Electron-Electron Scattering in TiS_2

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The a-axis, temperature-dependent electrical resistivity of high-purity, stoichiometric TiS_2 is proportional to T^2 from at least 10 to 400 K. This unique behavior is apparently caused by electron-electron scattering.

In 1937 Baber[1] predicted that electron-electron (or electron-hole) scattering could make a substantial contribution to the electrical resistivity of certain metals. Subsequent attempts to identify such scattering unambiguously in nonmagnetic materials have been moderately successful. Such electron-electron scattering will probably not be seen in the simple metals[2] but has been detected in certain transition metals[3] and in some semimetals.[4] In some nearly magnetic metals paramagnon scattering may dominate the electrical resistivity to temperatures well above room temperature.[5,6] In all of these cases the characteristic T^2 dependence of the resistivity predicted by Baber is restricted to lower temperatures, usually below 20 K. The layered semimetallic compound TiS_2 may offer the first case where electron-electron scattering causes the electrical resistivity to be proportional to T^2 to temperatures above 300 K.

Until recently, the semimetallic properties of TiS_2 have been attributed to deviations from stoichiometry in what would otherwise be a semiconducting material. But in 1972 Thompson, Pisharody, and Koehler[7] noted that this is not an adequate explanation since TiS_2 can be prepared as a stoichiometric compound. These results have been abundantly confirmed in studies of the titanium-sulfur phase diagram,[8,9] and the semimetallic properties of TiS_2 have been confirmed in independent measurements.[10,11] But the origin of these semimetallic properties has not been revealed through band-structure calculations that predict a 1-eV band gap in TiS_2.[12] The remaining questions regarding the band structure and the unusual transport properties of TiS_2 have stimulated the author to re-analyze the transport and magnetic measurements. I conclude from the composition-dependent magnetic susceptibility and thermoelectric power that the Ti_xS_2 nonstoichiometric compounds display nearly ideal, rigid, parabolic-band properties. At the same time the scattering of current carriers is quite unusual. The temperature-dependent resistivity, $\rho-\rho_0$, is proportional to T^2 from at least 10 to 400 K. Also, $\rho-\rho_0$ is roughly proportional to $n^{-5/3}$ where n is the carrier concentration. These relationships suggest that the resistivity is dominated by electron-electron scattering.

I will assume that the electrical resistivity can be factored into a mass-dependent factor representing the rigid-band, temperature-independent properties and a relaxation-time factor containing all of the temperature dependence. Thus

$$\rho(T)=[m^*/ne^2][1/\tau(T)]+\rho_0. \tag{1}$$

The magnetic susceptibility and Seebeck coefficient will be used to show that m^* is independent of composition. These data were presented in Ref. 8. Within a rigid-, parabolic-band model the Seebeck coefficient for a metal is proportional to[13] $m^*/n^{2/3}$, where m^* is the effective mass and n is the carrier concentration. Likewise, the magnetic susceptibility of the conduction electrons is proportional to[13] $m^*n^{1/3}$. Rather than deal with χ directly, I will follow Takeuchi and Katsuda[14] and study the changes in χ that occur when the composition is changed. The incremental susceptibility is defined as $\Delta\chi=\chi_{Ti_xS_2}-\chi_{TiS_2}$. A comparison of the experimental values of $\Delta\chi$ with the expected core diamagnetic contributions from the supernumerary titanium atoms shows that such core terms can be neglected so that $\Delta\chi$ reflects only the change in χ caused by changes in the number of conduction electrons. The $\Delta\chi$ and S equations can now be solved simultaneously to yield

$$|S|^{-1/2}=A+B\Delta\chi,$$

where A and B are functions of g, the spectroscopic splitting factor, and m^*, the effective mass. Thus, $|S|^{-1/2}$ would be expected to be proportional to $\Delta\chi$, provided that m^* and g are constant, i.e., provided that the rigid parabolic band model works. Then $|S|^{-1/2}$ is plotted versus $\Delta\chi$ in Fig. 1 for the Ti_xS_2 compounds. From the linearity of this relation I conclude that m^* and g

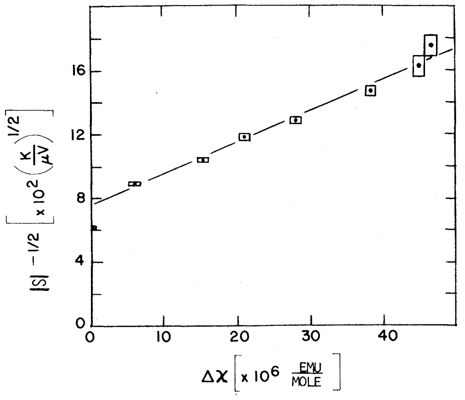

FIG. 1. The inverse square root of the Seebeck coefficient versus the change in the susceptibility on doping with titanium.

