

## Transport properties and the phase transition in $Ti_{1-x}M_xSe_2$ ( $M = Ta$ or $V$ )

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The transport properties of semimetallic  $TiSe_2$  are reexamined, and the limits of a two-band model are discussed. We conclude that the density of electrons and holes is  $5 \times 10^{20}/cm^3$  to  $10 \times 10^{20}/cm^3$ , in agreement with recent photoemission data. The second-order phase transition at 202 K in  $TiSe_2$  is suppressed by cation substitution with Ta or V. In both cases, about 7% substitution completely eliminates the transition. However, while Ta appears to donate carriers in the rigid-band sense, V has a magnetic moment which is concentration and temperature dependent. Furthermore, at low V concentrations the resistivity diverges at low temperatures, in contrast to the metallic behavior of the Ta-doped samples. The data suggest that the cation disorder is the major cause of suppression of the transition. Since the disorder is not directly related to the carrier density, we are unable to draw conclusions from these data concerning a possible electron-hole coupling mechanism to drive the transition.

It is now well established that a low-temperature, second-order phase transition occurs in the semimetal  $TiSe_2$ , below which the hexagonal  $a$  and  $c$  axes are doubled.<sup>1-5</sup> In the most stoichiometric materials this transition occurs close to 200 K. Several mechanisms of transformation have been proposed,<sup>1-5</sup> but the data are not sufficient to uniquely identify which is operative. It is known that the transition temperature  $T_0$  is suppressed by cation and anion substitution<sup>1-4</sup> and nonstoichiometry,<sup>1</sup> but a systematic study of the effects of cation substitution is lacking. Here we wish to present some new data and to further discuss transport measurements in  $TiSe_2$ .

In this paper we first consider the question of carrier densities and mobilities in  $TiSe_2$ . Then we present resistivity and magnetic susceptibility data for  $Ti_{1-x}M_xSe_2$ , where  $M=Ta$  or  $V$ . The properties of these cation-substituted alloys change rapidly with increasing  $x$ . At small  $x$ , V appears to form a local moment, while Ta does not. The onset temperature to the superlattice state is reduced with increasing  $x$ , at least partly due to the cation disorder. Because of the effects of disorder, these new data are still unable to unambiguously identify the mechanism of superlattice formation.

The samples were prepared from 99.9999% pure Se and 99.99% pure Ti (the dopants V and Ta were 99.9% pure). Powder samples were first prepared by reaction at 600 °C in a small excess of Se (1 mg excess per  $cm^3$  of reaction volume in a sealed evacuated quartz tube). These powder samples were homogenized in two subsequent steps. Each step consisted of grinding the reacted powder, pressing it into a pellet at 40 000 psi, and reheating it to 600 °C. Single crystals were grown by iodine vapor transport from these powders, again in excess Se of 1 mg/ $cm^3$ , to a growth temperature of 590 °C. We previously established that the most

stoichiometric  $TiSe_2$  (Ref. 1) and  $VSe_2$  (Ref. 6) are obtained at the lowest growth temperatures, 590 °C being the lowest consistent with reasonable growth rates.

### I. $TiSe_2$

In a previous paper,<sup>1</sup> we presented resistivity and Hall coefficient ( $R_H$ ) data from which we estimated a carrier concentration by assuming a carrier mobility of 15  $cm^2/V$  sec at 200 K. This procedure gave  $n_e = n_h = 10^{20}/cm^3$ . A better estimate can be obtained in the following way. The product of conductivity and Hall coefficient in a simple two-band model (which we assume applies here—discussion of this point comes later) is given by<sup>7</sup>

$$\sigma R_H = \frac{\mu_h}{c} \left( \frac{1 - (n_e/n_h)(\mu_e/\mu_h)^2}{1 + (n_e/n_h)(\mu_e/\mu_h)} \right), \quad (1)$$

where  $\mu_h$  and  $\mu_e$  are hole and electron mobilities, respectively. Since by definition  $\mu_h$  and  $\mu_e$  are positive, the quantity in large parentheses is less than or equal to one. When  $R_H$  is positive, we obtain then a *lower bound* on  $\mu_h \geq c\sigma R_H = \mu^*$ . Similarly when  $R_H$  is negative, Eq. (1) can be recast in a similar form to give a lower bound on  $\mu_e \geq |c\sigma R_H|$ . Using these bounds, *upper limits* on the number of carriers can be obtained from

$$\sigma = |e|(n_h\mu_h + n_e\mu_e), \quad (2)$$

by defining  $n^*$  from

$$\sigma = |e|n^*\mu^*. \quad (3)$$

Here  $n^*$  will be an upper limit on the density of holes (electrons) when  $R_H$  is positive (negative). Next we present transport data on our purest  $TiSe_2$  (iodine transported) and calculate  $n^*$  vs temperature.

