

THE LOW TEMPERATURE ELECTRICAL PROPERTIES OF 1T-TaS₂

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(Received 26 April 1977 by A.G. Chynoweth)

Measurements of the electrical resistivity of 1T-TaS₂ to 0.03 K show that the increase in resistivity below ~ 50 K is extrinsic. Below 2 K the resistivity is described by $\rho = \rho_0 \exp(T_0/T)^{1/3}$. Because of this fractional power law behavior, we conclude that the increase is due to Anderson localization by random impurity and/or defect potentials. Other difficulties in understanding the properties of 1T-TaS₂ are also pointed out.

THE CHARGE density wave (CDW) instability in layered compounds is qualitatively understood [1, 2] and in some cases semi-quantitative agreement with empirical free energy models is obtained [3, 4]. Yet there remain a number of problems in understanding the details. Here we consider 1T-TaS₂, which is unusual even within the group of materials that show CDW instabilities. While this paper concerns the low temperature properties, we would like to point out the general nature of the problems in understanding the properties of 1T-TaS₂.

Some of these problems are apparent from the electrical resistivity of 1T-TaS₂, especially in comparison to 1T-TaSe₂ (Fig. 1). While both compounds have a CDW onset temperature (T_0) to the incommensurate CDW state (ICDW) of approximately 600 K, only 1T-TaSe₂ behaves in a simple manner. The ICDW amplitude in 1T-TaSe₂ increases as the temperature is reduced below T_0 , until the CDW becomes commensurate (CCDW) with the lattice in a first order transition at $T_d = 473$ K. The resistivity increases (relative to a simple metal) below T_0 because of increasing gaps at the Fermi surface and they increase discontinuously at T_d . At low temperatures metallic behavior is observed from those portions of the Fermi surface not destroyed by gaps. In the ICDW the wave vector of the distortion is $\mathbf{q} = 0.28\mathbf{a}^* + \mathbf{c}^*/3$. That is, the basal plane projection of \mathbf{q} is parallel to the reciprocal lattice vector \mathbf{a}^* , and the CDW stacking produces a three-layer repeat. At T_d the basal plane projection of \mathbf{q} rotates by $13^\circ 54'$ to become commensurate with the lattice (in a $\sqrt{13}\mathbf{a}$ superlattice), and the CDW stacking changes so that it repeats every 13 layers [5]. In 1T-TaS₂ at the first order transition, $T'_d = 352$ K, \mathbf{q} rotates only by $\approx 11.5^\circ$ [1, 6], stopping short of the commensurate position. The CDW repeat remains at three layers. A CCDW superlattice, identical to that of 1T-TaSe₂, occurs below the transition at $T_d \approx 200$ K [6]. This intermediate state between T_d and T'_d (we have labelled this state with the

misnomer "quasicommensurate") is probably related to the retention of the 3-layer repeat and the appearance of secondary distortions [7, 8], similar to those that occur in 2H-TaSe₂ [3, 7].

The second unusual feature about the resistivity of 1T-TaS₂ is the high value attained below T_d , especially in comparison to 1T-TaSe₂. This high value may be due to an extremely low carrier concentration, trapping of the carriers by polaron formation [1], or some kind of Mott transition [9]. Further, the low temperature resistivity is temperature dependent. However, the magnitude of the increase, say from the minimum near 60 to 4.2 K is sample dependent, varying by as much as a factor of two, as also evidenced by the differences in published data [10–12]. We have determined the room temperature resistivity of 1T-TaS₂ more accurately than in reference [10], and find $\rho(295 \text{ K}) = 1.0 \times 10^{-3} \Omega$ and $\pm 5\%$ in better agreement with reference [11]. The temperature dependence, of course, remains the same as reference [10].

