

Electrical, structural and magnetic properties of pure and doped 1T-TaS₂

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ABSTRACT

A review of the available electrical and structural data on both pure and doped 1T-TaS₂ leads us to propose that the nearly commensurate to commensurate transition at 200 K is accompanied by Mott localization in two dimensions. One electron out of 13 in the Ta plane is localized onto the centre of a star of 13 Ta atoms. The picture helps in understanding the concentration dependence of the low-temperature resistivity in cation-doped samples, particularly the sharp maximum at an atomic fraction $x \sim 0.08$ for Ti doping. Examining recent resistivity data by Di Salvo and Graebner (1977) we find that at low temperatures the conduction mechanism assumes a three-dimensional character. The lack of a Curie-type susceptibility in spite of electron localization is ascribed to spin-orbit coupling, according to an earlier suggestion by Geertsma, Haas, Huisman and Jellinek (1972).

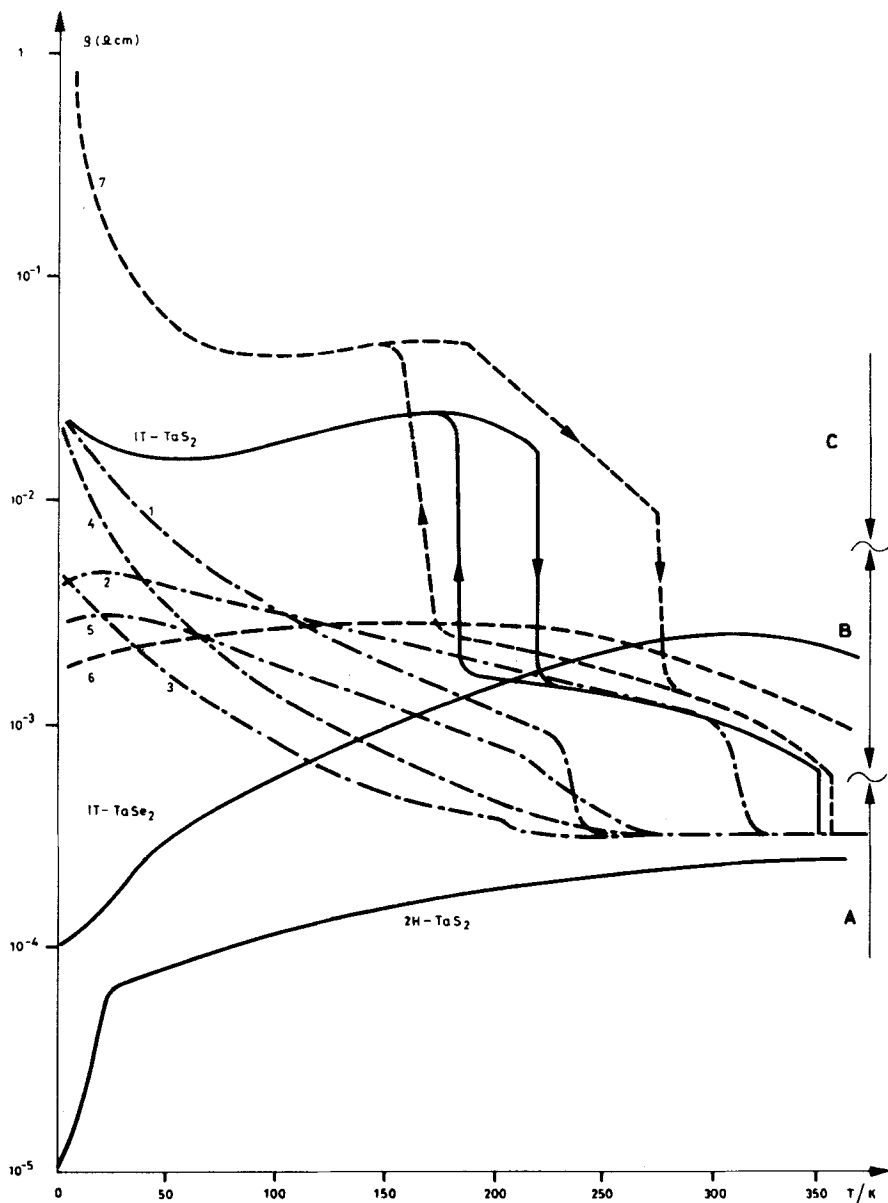
§ 1. INTRODUCTION

1T-TaS₂, 1T-TaSe₂, and the alloy systems based on them, stand out as a group of materials whose electrical and magnetic properties (Thompson, Pisharody and Koehler 1972, Benda 1974, Di Salvo, Wilson, Bagley and Waszczak 1975) are fairly difficult to interpret in a coherent fashion. Their structural transitions are thought to be reasonably well understood (Wilson, Di Salvo and Mahajan 1975), like those of other transition-metal dichalcogenides, in terms of Fermi surface (FS) driven charge-density-wave (CDW) instabilities, and their eventual lock-in with the underlying lattice. Although electron-electron interaction effects can, to some extent, be taken into account through $\chi(\mathbf{q})$, whose divergence signals the transition, the interpretation of the resulting low-temperature phase is usually attempted in terms of ordinary one-electron band theory, either as a fairly well conducting semimetal or as a conventional semiconductor.