The electrical resistivity (current parallel to the

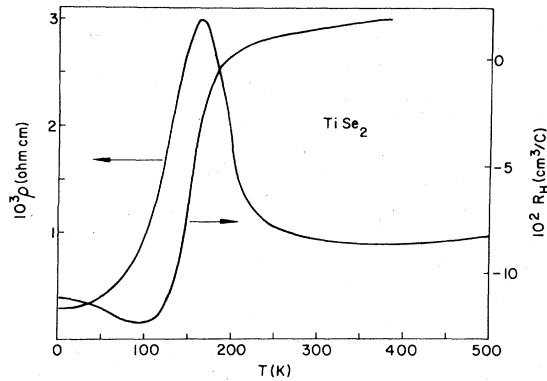


FIG. 1. Electrical resistivity and the Hall coefficient with the current parallel to the layers for a  $\text{TiSe}_2$  single crystal.

layers) and Hall coefficient (current parallel and magnetic field perpendicular to the layers) for  $\text{TiSe}_2$  are shown in Fig. 1. By carefully measuring sample dimensions and using thin voltage contacts on a number of samples, we have determined  $\rho(295 \text{ K}) = 0.95 \times 10^{-3} \Omega \text{ cm} \pm 5\%$ . This value is lower than our original estimate of  $\approx 1.15 \times 10^{-3} \Omega \text{ cm}$ . Above 450 K the resistivity increases linearly with temperature up to 700 K, and  $d\rho/dT = 5.6 \times 10^{-7} \Omega \text{ cm/K}$ . This increase is small when the logarithmic derivative is compared to metals, even other layered compounds. For example, at 450 K  $d(\ln\rho)/dT = 6.0 \times 10^{-4} \text{ K}^{-1}$  for  $\text{TiSe}_2$ , but is  $1.5 \times 10^{-3} \text{ K}^{-1}$  for  $2H\text{-TaSe}_2$  and  $2.4 \times 10^{-3} \text{ K}^{-1}$  for Cu.

Figure 2 shows  $|\sigma R_H|$ , converted to practical

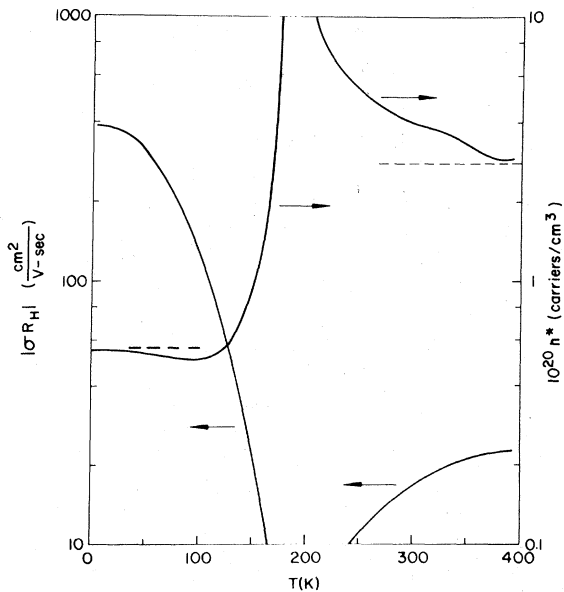


FIG. 2. Lower limit of carrier mobility  $|\sigma R_H|$  and the upper limit of carrier density  $n^*$  are shown versus temperature.

units for mobility, and  $n^*$  from Eq. (3). We expect  $n^*$  to be much larger than the actual density when  $\mu^*$  (i.e.,  $R_H$ ) goes through zero. When the temperature is well above  $T_0$ , we expect the actual density of carriers to be constant or perhaps to increase somewhat with increasing temperature due to thermal excitation of extra carriers. Thus the lowest value of  $n^*$  obtained above  $T_0 \approx 200 \text{ K}$  is the most realistic upper bound on  $n_e$  or  $n_h$ . From Fig. 2 the value obtained at the highest temperature of measurement is  $n^* = 2.8 \times 10^{20}/\text{cm}^3$ .