X-ray photoelectron spectroscopy of the Ta 4f core levels shows that the CDW amplitude at low temperatures in both 1T-TaSe₂ and 1T-TaS₂ is large, on the order of one electron per atom [13]. Thus the low temperature state may be described as a "valence disproportionation" of $\text{Ta}^{4+} \rightarrow \text{Ta}^{3+}$, Ta^{4+} and Ta^{5+} . The atomic displacements at room temperature are also large, up to 0.25 \AA [14]. An adequate description of how this state evolves from the small amplitude ICDW near T_0 is not available.

Another unusual feature of 1T-TaS₂ (and 1T-TaSe₂) is the strong diffuse scattering in the ICDW state apparent in the electron diffraction [1, 2]. First, this scattering is much stronger than observed in the 2H or 4Hb polymorphs. In fact, in pure 2H samples, no diffuse scattering is seen in the ICDW state. In the 1T polytypes the scattering is strongest for transverse displacements of \mathbf{q} (see Fig. 12, reference [1]). We interpret this as due to soft CDW excitations, which are soft in the

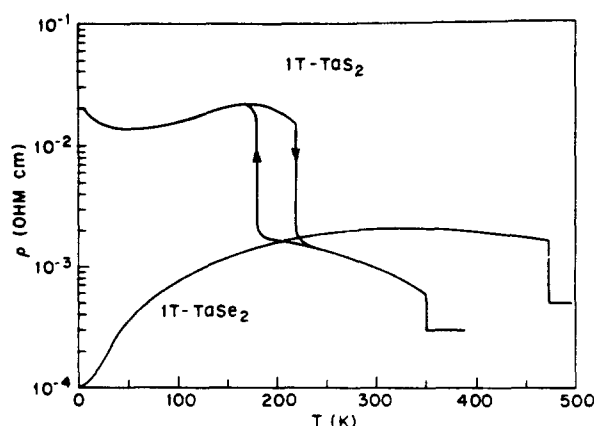


Fig. 1. The electrical resistivity of 1T-TaSe₂ and of 1T-TaS₂ at low temperature (to 4.2 K) are quite different, even though they both show the same CCDW superlattice.

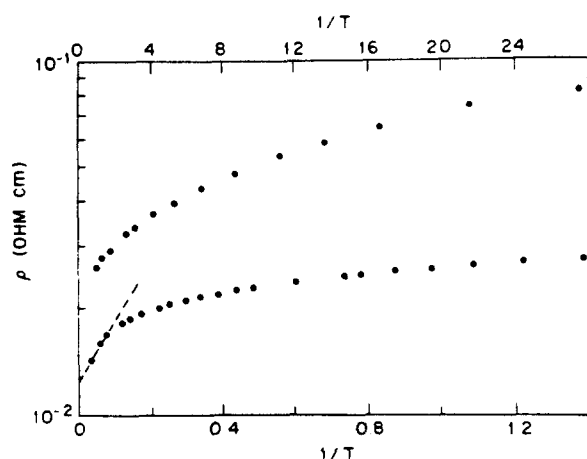


Fig. 2. The electrical resistivity of 1T-TaS₂ below 10 K is not exponentially activated over any significant temperature interval. The upper set of data points is referred to the upper scale of $1/T$.

direction toward which q rotates to become commensurate, consistent with the appearance of secondary distortions at lower temperatures. An alternate explanation has been given in terms of a bell-shaped Fermi surface with strong Kohn anomalies [6]. Further measurements of the diffuse intensity as a function of both wave vector and energy should aid in our understanding this phenomenon.

In this note we present very low temperature measurements of the resistivity of 1T-TaS₂. From the functional dependence of $\rho(T)$, we show that the increase in ρ below approximately 60 K is not intrinsic, but is due to Anderson localization. Thus the interpretation that the increase is due to small distortion induced gaps in the Fermi surface [11, 12] is not correct.