The difficulty with the above-mentioned group of materials is that, over wide ranges of temperature and composition, they conduct too well to be called ordinary semiconductors but too poorly to be called semimetals. The most conspicuous feature is the low-temperature resistivity anomaly (at $T \lesssim 60$ K)

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Fig. 1



A compilation of resistivity data for pure (full lines), cation-doped (dashed-dotted lines), and anion-doped (dashed lines) 1T-TaS₂ samples, from the works by Di Salvo *et al.* (1975), and Di Salvo and Graebner (1977). The result for 2H-TaS₂ is shown as an example of good metallic conduction in two-dimension. The curves are meant to illustrate trends rather than to duplicate accurately the results of measurements (curve 1 = Ta_{0.905}Ti_{0.095}S₂; 2 = Ta_{0.96}Ti_{0.04}S₂; 3 = Ta_{0.855}Ti_{0.145}S₂; 4 = Ta_{0.915}Hf_{0.085}S₂; 5 = Ta_{0.915}V_{0.085}S₂; 6 = TaS_{0.5}Se_{1.5}; 7 = TaS_{1.6}Se_{0.4}). Two-dimensional metallic conduction is excluded in range C. B is the range of two-dimensional metallic conductivity. Range A is where proper two-dimensional metallic conduction is possible.

in pure 1T-TaS₂ (see fig. 1, full line) which has been ascribed to a variety of causes : complete gapping (Di Salvo *et al.* 1975), Anderson localization (Di Salvo and Graebner 1977), and Mott localization (Fazekas and Tosatti 1976, Tosatti and Fazekas 1976). It would be mistaken, however, to try to explain away just this single phenomenon as if the rest of the behaviour were quite ordinary. In fact, the nature of the conduction processes is far from being clear even when the resistivity is lower, as is the case at higher temperatures, or in doped samples. (By doping we mean, following Di Salvo *et al.* (1975), introducing impurities which enter either the cation, or the anion, sublattice substitutionally.)

§ 2. THE THREE RESISTIVITY RANGES

We call attention to the fact that three rather well-defined ranges of resistivity seem to exist :

Range A : $\rho \lesssim 5 \times 10^{-4} \Omega \text{ cm}$;

Range B : $5 \times 10^{-3} \Omega \text{ cm} \gtrsim \rho \gtrsim 5 \times 10^{-4} \Omega \text{ cm}$; and,

Range C : $\rho \gtrsim 10^{-2} \Omega \text{ cm}$.

Most of the materials considered here (at least in a definite phase if there is a recognizable phase transition) can be unambiguously classified according to ρ , as belonging to one of the above ranges. In fig. 1, we give a compilation of resistivity data, taken from Di Salvo and Graebner (1977) for pure samples, and from Di Salvo *et al.* (1975) for doped samples. Since the high-temperature resistivity of 1T-TaS₂ is, according to Di Salvo and Graebner (1977), somewhat different from the value published earlier, we changed the $\rho(T)/\rho(360 \text{ K})$ ratios plotted by Di Salvo *et al.* (1975) so as to reobtain the original low-temperature values of ρ for the doped samples. One can see that most of the values fall in Range B which apparently has a special significance. Its nature can be immediately recognized by noting, as first pointed out by Di Salvo and Graebner (1977), that Range B is centred on $\rho \sim 3 \times 10^{-3} \Omega \text{ cm}$ —approximately the value one would obtain if all the sandwiches had the universal value (Licciardello and Thouless 1975) of the two-dimensional maximum metallic resistivity. (We mention that a somewhat similar classification scheme emphasizing the importance of the conductivity range near the minimum metallic conductivity has recently been advocated by Chudnovskii (1978), for three-dimensional conductors.)

With the exception of 1T-TaSe₂ below $\sim 150 \text{ K}$ (a case which calls for special consideration), conductivities better than the minimum two-dimensional (2D) value are seen only at high enough temperatures where the system is already in the incommensurate (I) phase. At sufficiently low levels of doping (i.e. at an atomic fraction $x \lesssim 0.14$) there is a recognizable phase transition into such a well-conducting state. Only this state can, in our opinion, be called a proper quasi-two-dimensional conductor.

Of more interest is the intermediate Range B which, as already mentioned, could be characterized as ' the poorest 2D metal possible '. It is interesting to note what a wide variety of systems ' chooses ' this range : 1T-TaS₂ in its intermediate phase ; 1T-TaSe₂ in the commensurate (C) phase above 150 K ; cation-doped TaS₂ below the transition at $\sim 300 \text{ K}$, if the dopant is pentavalent (Nb, V) ; also if the dopant is tetravalent and the concentration x is

sufficiently different from $x \sim 0.08$; 1T-TaS_xSe_{2-x} anion-doped samples for $x < 1$ below the transition temperature; cation-doped 1T-TaSe₂ in most cases.

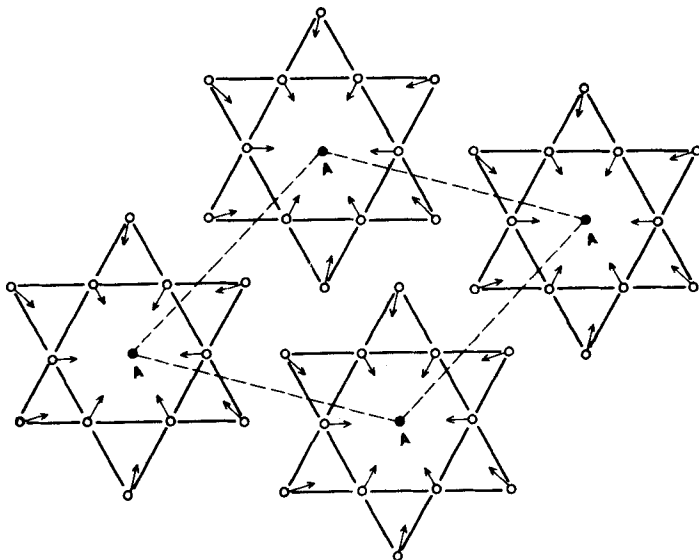
In contrast, higher resistivities falling in Range C are met only as exceptions: 1T-TaS₂ in its C phase; IVB-doped sulphide for $x \sim 0.08$; the low-temperature phase of 1T-TaSe_xS_{2-x} for $x \lesssim 0.8$. The very high resistivities found in Fe-doped samples (Di Salvo, Wilson and Waszczak 1976) seem to indicate an altogether different behaviour and are not considered here.

