Paramagnetic moments and localization in 1T-TaS_2

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The low-temperature magnetic susceptibility of 1T-TaS_2 is shown to have a contribution from localized paramagnetic moments that are not due to impurities. The density of paramagnetic moments increases as the preparation temperature is increased. This suggests that the moments are due to interstitial defects (intercalated Ta atoms). In some samples a weak remanent magnetization is observed below 4 K as the magnetic field is reduced toward zero, suggesting spin-glass-like ordering of the moments. Since the low-temperature electrical resistivity is dominated by Anderson localization, the magnitude of the resistivity at low temperatures also increases with increasing preparation temperature due to a higher defect density. These results are compared to recently proposed models.

I. INTRODUCTION

The low-temperature properties of 1T-TaS_2 have been the object of recent experimental and theoretical studies. This interest grew from the observation of a hoppinglike electrical resistivity (ρ) below approximately 2 K,[1] that fits the form

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

(with $n = \frac{1}{3}$). Other studies of the Hall effect,[2,3] magnetoresistance,[4,5] and nonlinear conductivity[6] have further illuminated this unusual low-temperature behavior. These experiments lead to the development of several different theoretical models.[7–9] Fazekas and Tosatti[7] propose that a Mott transition occurs when the charge-density wave (CDW) becomes commensurate at 200 K. This model requires a large Mott-Hubbard electron-electron intrasite repulsion U. Fukuyama and Yosida,[8,9] focusing on the low-temperature (<20 K) properties, proposed the existence of a small U in order to explain the low magnetic field behavior of the magnetoresistance. In both models, a nonzero U produces singly occupied states that are generally expected to be paramagnetic. These paramagnetic moments would be intrinsic to 1T-TaS_2 and their density would depend upon the magnitude of U. A temperature-dependent paramagnetic contribution to the susceptibility (Curie contribution) has been previously reported[10]; however, it was then believed that this contribution was due to impurities. In this paper we show conclusively that the Curie contribution is not due to impurities but rather to atomic defects and thus is not intrinsic to 1T-TaS_2. Our data suggest that the low-temperature properties are completely determined by these defects.

II. SAMPLE PREPARATION

Several different samples were prepared for this study. The first was a powder sample prepared from 99.999%-purity Ta sheet and 99.9999%-purity S by reaction in a sealed quartz tube at 950 °C in excess S ($\approx$1 mg/cm^3), annealed at 750 °C for 3 days, and quenched into water. The same part of the sample that was used for susceptibility measurements was spectroscopically analyzed for impurities. Those found were: Fe (5–10 ppm), Ni (1–5 ppm), Mg (1–5 ppm), Cu (1–5 ppm), and Al (5–10 ppm). A second sample consisted of ten single crystals of 1T-TaS_2 glued together so that the basal planes of each were parallel. These crystals were prepared from 99.95% purity Ta and 99.999% purity sulfur by iodine vapor transport (again with 1 mg/cc excess sulfur) at a growth temperature of 750 °C. The crystals were quenched into water from the growth temperature to maintain the metastable 1T polymorph. Several other powder samples were prepared at temperatures between 750 and 1000 °C from 99.95% pure Ta and 99.999% pure S and quenched into water from the preparation temperature.

III. MAGNETIC MEASUREMENTS

The magnetic susceptibility of the high-purity sample prepared at 750 °C is shown from 4.2 to 300 K in Fig. 1. The sharp decrease in susceptibility near 200

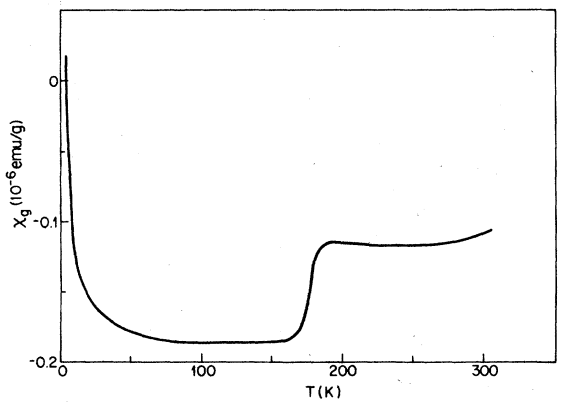

FIG. 1. The magnetic susceptibility of high-purity 1T-TaS_2 powder annealed at 750 °C is shown from 4.2 to 300 K.

