# CHARGE CARRIER LOCALIZATION IN PURE AND DOPED 1T–$TaS_2$

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We review experimental data on the low-temperature behaviour of pure, and cation-doped 1T–$TaS_2$, This suggests that the transition into the commensurate phase is accompanied by Mott-localization while below helium temperatures, conduction proceeds by variable range hopping in disorder-localized states lying in a region where the Mott–Hubbard subbands slightly overlap. Many properties of doped samples can be understood by assuming that the star-shaped atomic clusters characteristic of pure material are preferentially centred on impurities.

## 1. Introduction

Transition metal dichalcogenides have received much attention recently [1, 2], as an attractive group of materials for the study of the formation and properties of charge density waves (CDW). Most of the observed phenomena can be, in principle at least, understood by applying conventional one-electron band theory to describe the situation that arises as a result of CDW formation; i.e., either gapping is incomplete, and at low temperatures metallic behaviour is observed, or all the Fermi surface (FS) is eliminated and a conventional semiconductor is produced.

1T–$TaS_2$ seems to be an exception inasmuch as some kind of electron localization has to be invoked to explain its low-temperature properties [3]. At the moment it is a matter of controversy whether localization is primarily of a collective nature (Mott localization) or due to disorder (Anderson localization). Our feeling is that neither of these can be eliminated without leaving some of the results unexplained.

Our present purpose is to set up a conceptual framework which might conceivably encompass all available experimental data on pure, and as much as possible on doped 1T–$TaS_2$. Such qualitative understanding should be the prerequisite for developing a proper theory aiming at quantitative details.

## 2. Structural and electrical properties

Our considerations heavily rely on some details of the low-temperature structure of 1T–$TaS_2$, which are extensively discussed in review papers by Wilson et al. [1], and Williams [4]. Below 200 K, the $\sqrt{13}\times\sqrt{13}$ commensurate structure (fig. 1) is observed. It can be visualised as consisting of "stars" of 13 Ta atoms, with twelve atoms in two shells displaced towards the thirteenth, central atom. Since the Ta–S bond lengths are not easily changed, a warping of the S sheets accompanies the in-plane shifts of the Ta atoms, with swellings over star centres, and depressions in between the stars. Both Coulomb interaction and steric considerations suggest that the swelling of the next sandwich should fit into a depression of the sandwich below; in this way we can understand both the $\alpha\beta\gamma$ stacking sequence in the incommensurate phases, and the $13c_0$ repeat distance of the commensurate phase. Both XPS experiments [5] and theory [6] suggest

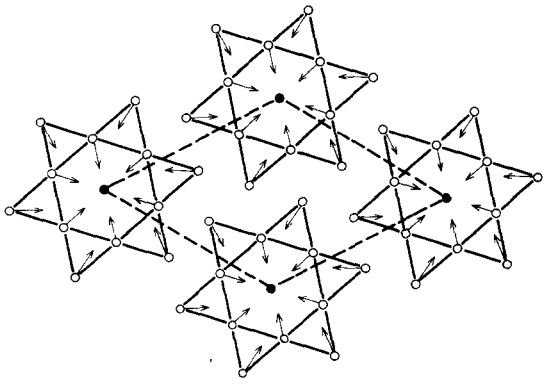

Fig. 1. Atomic displacements and star-shaped clusters of Ta atoms in the commensurate phase.

that a similar description applies to the nearly commensurate phase *locally*, only locked-in domains are separated by line defects (discommensurations) across which the CDW phase changes rapidly. We do not discuss the high-temperature phase.

It is important to realize that, in the commensurate phase, both the two-dimensional, and the three-dimensional unit cell contains an *odd* number of Ta atoms, and an equal number of 5d electrons in the conduction band. Consequently, though CDW gapping could conceivably withdraw 12 out of 13 electrons from the conduction process (both the structure, and comparison with isostructural 1T–$TaSe_2$ suggest that this may be so), it should certainly leave us with a partially filled band, leading to metallic conduction at low enough temperatures. However, according to resistivity measurements [7], such is not the case: below $\approx$60 K the resistivity is described by an Arrhenius plot, though with such a small activation energy (of the order of $10^{-4}$ eV) that is fairly difficult to interpret. (For convenience, this result is reproduced, along with some others for doped samples, in fig. 2.)