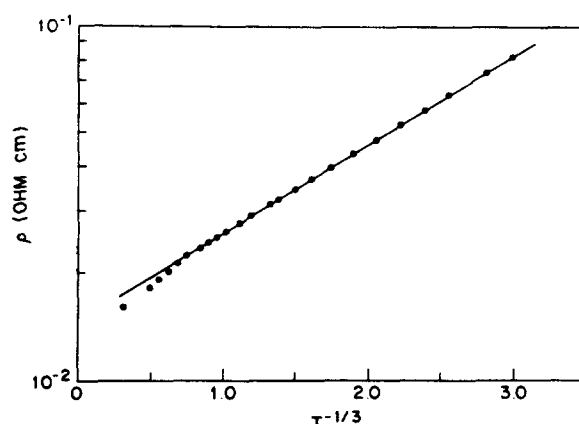


Fig. 3. The logarithm of the electrical resistivity of 1T-TaS₂ below 2.2 K is proportional to $T^{-1/3}$.

The electrical resistivity of 1T-TaS₂ with the current parallel to the layers is shown in Fig. 2 from 0.03 to 20 K vs T^{-1} . The sample was mounted in a He³-He⁴ dilution refrigerator equipped with a CMN-SQUID thermometer [15]. The sample current (30 Hz) was adjusted to keep the power dissipated in the sample to less than 10^{-15} W to avoid heating the sample. The sample resistance was independent of current when the latter changed by more than an order of magnitude.

It is clear that the resistivity does not fit the simple form $\rho = \rho_0 e^{-\Delta/T}$ expected for gap-like behavior. Since $\ln \rho$ vs T^{-1} has negative curvature, we fit the data to the relation

$$\rho = \rho_0 e^{(T_0/T)^n} \quad (1)$$

with $1 > n > \frac{1}{2}$ [16]. The best fit occurs for $n = \frac{1}{2}$ as shown in Fig. 3. The fit is good from 0.03 to 2.2 K, a approximately two orders of magnitude in temperature. While $n = \frac{1}{2}$ is expected in the simple case of two dimensional localization [16], the exponent also depends on the energy dependence of the density of states near the Fermi level [17]. Since the density of states in the CCDW state is not known, we cannot directly interpret the value of n as due to the quasi-two-dimensionality of the structure.

Before discussing these data further, we indicate why localization of the carriers occurs. Localization occurs when the amplitude of the random part of the lattice potential becomes of the order of the occupied bandwidth [16]. The theories suggest that the conductivity at $T = 0$ will decrease with increasing disorder until, at a critical value, the conductivity will decrease discontinuously from σ_{MIN} to zero. The $T = 0$ conductivity will be zero for any disorder greater than this value, the conductivity approaching zero as the inverse of equation (1) as $T \rightarrow 0$. The temperature range for

which equation (1) is valid also increases with increasing disorder. In this regime the conductivity is due to variable range hopping of the carriers from one potential minimum to another. This localization due to random potentials is called Anderson localization [16].

The occupied bandwidth of 1T-TaS₂ is expected to be considerably smaller than the 2 eV calculated for undistorted 1T-TaS₂ because much of the Fermi surface is destroyed by band gaps. Even in 1T-TaSe₂ we estimate from the resistivity and susceptibility that the carrier density is only 1/10 that of the normal metal, where there is 1 electron per Ta atom. In 1T-TaS₂ the random potential must come from impurities and/or crystal defects. Typical impurities in the Ta used are 10 ppm Fe, 60 ppm Nb and 60 ppm W. Also, some iodine is included in the crystal during crystal growth, presumably substituting for sulfur. Crystalline defects can also be seen in electron microscopy (Fig. 10 of reference [1]), but their density or type has not been studied in any detail. Finally, we note that the Curie-like increase in the magnetic susceptibility of 1T-TaS₂ (and 1T-TaSe₂) at low temperatures (see Fig. 1, reference [1]) is most likely due to paramagnetic impurities such as Fe. The moment calculated from this Curie term is much too small to be due to Mott localization of the expected remaining 1 carrier per 13 Ta atoms.