K is due to an incommensurate-to-commensurate charge-density wave transition.[11–13] Here we focus on the Curie-like increase observed in the susceptibility (χ_g) below 100 K. These data were fitted to the Curie-Weiss form from 6 to 85 K

$$\chi_g = \frac{C_g}{T+\Theta} + \chi_0 \ . \tag{2}$$

The parameters determined by a least-squares fit are: $C_g = 0.806 \times 10^{-6}$ emu K/g, $\chi_0 = -0.196 \times 10^{-6}$ emu/g, and $\Theta = -0.4$ K. Below 4 K the susceptibility is magnetic field dependent. For example, at 4.2 K the magnetization per gram $\sigma_P \equiv (\chi - \chi_0)H$ is slightly nonlinear in the magnetic field H, so that σ_P (12.8 kG) is about 4% lower than that extrapolated from lower fields. Below 4.2 K the susceptibility deviates considerably from Eq. (2), the measured susceptibility at 12.8 kG is lower than that calculated from Eq. (2). This is easily seen in Fig. 2 where $(\chi - \chi_0)^{-1}$ is plotted versus T. The nonlinearity is also quite evident at 1.45 K in σ_P vs H as shown in Fig. 3. At each data point the magnetic field is turned on then off, and the data were obtained successively from the highest to the lowest field. The curve in Fig. 3 is suggestive of paramagnetic saturation; however, the nonzero value of σ_P obtained by extrapolating to $H = 0$ is not consistent with such a simple picture. Before discussing these data further we present data for the other samples.

In Fig. 4 the magnetic susceptibility of the single-crystal sample is shown for the magnetic field parallel and perpendicular to the TaS_2 layers. While 1T-TaS_2 is nominally hexagonal, the presence of the commensurate CDW below 200 K lowers the symmetry to triclinic.[12,14] Consequently, the measured susceptibilities are not the principle values; nonetheless, anisotropy is apparent. This anisotropy appears to be connected mainly with an anisotropy in χ_0 of Eq. (2). Indeed a least-squares fit to the data from 6 to 85 K gives $C_g = +0.69 \times 10^{-6}$ emu K/g for H parallel to the layers and $C_g = +0.72 \times 10^{-6}$ emu K/g for H perpendicular to the layers. In both directions we find $\Theta = +0.6$ K. The values of the Curie constant C_g are about 12% lower than those obtained from the powder sample, and the Θ value is slightly positive rather than negative as for the powder sample. At 1.45 K σ_P is again nonlinear as seen in Fig. 5, but only when H is parallel to the layers does σ_P extrapolate to a nonzero value as $H \to 0$. This extrapolated value is lower than that obtained in the powder sample (Fig. 3) by about a factor of 3.

In an attempt to measure the g value of these paramagnetic moments an electron-spin resonance (ESR) signal at 12 GHz was searched for at 77, 4.2, and 1.6 K in one of the single crystals used to obtain the data of Figs. 4 and 5. No signal was observed over the range of applied magnetic fields, which was

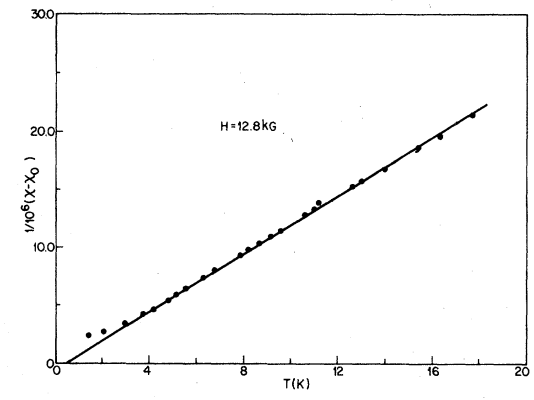

FIG. 2. A plot of the reciprocal susceptibility corrected for the diamagnetic contribution from 1.45 to 20 K shows the deviation from the simple Curie-Weiss behavior below 4.2 K.