The apparently unbounded rise of the low-temperature resistivity clearly cannot be described by band theory alone. A strong case can be made for Anderson localization [8] due to impurities and/or structural defects: the fractional power law dependence of the logarithm of resistivity at low temperatures [9, 10] is a clear indication of disorder effects. It is unlikely, however, that disorder alone would suffice to explain all that is seen. First, it would be difficult to understand why disorder should always affect 1T–$TaS_2$, and never the otherwise very similar 1T–$TaSe_2$ [3]. More important is perhaps to notice that introducing more disorder should *increase* the resistivity further; but the introduction of a small concentration ($\lesssim$1 per cent) of IVB or VB impurities (these are supposed to enter the Ta sublattice substitutionally) always *decreases* the resistivity by about an order of magnitude, to the level characteristic of the nearly commensurate phase [11] (fig. 2). We think this is a convincing evidence for the presence of a cooperative component of the localization mechanism, which should be effective in the entire temperature range below the lock-in transition [12]. This guess is corroborated by recent Hall effect measurements by Tanuma et al. [13], which show that in the commensurate phase, the carrier density is always smaller, by an order of magnitude at least, than 1/13 per Ta atom, which is the smallest concentration that could be attributed to CDW-created gaps.

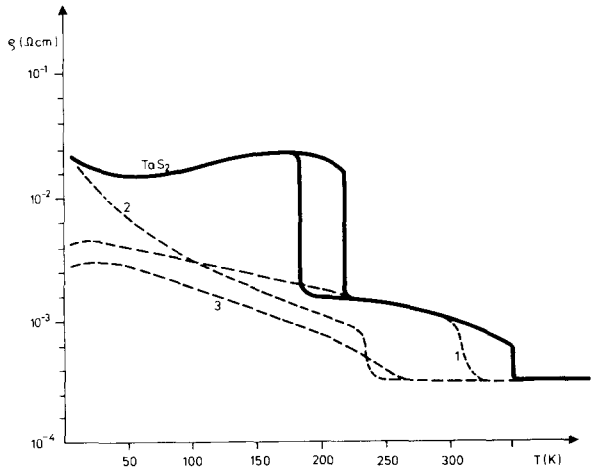


Fig. 2. Resistivity vs temperature plots for pure and doped 1T–$TaS_2$, after [11], curves (1) 1T–$Ta_{0.96}Ti_{0.04}S_2$; (2) 1T–$Ta_{0.915}Ti_{0.085}S_2$ and (3) 1T–$Ta_{0.915}V_{0.085}S_2$.

In the following section, we introduce a specific model for the electronic structure of 1T–$TaS_2$, which helps to understand why correlation effects may become important in this material.

## 3. Electron localization in star-centre orbitals

Since the structural investigations revealed the existence of clearly identifiable groups of atoms (the "stars" shown in fig. 1), it is tempting to think of these as quasimolecules with ordinary bonding characteristics. We have suggested [14] that twelve out of the thirteen electrons associated with a star are paired off in six star-bonding orbitals (as suggested by symmetry), and at low temperatures only the "thirteenth" electron, occupying a non-bonding orbital localized somewhere inside the star, can contribute to conduction or paramagnetism. We emphasize that the warping of the sulphur sheets plays an important role in shaping the charge density distribution: modulation of the $c/a$ ratio acts, through the hybridization of the crystal-field-split subbands [15], to accumulate charge on the outer belt of the star, and deplete charge in the star centre. This would identify electron density minima with atomic density maxima, and is thus

the exact opposite of, for instance, Wilson's [16] choice of CDW phasing. It seems, however, to be in accord with XPS measurements [17, 18].

If we further assume that the bands derived from the star-bonding orbitals do not overlap the band accommodating the thirteenth, star-centre electrons, we are left with a fairly narrow half-filled band, within which a Mott–Hubbard localization may occur. We infer from the experimental situation that indeed this is the case and identify the onset of electron localization with the lock-in transition at 200 K. This suggestion is corroborated by the observation that in the commensurate phase, conductivity is always substantially lower than what would correspond to each sandwich having the universal two-dimensional (2D) value [19] of minimum metallic conductivity (MMC), so low-temperature 1T–$TaS_2$ certainly could not be a 2D metal (as it is supposed to be). The already mentioned Hall effect measurements [13] also indicate some sort of electron localization below 200 K.