In the following we attempt a consistent, though qualitative, understanding of the electrical behaviour of systems with resistivities in Ranges B and C, based on the peculiar structural and electronic characteristics of the 1T polytype.

§ 3. LOCAL ORDER

The structure of 1T-TaS₂ (and of the isostructural 1T-TaSe₂) is most easily understood in the C $\sqrt{13} \times \sqrt{13}$ phase which appears below 200 K in pure samples (Wilson *et al.* 1975). In the Ta plane the structural unit is a 'star' (fig. 2) consisting of a central atom (A), of an inner ring of six Ta atoms moving towards A, and of an outer ring of six next-nearest-neighbour atoms which also shift inwards, only somewhat sideways. X-ray photoemission (XPS) studies (Wertheim, Di Salvo and Chiang 1975, Hughes and Pollak 1976 b), as well as our previous analysis (Tosatti and Fazekas 1976) lead us to believe that, considering the star as a quasi-molecule, the six low-lying 'bonding' orbitals will have a large weight in the outer region of the star, presumably between the two concentric rings of atoms. Hence it is reasonable to suppose that the energy gain associated with the formation of the $\sqrt{13} \times \sqrt{13}$ phase (and most

Fig. 2



Atomic positions, displacements, and 'stars' in the $\sqrt{13} \times \sqrt{13}$ phase, taken essentially from Wilson *et al.* (1975).

probably also with that of the nearly commensurate phase) comes mainly from the twelve electrons in the 'star-bonding' orbitals. It should be mentioned that recently Haas (1978) also considered this star structure, as one of the characteristic distortion patterns of the triangular lattice. However, he based his discussion upon assuming central forces between the atoms of a single (metal) layer. In contrast, in our picture, star formation is ascribed to the sandwich as a whole rather than to the Ta layer only: undulations of the sulphur sheets accompany the in-plane motion of the Ta atoms so as to prevent any significant changes in the lengths of the Ta-S bonds, and consequently the S sheets bulge out at the star centres. One may note that the inter-sandwich ordering of stars (the star centre in the next sandwich is probably $\mathbf{c}_0 + 2\mathbf{a}$, resulting in a one-sandwich monoclinic cell, and a repeat distance $13c_0$ along the c axis) may also be understood as the consequence of Coulomb repulsion between the S-sheet bulges on adjacent sandwiches. However, as pointed out by Bulaevskii and Khomskii (1977), inter-sandwich tunnelling can be of equal importance.

We note that Wilson (1978) recently analysed in detail the phasing taken by the periodic-structural distortion in a number of CDW-bearing materials and came to the conclusion that *maximum*, rather than minimum, electron density should be assigned to the star centre, thus bringing atom A near to configuration $5d^2$. It is a crucial point that we hold the exactly opposite view, associating charge **depletion** with the star centre. We recall that, according to our previous analysis (Tosatti and Fazekas 1976), modulation of the hybridization of the $3z^2 - r^2$, and $(x^2 - y^2, xy)$ sub-bands due to the periodic variation in the trigonal component of the crystal field plays a significant role in shaping the charge redistribution pattern, while Wilson considers it taking place in the tight-binding-like $3z^2 - r^2$ sub-band, essentially unaffected by the motion of the sulphur atoms. We return to further comparison with the work of Wilson (1978) in § 5, discussing the effects of cation doping.

To summarize, for the present purposes we adopt a local, quasi-chemical picture of the structural changes brought about by CDW formation. Even though in the high-temperature phase the incipient charge density wave (ICDW) is clearly associated with FS effects, the distortions can probably be understood (particularly below 350 K) locally as well, as star formation within a sandwich, plus star-star repulsion between sandwiches. After all, $2/\sqrt{3} \cdot |\mathbf{q}|^{-1}$ for the ICDW is never very different from the in-plane distance of nearest-neighbour star centres in the $\sqrt{13} \times \sqrt{13}$ phase. The 'soft CDW excitations' mentioned by Di Salvo and Graebner (1977), which rotate \mathbf{q} towards the commensurate direction in the intermediate phase, can be described by saying that CDW (negative) charge minima are trying to get in registry with the Ta sites. To make such an approach quantitative, one should probably apply the short-coherence-length limit of CDW theory, along the lines of the treatment of McMillan (1977) for the properties of 2H-TaSe₂.

§ 4. ANDERSON VERSUS MOTT LOCALIZATION

We argued earlier (Fazekas and Tosatti 1976, Tosatti and Fazekas 1976) that 12 out of 13 $5d$ electrons in the star-shaped cluster are paired off and do not give any essential contribution to electrical conduction or to paramagnetism.

Conduction within the layers, in particular, is only the thirteenth electrons' business. The resistivity measurements (Thompson, Gamble and Revelli 1971, Di Salvo *et al.* 1975) clearly show that even these electrons become localized by some mechanism below $T \lesssim 60$ K. There have been two suggestions as to how this might happen. We proposed (Fazekas and Tosatti 1976, Tosatti and Fazekas 1976) an explanation in terms of Mott localization. Alternatively, Di Salvo and Graebner (1977) suggested Anderson localization due to impurities and unspecified structural defects.

The argument in favour of an Anderson localization rests mainly on the fact that, for $0.03 \text{ K} \lesssim T \lesssim 2.2 \text{ K}$, the resistivity can be well fitted with $\ln \rho \sim T^{-1/3}$, the expression for variable-range hopping in two-dimension. However, if one assumes that electrons localize solely due to disorder, it is natural to expect that increasing disorder (for instance as caused by doping) leads to stronger localization, i.e. to higher resistivities. This indeed is the case for increasing anion disorder (doping with Se), but just the opposite is found for cation doping: for example, doping by 1% of Ti *reduces* the resistivity by an order of magnitude. This suggests that the resistivity anomaly in the pure material should rather be of a collective nature. However, the activation energy is probably very small (if there is any). We also point out that at sufficiently low temperatures, fractional power-law behaviour of the resistivity, indicating variable-range hopping, takes over even in wide-gap Mott insulators like NiO (Austin and Mott 1969), so that the $T^{-1/3}$ behaviour reported by Di Salvo and Graebner (1977) cannot be taken as evidence for the absence of collective electron localization.