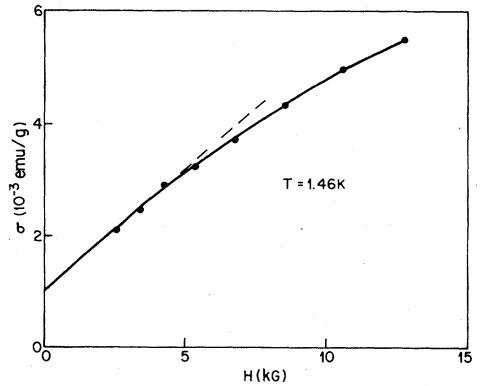

FIG. 3. The corrected magnetization $\sigma_P \equiv (\chi - \chi_0)H$ also shows nonlinear behavior at 1.45 K and an extrapolated nonzero magnetization as H approaches zero.

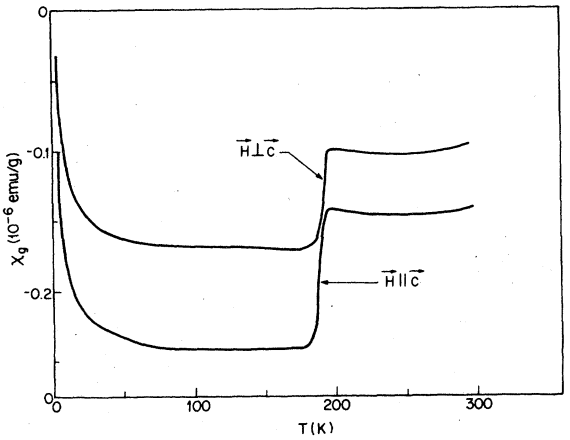

FIG. 4. The magnetic susceptibility of 1T-TaS_2 crystals with the field parallel and perpendicular to the c axis of the simple 1T-TaS_2 structure is shown from 4.2 to 300 K.

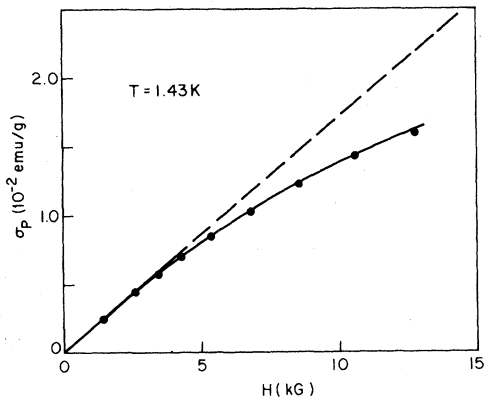

FIG. 6. The magnetization of 1T-TaS_2 powder prepared at 1000 °C shows nonlinear dependence on H at 1.43 K, but no apparent remanent magnetization as H approaches zero.

varied from zero to a maximum value so that states with $g \approx \infty$ down to $g \sim 0.18$ could be detected. This implies that the linewidth is larger than 5×10^3 G (for the noise levels in this spectrometer) or that $g < 0.18$. Large linewidths imply rapid spin-lattice relaxation, not an unlikely possibility, since Ta has a large spin-orbit interaction.

As is clear already from the data of Figs. 1 through 5 the susceptibility results are sample dependent. Consequently we examined the susceptibility of samples prepared at different temperatures. The susceptibility of a powder sample prepared at 1000 °C shows a larger Curie contribution than those prepared at 750 °C. The parameters of Eq. (2) obtained by a least-squares fit for a sample prepared at 1000 °C are: $C_g = 2.93 \times 10^{-6}$ emu/g, $\chi_0 =$ K/g, $\chi_0 = -0.194 \times 10^{-6}$ emu/g, and $\Theta = 0.3$ K. While Θ and χ_0 are similar to the previous results, the density of paramagnetic moments has increased by approximately a factor of 4. However, in contrast to the samples prepared at 750 °C, a plot of σ_P at 1.43 K shows no indication of a remanent magnetization as $H \rightarrow 0$ (Fig. 6).