Our picture offers an easy interpretation of certain observations on cation-doped samples [11]. First, since the impurities have an electronegativity somewhat different from that of Ta, they should lead to preferential centering of stars (either on, or off, impurities), thereby destroying long-range order, as observed. At the same time, in regions where conflicting requirements lead to quick variation of CDW phase, stars are broken up, and electrons released to screen out the Mott localization. It is the same mechanism that delocalizes electrons in the nearly commensurate phase and indeed, the resistivity vs temperature plot for lightly Ti doped $TaS_2$ looks just like the smooth extrapolation from the behaviour in the nearly commensurate phase (fig. 2, curve 1).

It is at first sight surprising that, with increasing Ti or Hf concentration, the low-temperature resistivity climbs back to the value characteristic of the pure material (fig. 2, curve 2). It can be understood, however, by assuming that the electron-deficient star-centres are preferentially centred on IVB impurities which then have the $M^{4+}$ configuration. (It should be added that, for M = Ti, $M^{3+}$ is sometimes advocated [20, 21]. For M = Hf, our choice is the experimental finding [18].) Such assignment leaves the bonding states of the star intact, only the "thirteenth" electron is missing. By the time the concentration reaches $x = 1/13 \approx 0.08$, on the average all stars are Ti-centred, and no star-centre electrons participate in the conduction process, just as in pure $TaS_2$, where the electrons are there, only they are localized. With further increase of $x$, lower values of resistivity are restored (fig. 3). We note that this explanation implies (for $x \approx 1/13$) that, at low enough temperatures, it is energetically advantageous for the Ti impurities to form a $\sqrt{13} \times \sqrt{13}$ superlattice of their own. Since by the time such a temperature is reached, atomic diffusion all but ceases, the process is not likely to take place [21].

In contrast, VB impurities are expected to donate their electrons like Ta does, and no maximum in the resistivity vs concentration curve should be seen (cf. fig. 2, curve 3).

## 4. Correlation versus disorder

Though Mott-localization of star-centre electrons seems to be essential for the interpretation of the properties of the commensurate phase in general, at low enough temperatures disorder effects become increasingly important. The very fact that correlation does not produce a clearly identifiable gap, suggests that the Hubbard subbands overlap to some extent, and the Fermi level $E_F$ is most likely to be found in a pseudogap. Anderson localization in the overlapping tails of Hubbard subbands is then an obvious possibility [22].

Low-temperature resistivity measurements [9, 10] have turned up evidence for variable range hopping (VRH) below $\approx 2$ K. Di Salvo and

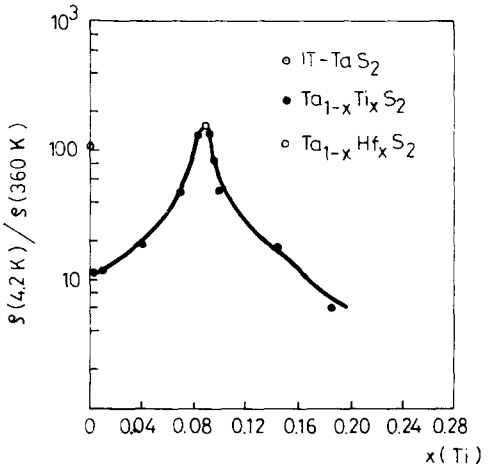


Fig. 3. Helium-temperature resistivity vs Ti concentration, after [11]. Open circle refers to a Hf-doped sample.