The data at 4.2 K yield  $n^* = 0.56 \times 10^{20}/\text{cm}^3$  and  $\mu^* = 390 \text{ cm}^2/\text{V sec}$ . From these data and those above  $T_0$ , we can estimate the fraction of carriers lost due to the transition at 200 K as

$$[n^*(380 \text{ K}) - n^*(4.2 \text{ K})]/[n^*(380 \text{ K})] = 0.8.$$

These data show that substantial portions of the Fermi surface are lost due to gap formation in the superlattice state and are consistent with recent  $\text{Se}^{77}$  NMR measurements,<sup>8</sup> changes in the free-carrier plasma frequency,<sup>9</sup> and the low-temperature electronic specific heat.<sup>10</sup>

What are the limits of this analysis? The first has to do with the  $\text{TiSe}_2$  itself. We know that iodine, used in the crystal growth, is incorporated at about 0.3 at.%,<sup>1</sup> or about  $0.4 \times 10^{20}$  iodine atoms/ $\text{cm}^3$ . If compensating Ti vacancies are not induced, each iodine is expected to donate one electron to the bands, increasing  $n_e$  and decreasing  $n_h$ . We estimate that  $n_e - n_h/n_e \approx 0.1$  from this donation. It is also possible that defects, similar to those proposed to exist in  $\text{TiS}_2$ ,<sup>2,11</sup> could change the ratio of electrons and holes. However, at present we have no way of measuring the density of these defects. (We return to this difficulty in Sec. III.)

A second problem with this analysis is the use of a simple two-band model. In particular, Kukkonen<sup>12</sup> has pointed out that electron-hole scattering will contribute to degrading the current and thus reduce the mobility for conductivity, but such scattering will not effect the Hall mobility. If electron-hole scattering dominates other relaxation processes, Eqs. (1) and (3) will underestimate  $n^*$ . At present we are unable to accurately ascertain this effect, but  $n_e = n_h \approx (5-10) \times 10^{20}/\text{cm}^3$  is possible.

If the carrier concentrations are this high, the occupied portion of the conduction band may be visible in photoemission data. The valence band x-ray photoelectron spectra of  $\text{TiSe}_2$  obtained with a Hewlett Packard 5950A Spectrometer using Al  $K\alpha$  radiation are shown in Fig. 3. The leading edge of the  $p$  bands usually decreases smoothly in group-IVb layered semiconductors such as  $\text{ZrS}_2$  (dashed portion of the curve). The extra lump near  $E = 0$  is most likely due to the conduction electrons in the  $d$  band. We estimate the occupied conduction band

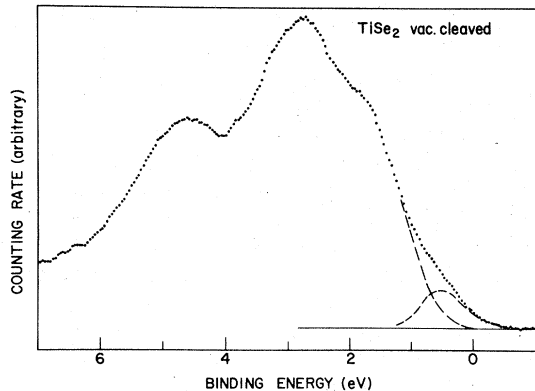


FIG. 3. X-ray photoelectron spectra (XPS) of  $\text{TiSe}_2$  showing the upper edge of the Se valence band. The Fermi level is taken as the zero of binding energy. The dashed lines show an approximate deconvolution of the emission from the  $p$  valence band and the partially occupied  $d$  conduction band.

width as  $\approx 0.25$  eV by the difference between the dashed curve and the data. This number has large uncertainty because the resolution of this apparatus is on the order of 0.5 eV. The large width of the  $d$  band emission is most likely due to the resolution and is sensitive to the shape assumed for the  $p$  band edge. Recent angle-resolved uv photoemission measurements with higher energy resolution yield a better value, i.e.,  $E_F^{(e)} \approx 0.1$  eV.<sup>13</sup> By comparison to band-structure calculations for  $1T\text{-TaS}_2$ ,<sup>14</sup> or  $\text{TiS}_2$ ,<sup>15</sup> we estimate from the above band width that  $n_e \sim 5\text{--}10 \times 10^{20}/\text{cm}^3$ . These values of  $n_e$  and  $E_F^{(e)}$  are an order of magnitude higher than our original estimate.<sup>1</sup>