While the density of paramagnetic defects increases with increasing preparation temperature, the data of Fig. 7 also indicate that the low-temperature resistivi-

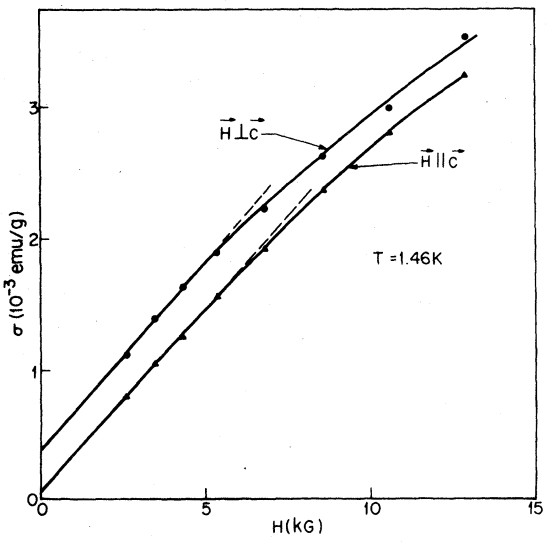

FIG. 5. The magnetization of 1T-TaS_2 crystals at 1.45 K shows nonlinear dependence upon the applied field, but only shows an extrapolated nonzero magnetization when H is parallel to the layers (i.e., $\vec{H}\perp\vec{c}$).

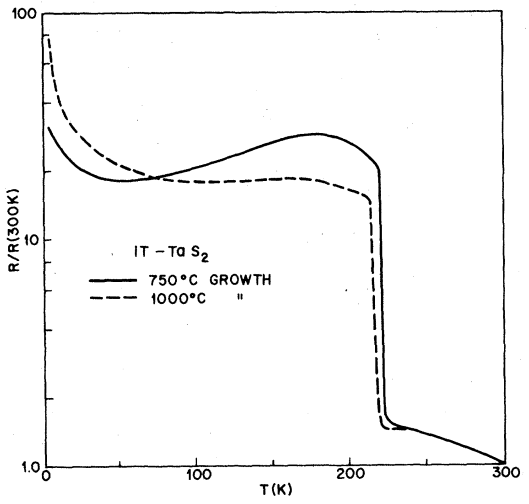

FIG. 7. 1T-TaS_2 crystals prepared at 1000 °C show a higher basal-plane resistivity at low temperatures than those prepared at 750 °C due to the higher defect density produced at the higher growth temperature (data taken with temperature increasing).

ty of $1T$-TaS_2 crystals grown at 1000 °C is higher than that of those grown at 750 °C. Since the increase in resistivity at low temperatures was previously shown to be due to random potentials[1] and since the resistivity increases with increasing preparation temperature, it appears that the paramagnetic defects observed in magnetic susceptibility are also responsible for the localized behavior seen in electrical transport properties. [One note of caution—as the defect density increases, the transition near 200 K becomes sluggish. Single crystals grown at 750 °C in excess S transform fully on cooling through the transition at rates of 1 to 2 K/min. Crystals grown at 1000 °C, however, must be cycled between a low temperature ($\approx$50 K) and 200 K several times before the transformation to the commensurate CDW (CCDW) state is complete. Such cycling was also necessary to obtain full transformation of the powder sample prepared at 1000 °C and studied by magnetic susceptibility.]

IV. DISCUSSION

Consider first the results from the high-purity powder sample prepared at 750 °C (Figs. 1–3). The measured Curie constant is too large to be accounted for by the observed impurities. It was previously shown that Fe substituted for Ta in $1T$-TaS_2 is nonmagnetic at low temperatures.[15] Due to the excess sulfur present during preparation it is very unlikely that the Fe is intercalated, although in that case it would have an effective moment of $\approx 5\mu_B$ per Fe.[16] As a worst case, however, we can assume that there is 10 ppm of Fe with a moment of $5\mu_B$. Also we can assume 5 ppm of Ni at $2.8\mu_B$ and 5 ppm of Cu at $1.7\mu_B$. This would lead to an absolute upper bound on an impurity-induced Curie constant of $C_g = +0.15 \times 10^{-6}$ emu K/g, a value that is more than a factor of 5 lower than that observed. Clearly, these impurities cannot be the source of the Curie contribution. Further, the Curie constant obtained from samples prepared from Ta 50 times less pure, such as the single crystals discussed here or in previous work,[10] are closely similar when the samples are prepared at the same temperature. Obviously the majority of impurities in Ta is nonmagnetic in $1T$-TaS_2. If these magnetic moments are *not* due to impurities, they must be due to defects in the sample or some mechanism intrinsic to $1T$-TaS_2. Since the results are dependent upon the preparation temperature, it seems most likely that the Curie contribution is due to paramagnetic defects. A parallel may be drawn to the structually related layered compounds $1T$-VSe_2 and VS_2. The compound VSe_2 may be more accurately described as $V_xV_{1-y}Se_2$ where x equals the concentration of interstitial (intercalated) V atoms and y equals the vacancy concentration in the normally full V layer. Detailed chemical studies show that x and y both increase with increasing preparation temperature, even in the presence of excess Se to values of several percent at 1000 °C.[17] Further, it is well established that paramagnetic moments are associated with the intercalated V atoms,[18–20] although this moment may be partially delocalized.[21] Since $1T$-TaS_2 and $1T$-VSe_2 or VS_2 are structually similar and since the Curie contribution increases with increasing preparation temperature in both $1T$-TaS_2, and $1T$-VSe_2, it seems very likely that interstitial and vacancy defects similar to those observed in $1T$-VSe_2 exist in $1T$-TaS_2 and that these produce the paramagnetic moments observed here.