§ 5. CATION DOPING

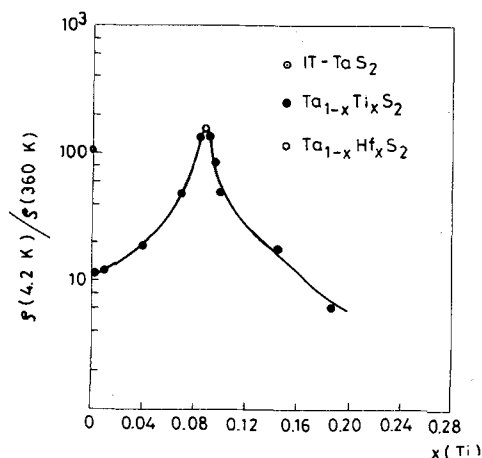
The local nature of star formation becomes particularly relevant when we consider alloy systems where cation impurities serve as natural nucleation centres for the stars. According to both XPS measurements (Wertheim *et al.* 1975, Hughes and Pollak 1976 a), and theoretical reasoning (Tosatti and Fazekas 1976), there is some charge depletion at the star centre; it thus seems clear that IVB impurities prefer to sit at the star centres. For Hf impurities, this is just the experimental finding by Hughes and Pollak (1976 b) and it seems safe to assume that the same would be found for Ti impurities.

The preferential centring of stars on IVB impurities explains at once why the C phase disappears at very low ($x \lesssim 0.005$) doping level (Di Salvo *et al.* 1975): part of the star centres will be fixed by the substitutionally disordered Ti atoms. The stars that still consist of Ta atoms only, will be pushed around thereby destroying their close packing. During the process, 'interstitial' Ta atoms appear between the stars. Their electrons remain essentially free to move and the screening effect they introduce destroys Mott localization. Hence the sudden drop of resistivity to the level of Range B, characteristic of the intermediate phase of the pure material. Indeed, for low Ti contents, the curves of ρ versus T look just like a smooth continuation of the behaviour in the intermediate phase of the undoped sulphide. It is therefore tempting to try to apply a similar picture to describe the situation in the intermediate phase in which structural defects, rather than impurities, give rise to the appearance of interstar Ta atoms. McMillan (1976) developed a theory of the I phase of

2H-TaSe₂, according to which the CDW is not uniform but instead locked-in regions are separated by discommensurations i.e. line defects in which the phase changes sharply. In the nearly commensurate phase of 1T-TaS₂, the presence of discommensurations was experimentally indicated in XPS work by Hughes and Pollak (1976 a), and later theoretically supported by Nakanishi and Shiba (1977). We guess that in doped samples, discommensurations become stabilized by Ti impurities down to 0 K. The importance of Ti disorder is also evident from the work by Wilson *et al.* (1975) who note that lock-in does not occur in doped samples in spite of the fact that for $x \sim 0.02$ – 0.03 , the FS diameter becomes, according to the rigid-band model, ideally suited for the $\sqrt{13} \times \sqrt{13}$ superlattice.

New phenomena appear when x increases towards $1/13 \sim 0.08$, i.e. when nearly *all* the stars are expected to be Ti-centred. In such circumstances there are very few star-centre *d*-electrons left to contribute to the conductivity —just as in the pure sulphide where the *d*-electrons are there, only they are Mott localized. Indeed, as Di Salvo *et al.* (1975) observe (see fig. 6 of their paper which we reproduce for easy reference as our fig. 3), the low-temperature resistivity grows with increasing x , becoming around $x \sim 0.08$ as high (or even higher by a factor of 1.5) as in the undoped material. For $x > 0.08$, ρ decreases (curve 3, fig. 1). Actually, one should expect a lower resistivity at the maximum if the Ti impurities were supposed to have random locations; this strongly suggests that the Ti (or Hf) atoms form a $\sqrt{13} \times \sqrt{13}$ superlattice of their own (see curves 1 and 4 in fig. 1). There seems to be no experimental evidence for the existence of a Ti superlattice at low temperatures but, to our knowledge, neither has it been ruled out. Wilson *et al.* (1975) remark that they did not perform diffraction measurements on doped 1T samples below room temperature, and also that, though they had conjectured cation-dopant

Fig. 3



The dependence of the low-temperature resistivity (in relative units) on the Ti concentration x . (Based on Di Salvo *et al.* 1975.) The empty circle at the peak refers to 1T-Ta_{0.915}Hf_{0.085}S₂.

superlattices might exist, they searched for them only for $x \geq 0.6$. On the theoretical side, McMillan (1975) demonstrated that impurity-impurity forces tend to bring impurities into registry with the CDW.

Here again, our interpretation is very different from that given by Wilson (1978). In his description, the star-tip atoms (which he denotes by C—see fig. 14 of Wilson's paper) are the most electron-deficient and therefore they are supposed to coincide with the Ti (or Hf) impurities. However, the concentration of star-tip atoms being $6/13$, this would leave the anomalous behaviour seen at $x \sim 1/13$ unexplained.

For isovalent impurities (V, Nb), one expects that differences in electronegativity still suffice to suppress the commensurate phase through preferential centring of the stars on impurities (or else off impurities, should that be more advantageous). However, these impurities carry as many electrons as does Ta, so all that happens is that the extra screening provided by the unbound electrons of the interstar Ta atoms eliminates electron localization. This pushes the resistivity down to the value corresponding to two-dimensional minimum metallic conductivity, characteristic of the intermediate phase (curve 5, fig. 1). Nothing peculiar happens when x grows past $1/13 \sim 0.08$, in agreement with our picture.