## II. $\text{Ti}_{1-x}\text{M}_x\text{Se}_2$ ( $M = \text{Ta}$ or $\text{V}$ )

Previous studies showed that the transition temperature of  $\text{TiSe}_2$  is suppressed by cation substitution with Ta.<sup>3,4</sup> However, these crystals were grown above 600 °C, where nonstoichiometry is known to result.<sup>1</sup> The resistivity of  $\text{Ti}_{1-x}\text{Ta}_x\text{Se}_2$  crystals (parallel to the layers) grown at 590 °C is shown in Fig. 4. With increasing  $x$ , both the transition temperature and the magnitude of the resistive anomaly are reduced, so that at  $x=0.07$  the transition is not visible in the resistivity. The transition temperature, determined from the resistivity slope as described previously,<sup>1</sup> decreases initially at  $dT_0/dx = 18 \pm 3$  K/at.%. Magnetic susceptibility measurements show these compounds to be weakly diamagnetic or paramagnetic. No local moments are observed in these measurements, beyond that due to a small amount of Fe impurity (50–80 ppm). This implies that the remaining  $d$  electron of the  $\text{Ta}^{4+}$  is delocalized into the Ti  $d$  band, increasing  $n_e$  and decreasing  $n_h$  (in

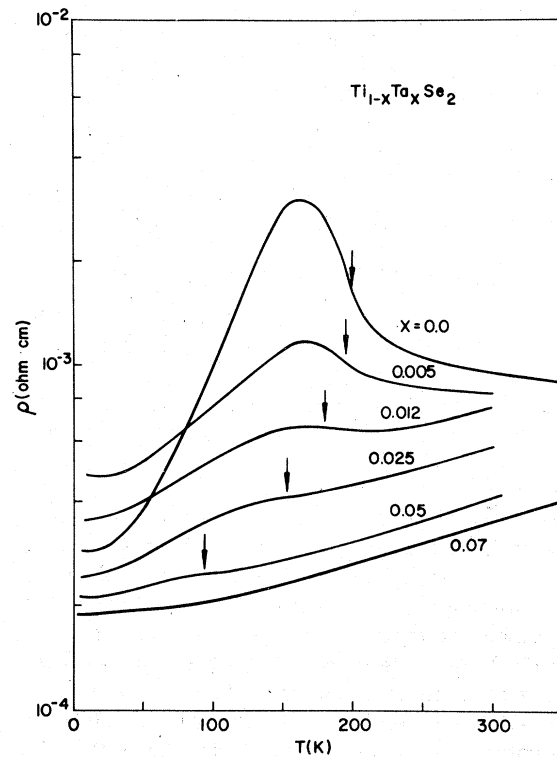


FIG. 4. Electrical resistivity of  $\text{Ti}_{1-x}\text{Ta}_x\text{Se}_2$  single crystals with the current parallel to the layers shows the rapid suppression of the phase transition with increasing  $x$ . The arrows mark the transition temperature.

the rigid-band approximation).

Similar resistivity measurements of  $\text{Ti}_{1-x}\text{V}_x\text{Se}_2$  single crystals (parallel to the layers) show quite different results, as shown in Fig. 5. At low concentrations of V, the resistivity increases rapidly at low temperatures; the largest increase occurs near  $x=0.01$ . The low-temperature resistivity near  $x=0.01$  is very sensitive to small changes in concentration. Several samples from the same growth batch, having the same V concentration to within measurement error ( $\pm 20\%$ ), show the same resistivity above 200 K. However, the resistivity can differ by a factor of 2 by 77 K and at 4.2 K can be larger than that shown in Fig. 5 by several orders of magnitude. The measurements suggest that  $T_0$  is reduced in these samples at nearly the same rate as for Ta, since the transition is no longer apparent when the V concentration is greater than 0.075.

Magnetic susceptibility measurements (Fig. 6) by the Faraday method on powder samples show that the V atoms have a magnetic moment. However, the moment per vanadium atom decreases with increasing concentration and the effective mo-