We have attempted to estimate the density of the paramagnetic moments in $1T$-TaS_2 in several ways. The Curie constant C_g of Eq. (2) is given by $Ng^2S(S+1)/3k$ where N is the density of moments per gram, g is the gyromagnetic ratio, S is the spin, and k is the Boltzman constant. Consequently, S, N, and g cannot be individually determined from this experiment alone. Without ESR data, some assumptions about the nature of the moments need be made. If we assume the nonlinearity in Fig. 6 is entirely due to paramagnetic saturation, we can estimate the g value assuming a spin by comparing the data to the Brillouin function.[22] We find that if $S = \frac{1}{2}$, $g \sim 1.4$. This would lead to a density of paramagnetic moments of about one in 2×10^3 Ta atoms in the sample prepared at 1000 °C. This number is within a factor of 2 or 3 of the density of carriers determined from the Hall effect assuming a one-carrier model.[2,3] If these moments are indeed associated with interstitial Ta defects, their density is more than an order of magnitude lower than in VSe_2 (Ref. 17) prepared at the same temperature. On the other hand, the data of Fig. 3 suggest the paramagnetic saturation may not be an adequate explanation of the nonlinearity of σ_P vs H, at least in some samples, since there appears to be a remanent magnetization in some cases. Since there is such a large spin-orbit interaction in Ta, the g value may be quite small (even zero) or could easily be as large as four. Consequently, without further information it would be difficult to even semiquantitatively determine the density of paramagnetic defects.

The apparent remanent magnetization is also sample dependent. It seems particularly puzzling that no remanent magnetization is observed in the sample with the largest concentration of paramagnetic moments. The Θ values obtained by fitting to Eq. (2) are quite small for all samples, suggesting that to where remanent magnetization is observed, it is due to a spin-glass-like arrangement of the moments. However, in light of the large difference in results for

different samples, further speculation is unwarranted.

Finally we discuss these data in light of the two models that have been proposed to explain the low-temperature properties of $1T$-TaS_2. Fazekas and Tosatii[7] propose that a Mott transition occurs when the CDW becomes commensurate at 200 K and that one electron is localized on each 13-atom Ta cluster that forms in this state.[14] This localized electron would have a paramagnetic moment and produce a Curie tail in the susceptibility. Assuming negligible exchange interactions, and using the above density of moments and assuming $S=\frac{1}{2}$, we find from our values of C_g that $g<0.25$. However, since the values of C_g are sample dependent and appear to be related to defects, the g value of the electron localized in 13 Ta atom clusters must be much smaller (say less than 0.1), if this model is correct. Alternatively, one could suppose that the localized moments have an exchange interaction energy on the order of or greater than 200 K, so that little temperature dependence would be observed at low temperatures. Well below the Mott transition, gaplike behavior is expected in the resistivity [i.e., $n=1$ in Eq. (1)]. However, the gaps obtained from resistivity[1-6,23] are very small ($\approx$20 K). Such a small Mott-Hubbard gap is not impossible, but our magnetic data suggest an alternative view. If this Mott model is correct, the defects seen here would produce carriers (holes and/or electrons) in the lower or upper Mott band. These carriers become localized at low enough temperatures ($T \lesssim 3$ K) due to the random potential of the defects, and show an activated behavior in an intermediate temperature range (3 K $\lesssim T \lesssim$ 20 K) due to the difference between the mobility edge and the Fermi energy, and finally show "unimpeded" motion at higher temperatures (20 k $\lesssim T \lesssim$ 200 K). Thus within this model the defects explain both the sample and preparation dependence of the localized behavior at low temperatures and the absence of a measurable Mott-Hubbard gap below 200 K.