We return to an analysis of the data of Figs. 2 and 3. We first assume it appropriate to analyze the data in terms of two-dimensional hopping, and later consider the three-dimensional case. When the temperature is above the variable range hopping regime a plot of $\ln \rho$ vs T^{-1} should extrapolate to $1/\sigma_{\text{MIN}(2D)}$ as T^{-1} approaches zero (see Fig. 3(a) of reference [16]). $\sigma_{\text{MIN}(2D)}$ is the minimum metallic conductivity in two dimensions. The theory suggests that $\sigma_{\text{MIN}(2D)}$ is related only to fundamental constants, and should be independent of material parameters at $\sigma_{\text{MIN}(2D)} = 2 \times 10^{-5}$ mhos per square per layer. Converting to a resistivity for this "multilayer sample" we obtain 3×10^{-3} ohm-cm. The value obtained from Fig. 2, using the data from 10 to 30 K, is 1.25×10^{-2} ohm-cm. This value is somewhat larger than that predicted, but recent experiments with MOS devices indicate that $\sigma_{\text{MIN}(2D)}$ may not be a universal constant [18].

As we previously pointed out the $n = \frac{1}{2}$ exponent may occur in three-dimensional variable range hopping, if the density of states has the proper energy dependence. While the density of states in the CCDW state is

not known, we expect the conductivity anisotropy to be only on the order of 10, as it is in other metallic layered compounds [19]. Because of this fact and the somewhat low value of $\sigma_{\text{MIN}(2D)}$ obtained, we next consider the three-dimensional model. In this case the plot of $\ln \rho$ vs T^{-1} should extrapolate to a value greater than $1/\sigma_{\text{MIN}(3D)}$ (see Fig. 3(b), reference [14]). Within the theoretical models, $\sigma_{\text{MIN}(3D)}$ will depend on sample parameters. In one model $\sigma_{\text{MIN}(3D)} = (600/a)$ ohm⁻¹ cm⁻¹, where a is the separation between localizing centers (in Å). For our samples, the average impurity separation is about 60 Å giving $1/\sigma_{\text{MIN}(3D)} = 10^{-1}$ ohm-cm, an order magnitude greater than the experimental intercept of $\ln \rho$ at $T^{-1} = 0$. Considering the uncertainty of calculating $\sigma_{\text{MIN}(3D)}$, we cannot rule this possibility out.

If the three-dimensional model applies, $\sigma_{\text{MIN}(3D)}$ should not be much greater than 80 ohm⁻¹ cm⁻¹, since variable range hopping sets in only below 2 K. We then conclude that the experimental σ_{MIN} of 1T-TaS₂ is on the order of 10^2 ohm⁻¹ cm⁻¹, independent of the dimensionality of the hopping. We are still unable, however, to explain the great difference in properties of 1T-TaS₂ and 1T-TaSe₂, since the latter is expected to have impurity and defect levels similar to the former.

It seems likely that this same localization mechanism is also responsible for the much larger increase in resistivity at low temperatures of the mixed anion compounds 1T-TaS_{2-x}Se_x ($x \leq 0.6$) [10], where the anion disorder will add to the impurity and defect potentials. It is also known that cation disorder produces localization, as in the 1T-Ta_{1-x}Fe_xS₂ compounds, where the transition at T_d has been eliminated [20]. Finally, we comment on the specific heat of 1T-TaS₂. At low temperatures the specific heat increases over the $C = \gamma T + \beta T^3$ extrapolated from above 3 K [21]. This excess specific heat may be related to the random potential. We also note that the electronic specific heat coefficient γ obtained is similar to that of 1T-TaSe₂ [22], whose resistivity is two orders of magnitude lower. The present results as well as those published [10, 20] indicate that the electrical properties of 1T-TaS₂ are particularly sensitive to disorder.

In conclusion, we have shown that the low temperature resistivity of 1T-TaS₂ is extrinsic. The low temperature resistivity is characterized by variable range hopping in the random potential of impurities or defects.

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