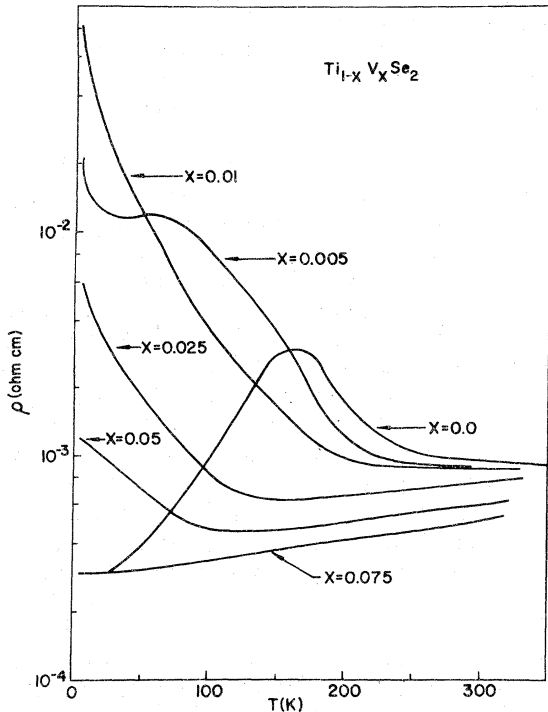


FIG. 5. Electrical resistivity of  $\text{Ti}_{1-x}\text{V}_x\text{Se}_2$  single crystals with the current parallel to the layers shows a low-temperature divergence when  $0.005 < x < 0.3$ .

ment appears to be temperature dependent (Table I). Because of this temperature dependence, the susceptibility does not fit the simple Curie-Weiss form [Eq. (4)] over the entire range of measurement:

$$\chi = \chi_0 + (N\mu_{\text{eff}}^2)/[3k(T + \Theta)]. \quad (4)$$

The effective moment  $\mu_{\text{eff}}$  appears to decrease smoothly as the temperature is decreased below  $T_0$ . Table I lists  $\mu_{\text{eff}}$  for  $T > 250$  K determined from Eq. (4) with  $\Theta = 0$  and  $\mu_{\text{eff}}$  when  $100 > T > 10$  K with a  $\Theta$  determined in this region. The values of  $\mu_{\text{eff}}$  in Table I are not corrected for Fe impurities. At the lowest vanadium concentration these impurities account for 10–15% of the given  $\mu_{\text{eff}}$ . Studies on single crystals show that  $\mu_{\text{eff}}$  is anisotropic with  $\mu_{\text{eff}}(\vec{H} \perp \vec{c})/\mu_{\text{eff}}(\vec{H} \parallel \vec{c}) \approx 1.07$ . The effective moments of Table I are obtained assuming that the host susceptibility is temperature independent. This is certainly not the case for pure  $\text{TiSe}_2$ ,<sup>1</sup> and we expect the vanadium to change this temperature dependence at least by suppressing the transition temperature. For this reason the effective moments listed in Table I may be somewhat in error, especially at low vanadium concentrations and at higher temperatures ( $T > 250$  K).

While the measured moments and anisotropies at  $x = 0.01$  are consistent with a localized  $d^1 V^{4+}$  in

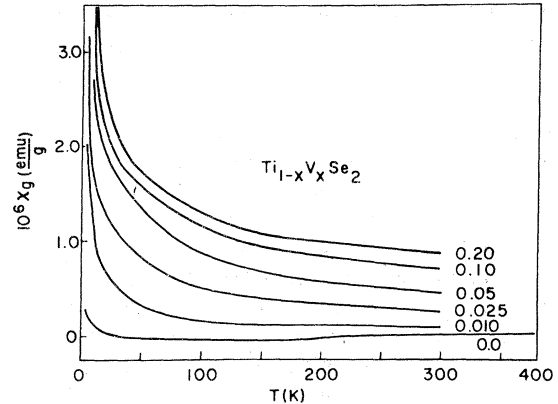


FIG. 6. Magnetic susceptibility of  $\text{Ti}_{1-x}\text{V}_x\text{Se}_2$  powders shows that the V has a magnetic moment.

an axially distorted cubic field,<sup>16</sup> it is also possible that some of the vanadium atoms reside between the layers in the Van der Waals gap (i.e., “intercalated vanadium”). These vanadium atoms are also expected to have a magnetic moment, but are probably  $d^2 V^{3+}$  as in  $\text{V}_5\text{Se}_8$ .<sup>17</sup>