§ 5. CONDUCTION IN PURE 1T-TaS₂: COEXISTENCE OF MOTT AND ANDERSON LOCALIZATIONS

The conventional view has so far been to regard the three consecutive phases of 1T-TaS₂ as three semimetals with a decreasing area of free FS left as the temperature is lowered. The supposedly metallic behaviour has been described as quasi-two-dimensional, referring to the assumption that the FS does not change much along the k_z direction. Calculations have confirmed that, particularly in the sulphide, the FS is very little k_z -dependent (Myron and Freeman 1975). More recently, Woolley and Wexler (1977) came to the same conclusion, recognizing at the same time that, in the selenides, the more three-dimensional character is related to the k_z -dependent trigonal splitting of the t_{2g} level. One can then argue that the CDW transitions are related to the two-dimensional aspects of the FS and cannot ever produce complete gapping since the two-dimensional unit cell has an odd number (13) of electrons in it. So, *for band-structure effects alone*, 1T-TaS₂ should always be describable as a quasi-two-dimensional metal.

However, in the commensurate phase, the resistivity is always larger (by a factor varying between three and ten) than the value corresponding to two-dimensional minimum metallic conductivity in the sandwiches:

$$\rho_{2D} \sim 3 \times 10^4 c_0 \sim 3 \times 10^{-3} \Omega \text{ cm.}$$

Consequently, this phase *cannot* be described as a two-dimensional conductor, at any temperature between 0 and 200 K. We are thus compelled to make the assumption that *the 200 K phase transition is accompanied by a Mott localization* (in two-dimension, at least), and that the residual conduction below this transition takes place primarily between the sandwiches.

The above suggestion, which supplements and replaces our earlier one (Fazekas and Tosatti 1976, Tosatti and Fazekas 1976), can be elaborated as

follows. Exactly what we mean is that the lock-in transition takes the material into a state which, upon further cooling, approaches, without crossing any more phase boundaries, a ground state in which the electrons are Mott localized. This is tantamount to saying that in the course of the structural transition the ratio of carrier bandwidth to interaction strength changes in such a manner as to satisfy, even if only marginally, the criterion for Mott localization (Mott 1974). (Another possibility is a progressive shrinkage of the band owing to polaron formation which would not entail symmetry change either.) If there is a Mott transition in the thermodynamic sense, it must coincide with the first-order lock-in transition at 200 K. (We do *not* suggest that Mott localization is the 'driving force' of the lock-in transition but rather that it is an accidental consequence of the latter. As discussed by Wilson (1978), 13-atom stars, and other apparently chemically bonded structural units, frequently form in layer materials and are compatible with metallic behaviour as well as with insulating properties.)

We would like to mention the presently rather speculative possibility that, at 200 K, Mott localization sets in without there being a Mott-type phase transition, either at 200 K, or at lower temperatures. Since a paramagnetic insulator and a metal can have the same symmetry, the phase boundary between them may end in a critical point, as it actually does in the case of Cr-doped V₂O₃ (Jayaraman, McWhan, Remeika and Dernier 1970). If some mechanism, such as the lock-in transition in the case dealt with here, changes the parameters abruptly at a temperature for which the (isomorphic) Mott transition in itself would be *supercritical*, it is perfectly possible to proceed from the itinerant to the localized phase with a phase transition that is *not* a Mott transition. The surprising thing is that, on lowering the temperature, we do not meet the paramagnetic insulator/antiferromagnetic insulator phase boundary which is there in the case of the (V_{1-x}Cr_x)₂O₃ system. However, in § 8 we shall indicate why localized electrons in 1T-TaS₂ may behave essentially non-magnetically. Later in this section, Hall coefficient measurements will be discussed, from which evidence is found for such a sudden drop in charge carrier concentration at 200 K, which would, in our opinion, be difficult to explain in any way other than by invoking incipient Mott localization.

The situation is further complicated by having to consider more than one kind of orbital at every star centre. As will be discussed in § 8, the simultaneous presence of a rather strong spin-orbit coupling and a comparable trigonal component of the crystal field splits the sixfold degenerate t_{2g} level into three doubly degenerate levels, each with a partial quenching of the spin + orbital magnetic moment. These levels are probably not far removed from each other, so they have to be treated on an equal footing at finite temperatures. As has been pointed out to us by N. F. Mott (private communication 1978), in this respect there may be a similarity to the case of Ti₂O₃, in which a band-crossing transition takes place continuously (Mott 1974). However, while in Ti₂O₃ actual localization of the electrons is prevented by the screening provided by the much lighter holes, in 1T-TaS₂, at low enough temperatures at least, only heavy carriers seem to be present, and charge localization becomes possible.

The conductivity immediately below the 200 K transition can, of course, remain relatively high if the crossing into the Mott-insulating phase is indeed

supercritical, i.e. the associated Mott–Hubbard gap is rather less than 200 K. The behaviour can perhaps even appear metallic because of inter-sandwich tunnelling; but it certainly cannot be two-dimensional *and* metallic.

Actually, we can find support for the idea of three-dimensional conduction in 1T-TaS₂ from measurements by Di Salvo and Graebner (1977). The inverse of the minimum metallic conductivity deduced from the ρ versus T^{-1} plot by extrapolating to $1/T=0$ is $1.25 \times 10^{-2} \Omega \text{ cm}$. Having had to abandon the idea of identifying it with the universal two-dimensional value, Di Salvo and Graebner (1977) fitted this value with the expression valid for three-dimension, which contains a , the average separation between localization centres. This yields $a \sim 7.5 \text{ \AA}$ which compares badly with the estimated value of the average distance between impurities, estimated as $\sim 60 \text{ \AA}$. It is, however, in reasonable agreement with the distance between the nearest-neighbour star-centres *across* the van der Waals gap, which is about 8.5 \AA (a star's nearest neighbour is in the next sandwich!). This corroborates our twin ideas that the localization centres are the star centres and that conduction proceeds by inter-sandwich hopping.