The second model by Fukuyama and Yosida[8,9] focuses on the low-temperature ($\lesssim$20 K) properties. They first were able to semiquantitatively explain the observed magnetoresistance by considering the effect of magnetic field induced Zeeman splitting of the states in the region near the Fermi energy and the mobility edge. In a later publication[24] they have also included the possibility of a magnetic dependence to the mobility edge. These models are able to explain much of the low-temperature experimental data. However, in an attempt to explain a few discrepancies at low magnetic fields, they also proposed[9] that the states near the Fermi level were singly occupied due to a small Mott-Hubbard electron-electron repulsion energy (U), whose magnitude was on the order of 20 K. If this were the case, the singly occupied states would be paramagnetic and would lead to an intrinsic Curie contribution to the susceptibility. This suggestion of a small U is different from the picture of Fazekas and Tosatti in which a large U is responsible for the tenfold increase in resistivity at the 200-K transition to the commensurate CDW state. Our present experiments as well as other data suggest that the small U model is incorrect, as we point out next.

In the small U model, the number of singly occupied states is proportional to the density of states at the Fermi level times U. Within this model, however, it is difficult to explain why the results of both magnetic and electrical measurements[1-6,23] should be sample (or preparation) dependent. That is, U should be an *intrinsic* property of the material. Also, the aptness of this model hinges upon estimating a correct value of U. Fukuyama and Yosida[9] estimate U independent of the transport properties by using the magnitude of the Curie contribution and the density of states near the Fermi level obtained from the specific heat. For $1T$-TaS_2, however, there is some difficulty in interpreting the specific-heat data. In most nonsuperconducting metals the low-temperature specific heat is given by $C/T=\gamma+\beta T^2$ [Eq. (3)], where the electronic specific-heat coefficient γ is proportional to the density of states at the Fermi energy. However, the low-temperature specific heat of $1T$-TaS_2 and of $1T$-TaS_2 is not fitted by such a simple form rather there is "excess" specific heat at low temperatures. Also the measured specific heat is *sample dependent* for $1T$-TaS_2.[25,26] In semimetallic $1T$-TaS_2 the low-temperature specific heat follows Eq. (3) from 4 to 10 K (Ref. 27) (a factor of 6 in T^2). The value of γ used by Fukuyama and Yosida[9] (2.0 mJ/mole K^2) for $1T$-TaS_2 was extracted from data presented only up to 5 K.[18] However, data up to 10 K (Ref. 25) do not fit Eq. (3) over any large temperature interval. Consequently, the value of γ given in Ref. 26 may be rather unreliable. Further, the γ value obtained from $1T$-$TaSe_2$ (from 4 to 10 K) is only 0.3 mJ/mole K^2.[27] It seems unlikely that $1T$-TaS_2 would have a γ value almost an order of magnitude larger than that of $1T$-$TaSe_2$.

V. SUMMARY

We experimentally show that the Curie contribution to the susceptibility of $1T$-TaS_2 is not due to impurities, but rather to defects whose density increases with increasing preparation temperature. Since no ESR signal could be observed, an accurate determination of the density of magnetic centers is not possible. However, if we assume that $g\approx 2$, their density is on the order of one in a thousand Ta atoms. In some samples there appears to be a remanent magnetization at 1.45 K at $H\rightarrow 0$, suggesting a spin-glass-like arrangement of the spins. The wide variation in reported electrical properties of samples

prepared under different conditions also supports a defect model. At present, the best description of 1*T*-TaS_2 appears to be given a combination of the Fazekas and Tosatti model[7] and the small mobility gap model of Fukuyama and Yosida[6] (excluding their suggestion of a small U[9]). The carriers as well as the random potentials are supplied by the defects. Further work to determine their exact density, g value, and magnetic structure at low temperatures (<1 K) is clearly desirable.

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