We are presently unable to prove that only the former possibility (substituted  $d^1 V^{4+}$ ) occurs here. However it seems likely for two reasons. (i) Both  $\text{TiSe}_2$  and  $\text{VSe}_2$  can be grown stoichiometrically at the growth temperatures used here. (ii) Local moments on *intercalated* atoms do not produce large effects in the resistivity of other metallic layered compounds.<sup>18,19</sup> If we accept the substituted hypothesis, it may still appear surprising that V has a magnetic moment in  $\text{TiSe}_2$ , since  $\text{VSe}_2$  shows only enhanced Pauli paramagnetism ( $1.43 \times 10^{-6}$  emu/g).<sup>5,20,21</sup> The V moment may be due in part to the larger intralayer metal-metal distance in  $\text{TiSe}_2$  (3.54 Å) compared to  $\text{VSe}_2$  (3.35 Å). Also the metal-selenium distance is larger in  $\text{TiSe}_2$  (2.53 Å) than in  $\text{VSe}_2$  (2.46 Å). Both these factors, in light of the enhanced susceptibility of  $\text{VSe}_2$ , may lead to local moment formation of the  $d^1 V^{4+}$  in  $\text{TiSe}_2$ . The

TABLE I. Effective magnetic moment per vanadium atom in  $\text{Ti}_{1-x}\text{V}_x\text{Se}_2$  determined from the slope of the magnetic susceptibility. The moment determined in this way is larger at high temperatures ( $> 200$  K) than that determined below 100 K. The small contribution to  $\mu_{\text{eff}}$  from Fe impurities has not been subtracted out.

$x$	$\mu_{\text{eff}}/V$ ( $\mu_B$ ) ( $T > 200$ K)	$\mu_{\text{eff}}/V$ ( $\mu_B$ ) ( $100 > T > 10$ K)	$\Theta_{\text{low}}$ (K)
0.01	2.3	1.5	2.5
0.025	1.9	1.3	5.0
0.05	1.8	1.1	7.0
0.10	1.3	0.9	10.0
0.20	0.9	0.7	10.0

lack of a local moment on Ta in  $\text{TiSe}_2$  is consistent with this picture, since  $1T\text{-TaSe}_2$  has metallic conductivity and the average metal-metal distance is 3.48 Å. In an attempt to resolve the question of where the V resides we tried to obtain the V ESR spectra, but no signal was observed between 6 K and 300 K in powders or single crystals.

The resistivity diverges in  $\text{Ti}_{1-x}\text{V}_x\text{Se}_2$  when  $x \lesssim 0.03$  as the temperature is reduced. Note that when  $0.03 < x < 0.07$ , the resistivity increases at low temperatures, but remains finite as  $T \rightarrow 0$ . Two mechanisms for this behavior suggest themselves: Anderson localization<sup>22</sup> and spin disorder scattering.<sup>23,24</sup> There are several examples of the former in layered compounds.<sup>25,26</sup> Figure 7 shows the resistivity of a nominal  $\text{Ti}_{0.99}\text{V}_{0.01}\text{Se}_2$  crystal below 70 K down to 1.05 K. This crystal shows a much larger increase in resistivity at low temperatures than the one shown in Fig. 5. Also in Fig. 7 is shown the field dependence of the resistivity with the magnetic field *parallel* to the current at 4.2 and 1.6 K. The large negative magnetoresistance suggests that the increasing resistivity is in part connected with the existence of a magnetic moment on the V atoms.

We return now to the phase transition itself and its behavior versus substitution. In general we ex-

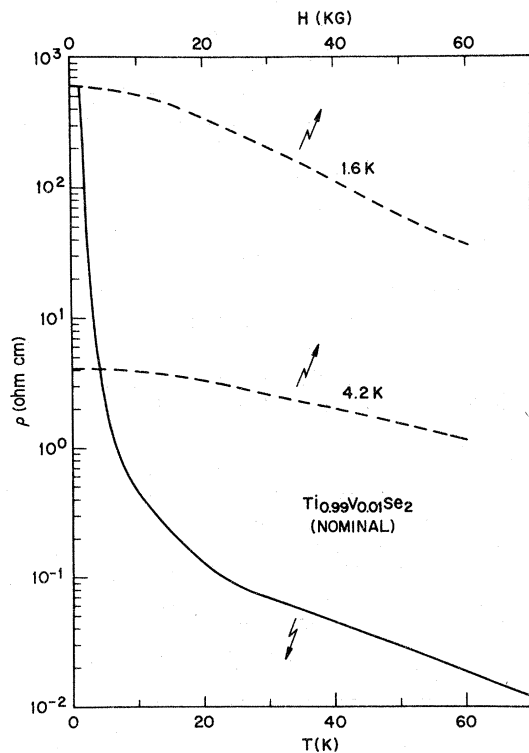


FIG. 7. Electrical resistivity and magnetoresistance of a nominal  $\text{Ti}_{0.99}\text{V}_{0.01}\text{Se}_2$  single crystal from 1.05 to 70 K.

pect that the transition temperature could be changed either by changing the carrier concentration or as a result of cation disorder.<sup>27</sup> In a previous paper,<sup>1</sup> we suggested that the transition in  $\text{Ti}_{1+x}\text{Se}_2$  was suppressed by the excess carriers produced from the excess ( $x$ ) Ti atoms. From resistivity data we estimated that  $T_0$  is reduced to zero at  $x = 0.035 \pm 0.005$ . In the case of excess Ti the initial rate of suppression of  $T_0$  is  $dT_0/dx|_{\text{excess}} \approx 35 \pm 5 \text{ K/at.}\%$ .