Of course, the present interpretation is not free of difficulties. Foremost is the lack of any clearly identifiable activation energy, i.e. of a Mott–Hubbard gap. In principle, one could have an insulating ground state with the two Hubbard subbands (Hubbard 1963) just touching, as in a zero-gap semiconductor, and then one could still have (at any finite temperature) additional Anderson localization due to disorder. For that matter, the amount of disorder that seems to play a role here, is pretty small: it can be deduced from considering the temperature range just above the variable-range hopping regime, where the $\ln \rho \sim 1/T$ relationship is satisfied. In this range, the electrons always hop to the nearest localization centre, and the slope of the $\ln \rho$ versus $1/T$ plot is proportional to W , the average disorder potential. We find such a range between ~ 10 and $\sim 30 \text{ K}$, and the slope gives an average disorder potential of $\sim 3 \text{ K} \cong 0.3 \text{ meV}$. In a way, this corroborates the idea that Mott localization must also be at work; Anderson localization alone would require an improbably small bandwidth. That could still result from small polaron formation (Holstein 1959); but this would again lead to predicting Mott localization.

A second question is, why should the exponent for variable-range hopping be $\frac{1}{2}$, characteristic of two-dimensional conduction? As Di Salvo and Graebner (1977) have pointed out, the answer may be found in the work by Hamilton (1972) who calculated that, if $N(E) = N_0 |E|^p$, where E is the energy measured from the Fermi level, and $N(E)$ is the density of states, then $\ln \rho \sim T^{-(p+1)/(p+4)}$. It follows that in order to fit the data of Di Salvo and Graebner (1977), one must have $p = \frac{1}{2}$, i.e. the Fermi level is *at the edge* of a **parabolic band**.

Actually, we can go further and conclude that the Fermi level must lie at the touching point of two parabolic band edges since, for a finite gap, the Fermi level should be found in the middle of the gap. This is in accordance with our previous suggestion of an almost exactly zero Mott–Hubbard gap, improbable as it might sound.

Very recent Hall coefficient measurements for pure 1T-TaS₂ by Tanuma, Suematsu, Higuchi, Inada and Onuki (1978) seem to support the idea that something more than just ordinary CDW gapping must be at work in the commensurate phase. **The model presented here seeks to ascribe the observed**

resistivity changes predominantly to corresponding changes in the charge carrier concentration, rather than to mobility effects. Let us recall that, from the I phase to helium temperatures, the resistivity increases by over two orders of magnitude, while in the isostructural 1T-TaSe₂, where the CDW explanation appears to be satisfactory, the number of carriers drops by only one order of magnitude (Di Salvo and Graebner 1977). Assuming for simplicity's sake that only one kind of charge carrier is present, we have used the Hall data of Tanuma *et al.* (1978) to plot $1/n$ versus T which is shown in fig. 4. (n is the number of charge carriers in 1 cm^3 . Note that the carriers are hole-like below the lock-in transition, but electron-like above it.) For easy comparison, we show, by a dashed line, the ρ versus T plot in the same figure (right-hand scale). It immediately transpires that, in the undoped material at least, the resistivity transitions are basically $1/n$ transitions. In fact, at the 200 K transition, n decreases by about two orders of magnitude, so there must be a concomitant *increase* in mobility to partially compensate its effect. Upon reaching the commensurate state, n drops to $\sim 10^{20} \text{ cm}^{-3}$, i.e. it is an order of magnitude smaller than what would correspond to one carrier per star (indicated by the horizontal dashed line). Such a small value of n would be very difficult to account for in terms of CDW-created gaps alone.

In contrast, the two sets of Hall coefficient data (Di Salvo *et al.* 1975) for 1T-Ta_{0.915}Hf_{0.085} (at 90 and 300 K; denoted by crosses in fig. 4) indicate a charge carrier concentration several times higher than one carrier per star. Looking at the resistivity curve (fig. 1, curve 4), however, will at once show that 90 K is still a rather high temperature for this doped material; its resistivity reaches Range C only at $\sim 40 \text{ K}$. Above that temperature, there is no particular reason to expect a significant drop in n .