Graebner [9] find $\ln \rho \sim T^{-1/3}$ which would nicely fit to Mott's law [23] for 2D if the extrapolated value of MMC were not in contradiction with the assumption of two-dimensionality. As discussed elsewhere [12], the average separation of localization centres (≈8 Å), derived assuming three-dimensional hopping, is just the separation of star centres across the van der Waals gap, which supports the idea of electron localization on the star centres and shows that, for hopping conduction, the material loses its 2D character. To be able to use the 3D formula for MMC, and still to justify the exponent 1/3, a density of states of the form $N(E) \sim \sqrt{|E - E_F|}$ had to be assumed [24], which seems compatible with the idea of $E_F$ located between two Hubbard subbands with overlapping edges. The situation has become more complicated by Kobayashi and Muto's [10] finding that for their samples the VRH exponent is 1/2 rather than 1/3. In our picture, this could be explained by claiming that the latter samples are more disordered and it is the tails, rather than edges, of the subbands that overlap, so the density of states becomes like $N(E) \sim (E - E_F)^2$, and still Hamilton's formula [24] can be used for 3D hopping. Indeed, Kobayashi and Muto quote a value for the resistivity at 4.2 K, that is about four times higher than what Di Salvo and Graebner [9] report.

At this point, our interpretation is rather different from the picture that emerges from recent works by Fukuyama and Yosida [25]. Discussing recent findings [10, 26] of large negative magnetoresistance in 1T–$TaS_2$, these authors also emphasize that both disorder and correlation are important for a full explanation. However, according to their interpretation disorder is the far stronger effect: $E_F$ is separated by only ≈0.4 meV from the mobility edge $E_C$, and lies in a region of high density of states (comparable to that of 1T–$TaSe_2$). In comparison, the Hubbard $U$ derived from ascribing the low-temperature susceptibility increment to Anderson-localized states, is merely 28 K. This point of view certainly offers an easy explanation for the comparable electronic specific heats of 1T–$TaS_2$, and metallic 1T–$TaSe_2$ [20, 27]. However, a few objections can be made. The high value of $N(E_F)$ implies that both $E_F$ and $E_C$ have comparatively large values (of order of 0.1 eV, as in 1T–$TaSe_2$) and it is difficult to see, how their difference $E_C - E_F$ could turn out to be a nearly *sample-independent* 0.4 meV, while the low-temperature resistivities can vary by an order of magnitude, attesting to rather different degrees of disorder. Also, if one takes the problem of the extrapolated MMC seriously, 3D hopping has to be assumed and then either exponent of VRH requires a very low $N(E_F)$. As for the question of specific heat, it might be interesting to refer to Kamimura and Yamaguchi's [28] work who find that the specific heat (in contrast to susceptibility) is, at low temperatures, virtually unaffected by correlation.

It should be added that in discussing localization and VRH, we were thinking in terms of the simplest Mott–Thouless [19, 23] picture. In fact, the theoretical questions are far from being settled and, for 2D, the very existence of an Anderson transition is a matter of controversy. A number of authors [29–31] recently arrived at the conclusion that in 2D an arbitrarily small disorder induces localization, and that no MMC exists in 3D (though Lee [32] reaffirmed the existence of both localized and extended states in 2D). The discussion by Götze et al. [31], however, suggests that still a fairly sharp transition takes place between a strictly localized and a quasi-metallic phase; in the latter, localization lengths are extremely long, so the coherence of the wave function is destroyed at a much smaller scale by thermal agitation. It seems likely that for practical purposes, the original Mott–Thouless picture remains valid.

## 5. Magnetic properties

The surprising thing about 1T–$TaS_2$ is that it shows ample evidence of electron localization but very little magnetism [1], though the two should go together. Fukuyama and Yosida [25] come to grips with this problem when introducing a very small Hubbard $U$ in accordance with the observed small paramagnetic susceptibility below ≈60 K. In our picture, 1/13 of all the electrons are supposed to be localized, and an explanation for the lack of a corresponding number of localized spins has to be found.

We have taken up a suggestion made by Geertsma et al. [33] about the possible role of spin–orbit coupling. Ta being a heavy element, the spin–orbit coupling constant is expected to be at least comparable to the trigonal component of the crystal field. For a purely octahedral

environment, the ground state configuration would be a fourfold degenerate state with vanishing first-order Zeeman splitting, so this looks a good starting point to explain why magnetism is all but absent in 1T–$TaS_2$.

Ordering is another matter. Even though the spin–orbit coupling manages to mix nonmagnetic states, the ionic ground state will be at least two-fold degenerate and the mechanism of superexchange will favour that different states be occupied at nearest-neighbour sites (though the difference will not be that of magnetic moment). This should answer the question why 1T–$TaS_2$ does not behave like other Mott-insulators and becomes antiferromagnetic; in fact it might do something similar.

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