If the suppression of the transition temperature were due to an increase in electron concentration (and a decrease in hole concentration) by electron donation from the excess Ti, we should be able to calculate the rate of suppression for Ta and V doping due to a similar electron donation to the bands. However, we need to know the valence of the excess Ti (how many electrons donated per Ti). We attempted to observe a difference in chemical shift between the excess Ti and host Ti in  $\text{Ti}_{1.08}\text{Se}_2$  by x-ray photoelectron spectroscopy. The narrowest Ti core levels are the  $2p$  levels and the results are shown in Fig. 8 in comparison to  $\text{TiSe}_2$ . Also shown is the first  $p$ -level center position in Ti metal and in  $\text{TiO}_2$ . The chemical shift for  $\text{Ti}^{4+}$  in  $\text{TiSe}_2$  is only 1.56 eV in comparison to 4.9 eV for the more ionic  $\text{Ti}^{4+}$  in  $\text{TiO}_2$ . A second Ti site is not observed in Fig. 8 for  $\text{Ti}_{1.08}\text{Se}_2$ ; rather, the width of the peaks increases by  $\approx 20\%$  over  $\text{TiSe}_2$  or Ti metal. It is difficult to assess the meaning of these data, but to first order it appears that all the Ti are equivalent.

Assuming then that the excess Ti are tetravalent, we would expect Ta to suppress  $T_0$  at  $\approx 9 \pm 1 \text{ K/at.}\%$ , if this suppression were due to changes in the carrier density alone. For both the Ta and V substituted samples we find  $dT_0/dx|_{\text{subs}}$  is about twice this value ( $18 \pm 3 \text{ K/at.}\%$ ). It is somewhat surprising

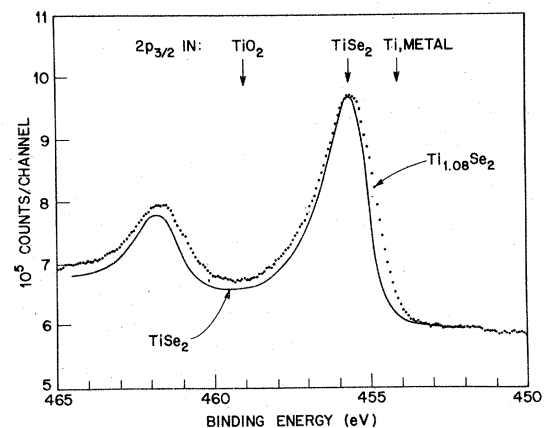


FIG. 8. XPS spectra of the Ti  $2p$  levels in  $\text{TiSe}_2$  (solid line) and  $\text{Ti}_{1.08}\text{Se}_2$  (dots). The arrows indicate the center position of the  $2p_{3/2}$  peak in Ti metal,  $\text{TiSe}_2$ , and  $\text{TiO}_2$ .

that Ta and V suppress the transition at the same rate, since the  $d$  electron may be localized on the V at low concentrations, but not on the Ta. Further since the transition involves the freezing in of a particular phonon,<sup>1</sup> one might expect the disruptive effect of V and Ta to be dissimilar because the former has a mass close to that of Ti while the latter has a much larger mass. Because we are not able to determine the relative importance of changing the electron and hole concentrations and of disorder in suppressing the transition, it is difficult to use these data to help determine the mechanism of transformation.