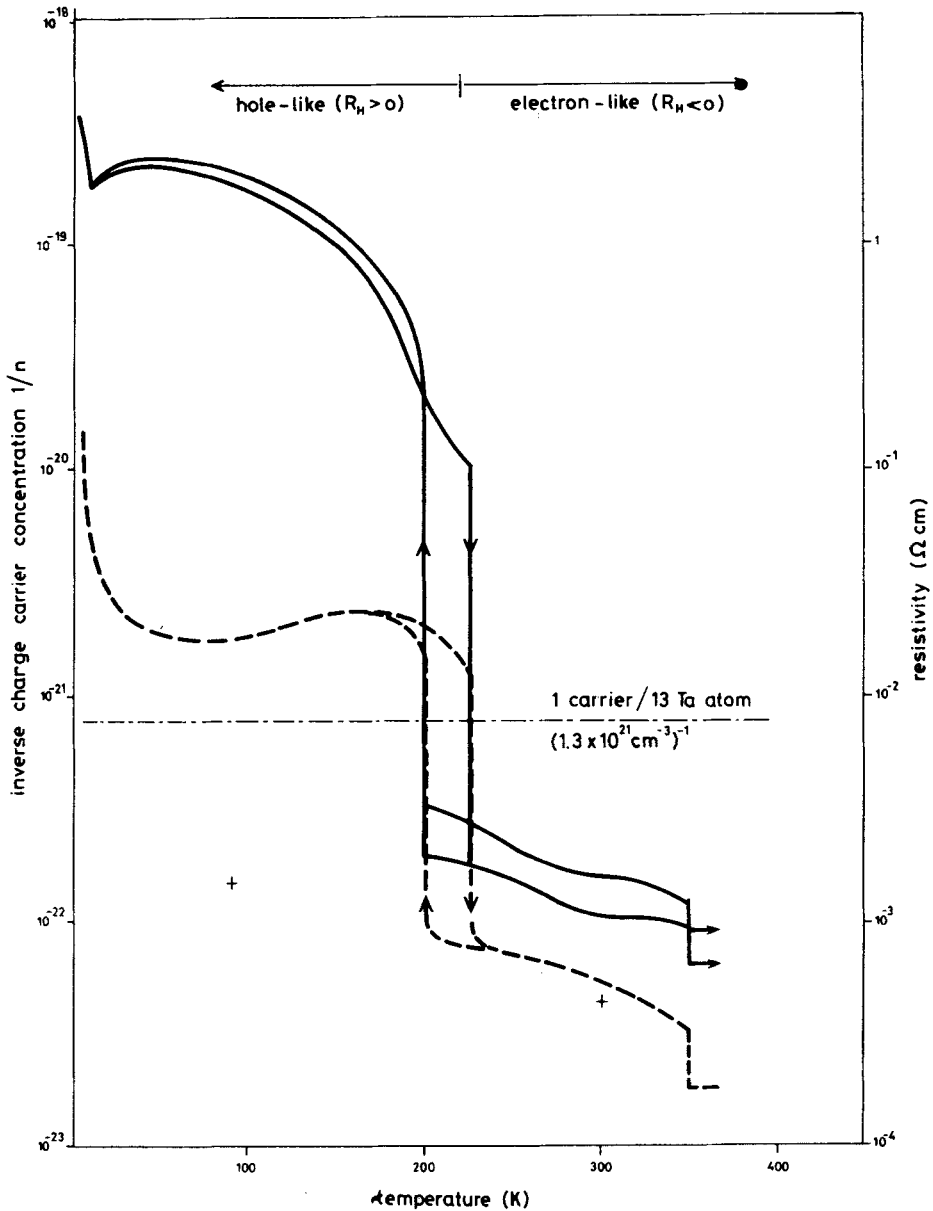
It would not be meaningful to attempt to interpret the finer details of the $1/n$ versus T plot, seen below 200 K, without admitting the possibility that several kinds of charge carriers might exist. As will be discussed in § 8, even if we completely neglect thermal excitation of the 'star-bonding' electrons, at least four, but more probably six, spin-orbitals have to be assigned to a star.

§ 7. ANION DOPING

Let us now consider briefly the effect of anion doping. One example is 1T-TaS_{1.6}Se_{0.4}; its resistivity versus temperature is shown as curve 7 in fig. 1. The significant increase in resistivity can be attributed to increased disorder. The Se²⁻ ion is considerably bigger than the S²⁻ ion, which also shows up in the c_0 values for the pure materials. (6.27 Å for TaSe₂, 5.86 Å for TaS₂). Thus replacing some of the S atoms by Se atoms is bound to cause large local fluctuations in the c/a ratio which, in turn, is known to have a significant effect on the energy levels (Tosatti and Fazekas 1976), and on CDW formation in general (Thompson 1975).

It might be interesting to point out that further experimental study of Se-doped (but S-rich) samples should provide valuable insight into the nature of conduction at low temperatures. Since conduction is obviously disorder-controlled, we expect that the $\ln \rho \sim T^{-1/3}$ behaviour found in nominally pure samples remains valid. If the minimum metallic conductivity deduced from measurements on Se-doped samples turns out to be roughly the same as

Fig. 4



Inverse charge-carrier concentration $1/n$, as a function of temperature T , based on Hall coefficient measurements by Tanuma *et al.* (1978). For the sake of easy comparison, the resistivity ρ is also shown (dashed line, right-hand scale). Crosses refer to data on $1T\text{-Ta}_{0.915}\text{Hf}_{0.085}\text{S}_2$ (Di Salvo *et al.* 1975). The horizontal dashed line refers to the situation when all star-bonding electrons are excluded from conduction (i.e. $n = \text{one carrier per 13 Ta atoms}$). Hall measurements are for two samples with slightly different properties.

obtained by Di Salvo and Graebner (1977), it can be interpreted either by identifying it with the universal two-dimensional value (but we have seen this is unlikely) or by saying that, though hopping is essentially three-dimensional, all the charge carriers are localized just as in pure samples, and so their average separation (the star-centre distance) must also be the same as in pure samples. Finding a minimum metallic conductivity appreciably different from the previously observed value, would rule out both our interpretation, and the idea of two-dimensional Anderson localization. A small variation is, of course, foreseen, because of the change in the average thickness of sandwiches or, alternatively, in the average star-star distance.

§ 8. MAGNETIC PROPERTIES

At first sight it might appear that any picture of the behaviour of 1T-TaS₂, based on the idea of electron localization (be it of the Anderson or Mott type) should necessarily run into serious difficulties when trying to interpret the apparent lack of free spins at moderately low temperatures. We can, however, turn to the interesting paper by Geertsma, Haas, Huisman and Jellinek (1972), which deals with the effect of spin-orbit coupling. The essential point is that the ground state of a single *d*-electron in a cubic environment is a fourfold degenerate state for which the first-order Zeeman splitting is zero.

The argument leading to the above statement is elementary crystal-field theory but we briefly sketch it for the sake of convenience. More details can be found in the book by Sugano, Tanabe and Kamimura (1970). The environment of the Ta⁴⁺ ion in 1T-TaS₂ is primarily octahedral, with a rather large crystal-field splitting between the *t*_{2g} and *e*_g levels. (Estimates of the crystal-field parameters can be extracted from the work of Mattheiss (1973).) Let us first neglect the trigonal component of the crystal field.

Choosing a proper coordinate system, the *t*_{2g} representation has the basis functions $\xi \sim yz$, $\eta \sim xz$, $\zeta \sim xy$. The quenching of the orbital moment is partial only, inasmuch as for the matrix of **L** on the *t*_{2g} basis we have

$$\mathbf{L}(t_{2g}) = -\mathbf{L}(p)$$

where **L**(*p*) is the matrix of **L** on a *p*-state basis (*x*, *y*, *z*). We exploit the assumption that the cubic field is large by neglecting matrix elements of **L** connecting *t*_{2g} states with *e*_g states.

Introducing the spin-orbit coupling $\mathcal{H}_{so} = G\mathbf{L} \cdot \mathbf{S}$, and diagonalizing it on the basis *t*_{2g}α, *t*_{2g}β, where α and β are the usual spin-½ eigenfunctions, one obtains for the ground states the following four degenerate states

$$\begin{aligned}\phi_1 &= \frac{z}{\sqrt{2}} \rho \exp(-i\varphi)\alpha & (L_z = -1, S_z = \tfrac{1}{2}), \\ \phi_2 &= \frac{z}{\sqrt{2}} \rho \exp(i\varphi)\beta & (L_z = 1, S_z = -\tfrac{1}{2}), \\ \phi_3 &= \frac{1}{\sqrt{6}} \left\{ z\rho \exp(-i\varphi)\beta + \frac{\rho^2}{2} [\exp(2i\varphi) - \exp(-2i\varphi)]\alpha \right\}, \\ \phi_4 &= \frac{1}{\sqrt{6}} \left\{ z\rho \exp(i\varphi)\alpha - \frac{\rho^2}{2} [\exp(2i\varphi) - \exp(-2i\varphi)]\beta \right\},\end{aligned}$$

where $\rho = \sqrt{(x^2 + y^2)}$, $\tan \varphi = y/x$, and spherically symmetric factors are omitted. As to ϕ_1 and ϕ_2 , one can immediately see that $\mathbf{L}_z + 2\mathbf{S}_z = 0$; the vanishing of the other matrix elements of $\mathbf{L} + 2\mathbf{S}$ in the above set can be easily checked.

The lack of a first-order Zeeman effect can at once explain the susceptibility data if we apply it to the Mott-localized electrons. The original suggestion was made in quite a different context. Geertsma *et al.* (1972) envisaged Mott localization of *all* electrons due to the spin-orbit enhancement of the effective Hubbard U . We are concerned with the localization of the star-centre electrons only; it is true, however, that in a proper evaluation of the 'on-star' electron-electron interaction, spin-orbit coupling should also be taken into account.

Of course, a complete lack of first-order Zeeman splitting should be expected only for an ideal octahedral environment, with very large $t_{2g} - e_g$ splitting. In fact, we expect the trigonal component of the crystal field and the spin-orbit coupling constant to have roughly the same order of magnitude. Moreover, if the orbit of the localized electron extends, as we imply, over the inner seven atoms of the star, the crystal field may be predominantly trigonal. In either case, the more complicated analysis by Ballhausen (1962) has to be applied. The likely outcome is an *anisotropic* susceptibility which is, however, still considerably smaller than what one would obtain from 1/13 of all Ta sites having free spins.

If the role played by spin-orbit coupling is indeed as relevant as it appears from the above, one must take seriously its effect on the electronic structure from the outset. For reasonable values of the spin-orbit coupling constant, the band structure of the undistorted state as calculated by Mattheiss (1973), becomes essentially modified, with states around the zone-centre Γ point being pushed below the Fermi level (J. Kollár, private communication 1978). This may have profound effect upon FS-based descriptions of the CDW instability.

§ 9. CONCLUSIONS

We have found that it is possible to give a coherent qualitative interpretation of most of the electrical, structural and magnetic properties of pure 1T-TaS₂, and of samples doped by group IVB or VB, cations or by Se. The central idea is that CDW formation is essentially a local structural instability leading to the appearance of 13-atom clusters ('stars') in the Ta planes. Twelve $5d^1$ electrons are paired off in 'star-bonding' orbitals and the thirteenth electron is localized well inside the star. Only these central electrons are expected to give any essential contribution to electrical conductivity, or magnetism.

Because of their large separation, it is natural to expect that, in the sub-band of the central electrons, a Mott localization may take place; we suggest that the lock-in transition at 200 K creates circumstances in which Mott localization becomes possible. The conductivity drops below the universal two-dimensional value right at the transition and, on lowering the temperature, the system approaches a ground state in which all the star-centre electrons are Mott localized. The idea of electron localization finds strong support in recent Hall coefficient data by Tanuma *et al.* (1978), which show that, upon entering the commensurate phase, the charge carrier density becomes one order of magnitude smaller than what could be ascribed to CDW-created gaps.

Analysing the low-temperature resistivity data by Di Salvo and Graebner (1977) we found that the Mott–Hubbard gap should be extremely small, and that the $\ln \rho \sim T^{-1/3}$ behaviour is associated with three-dimensional variable-range hopping in the two almost touching Hubbard sub-bands. Thus, Mott and Anderson localizations coexist, but Anderson localization alone could not account for the sudden drop of resistivity, produced by slight cation doping.

Cation doping has the same effect as the appearance of discommensurations in the intermediate phase of the pure material: it creates unbound electrons which destroy Mott localization. Preferential centring on impurities explains the rapid disappearance of the commensurate phase. For IVB doping the lack of central electrons gives a natural explanation for the low-temperature resistivity maximum around $x = 1/13 \sim 0.08$, seen in Ti-doped samples. Anion doping, on the other hand, leads to increased disorder due to fluctuating c/a ratios, hence enhancing Anderson localization.

The lack of a Curie-type contribution to the magnetic susceptibility, such as one expects from localized electrons, can be explained by taking into account the effect of spin–orbit coupling on the Mott-localized star-centre electrons, along the lines of reasoning by Geertsma *et al.* (1972).

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