### III. DISCUSSION

We return again to the properties of undoped, stoichiometric TiSe<sub>2</sub>. One concern in understanding the physical properties of TiSe<sub>2</sub> is the possible presence of crystalline defects, which may produce carriers. These might be, for example, Ti vacancies in the TiSe<sub>2</sub> layer with an equal number of Ti atoms in the Van der Waals gap. These defects are observed in TiS<sub>2</sub> when prepared at high temperatures.<sup>11</sup> While we cannot directly measure the concentration of such defects, the present data suggest that the concentration of these and other defects must be low. Both Figs. 1 and 4 of Ref. 1, show that the resistivity is rather severely changed from that of the "best" TiSe<sub>2</sub> even at very small levels of doping or nonstoichiometry. For example, the peak in the resistivity of Ti<sub>0.995</sub>Ta<sub>0.005</sub>Se<sub>2</sub> has dropped by more than a factor of 4 from that of TiSe<sub>2</sub> relative to the "background" extrapolated from high temperature. Such large changes with small doping concentrations seem unlikely if a large amount of disorder by "self-doping" is already present. For this reason it is believed that the data shown in Fig. 1 are close to, or representative of, "intrinsic, high purity, defect-free TiSe<sub>2</sub>."

It is tempting to associate the increase of the resistivity over the linear extrapolation from above 450 K with pretransition fluctuation effects.<sup>3</sup> This effect must then extend to twice the transition temperature, or in absolute terms at least for 200 K above  $T_0$ ! It is clear that the resistivity itself does not diverge at  $T_0$ ; rather, the resistivity peaks approximately 35 K below  $T_0$ . As in many magnetic transitions<sup>28</sup> or charge-density-wave (CDW) transitions in  $2H$  group-V $b$  dichalcogenides,<sup>29</sup> the transition in TiSe<sub>2</sub> at  $T_0$  is accompanied by a negative peak in  $dp/dT$ . At present it is difficult to say if these effects, especially well above  $T_0$  are associated with dynamic fluctuations or if they are due to impurity induced static distortions.<sup>27</sup> Either case may be consistent with the "streaking" around the  $2a_0$  superlattice points observed in electron

diffraction even at room temperature.<sup>2-5</sup>

Finally, we consider the mechanism of the transition. A number of models have been proposed. These include an electron-hole coupling from  $\Gamma$  to  $L$  by either the electron-phonon interaction<sup>1,10</sup> or by an excitonic Coulomb coupling.<sup>2</sup> Also suggested is a band Jahn-Teller effect<sup>30</sup> and a direct phonon instability that would occur in the *absence* of carriers.<sup>3,31</sup> The last model has also been combined with the first by suggesting that the transition temperature is enhanced by the presence of carriers.<sup>3</sup> It is clear from the electrical resistivity, magnetic susceptibility,<sup>1</sup> Se<sup>77</sup> NMR,<sup>8</sup> and optical reflectivity<sup>9</sup> that the number of carriers is reduced by a factor of 3-10 when well below  $T_0$ . Also the size of the specific heat anomaly at the 200-K transition is consistent with the transition being driven by the carriers.<sup>10</sup> However, the rounded shape of the specific-heat anomaly and critical scattering observed in elastic neutron scattering and x-ray measurements suggest a short correlation length for fluctuations of 15-20 Å.<sup>32</sup> Such a short correlation length implies that the phonon entropy cannot be neglected in determining the transition temperature or the nature of the fluctuations. A model similar to that developed by McMillan for  $2H$ -TaSe<sub>2</sub> where the correlation length is only 4 Å,<sup>33</sup> presumably will apply to TiSe<sub>2</sub>. In TiSe<sub>2</sub> this length is about four times longer than in  $2H$ -TaSe<sub>2</sub>, and the temperature exponent of the order parameter in TiSe<sub>2</sub> is close to the mean field value of 0.5.<sup>1</sup> Consequently, we expect that the phonons are less important in TiSe<sub>2</sub>. Although all the available data suggest to us that the driving force for the transition arises from the presence of the carriers, we cannot disprove other proposed models.

### IV. SUMMARY

A reexamination of the transport data, the possible inadequacy of a simple two-band model in interpreting the data, and recent photoemission measurements lead us to expect carrier densities in TiSe<sub>2</sub> of  $(5 \text{ to } 10) \times 10^{20}/\text{cm}^3$  when the temperature is above the second-order transition at  $T_0 \approx 200$  K. Both cation and anion substitution, as well as nonstoichiometry, suppress the transition. However, this suppression appears to be mostly due to the disorder created by such changes. Vanadium atoms, when substituted in TiSe<sub>2</sub>, have a magnetic moment and cause a large increase in the low-temperature resistivity. This behavior is in marked contrast to that of Ta substitution, where no moments are seen and simple metallic conduction occurs. However, we have been unable to unambiguously determine the driving force of the transition from these data, since the cation

disorder appears to dominate the suppression of the transition.

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