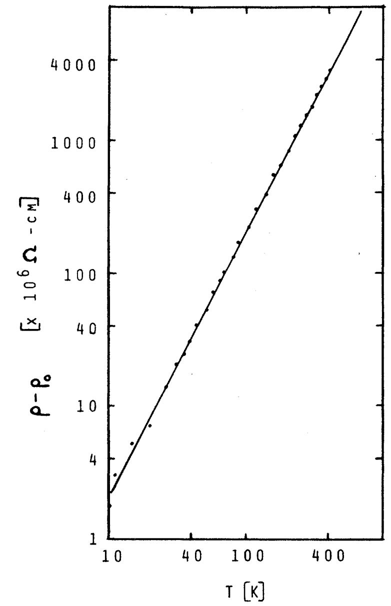

FIG. 2. A log-log plot of the a-axis electrical resistivity versus temperature for TiS_2. The solid line has a slope of 2.

are constant with $m^* = 1.5m_e$ and $g = 4.3$. (Here m^* is the net density-of-states effective mass.) The paramagnetic enhancement has been somewhat arbitrarily lumped into the value of g but this would seem to be a reasonable parametrization. In other semimetals where the relevant direct band gaps are comparable to the spin-orbit splitting, very large values of g are obtained.[15] Support for this parametrization follows from the observation that $m_s \equiv 2/g \cong m_0$ for TiS_2, where m_s and m_0 are the spin and orbital effective masses as defined by Cohen and Blount.[16] This equivalence leads to $\chi_{\mathrm{Pauli}} \cong 3\chi_{\mathrm{diamagnetic}}$ for the conduction electrons and hence a positive susceptibility as observed. Exchange-enhancement domination of χ would not seem to be consistent with the linear correlation between $|S|^{-1/2}$ and $\Delta\chi$ since such an enhancement would introduce a substantial composition-dependent factor.

The τ factor in Eq. (1) will be determined from the dependence of ρ on temperature and composition. Benda[10] and Takeuchi and Katsuda[14] have each reported that $\rho - \rho_0 \propto T^2$ in TiS_2 but in both cases the proportionality is over a limited temperature interval and, in the absence of corroborating evidence, is inconclusive of new scattering mechanisms. But when TiS_2 crystals are grown from high-purity elements by sulfur-vapor transport, $\rho - \rho_0 \propto T^2$ from 10 to 400 K. (The highest temperature is presently limited by chemical reaction with the contacts and the lowest temperature by the large value of ρ_0.) This result is shown in Fig. 2. There $\log(\rho - \rho_0)$ is plotted versus $\log T$. I find $\rho(T) = 1.95\times10^{-4}\ \Omega\ \mathrm{cm} + (2.0\times10^{-8}\ \Omega\ \mathrm{cm/K^2})T^2$. For this particular sample $\rho(300\ \mathrm{K})/\rho_0 = 10$. This T^2 behavior has been observed in materials with resistance ratios of 9.5 to 11 while in impure-nonstoichiometric samples with resistance ratios of 3 to 8, I find that the T^2 behavior is restricted to a smaller interval in T.

The value of the exponent on T is mildly sample dependent. For the sample shown in Fig. 2 the exponent is 2.00 ± 0.04. In samples with resistance ratios between 11 and 12, the exponent appears to be slightly larger, reaching values as large as 2.1. In these cases the determination of the exponent is complicated by a subtle plateau in the curve of ρ versus T^2 near 120 K. This plateau occurs near the distortion temperature predicted by Thompson[17] from systematics of charge-density-wave distortion temperatures in the layered dichalcogenides. The highest purity TiS_2 would then seem to fit the same systematics established for the metallic layered dichalcogenides.

Recently Lawrence and Wilkins[2] have reported a theoretical study of electron-electron scattering in the simple metals. They find for a parabolic band model that $\rho_{ee} \underset{\sim}{\propto} n^{-5/3}T^2$. We have tested this equation in the $Ti_{1+x}S_2$ compounds by plotting $\rho(399\ \mathrm{K})$ versus $n^{-5/3}$ as in Fig. 3. The value of n is calculated by assuming that the interstitial titanium atoms each donate four electrons to the conduction band. As shown in Fig. 3, ρ(300

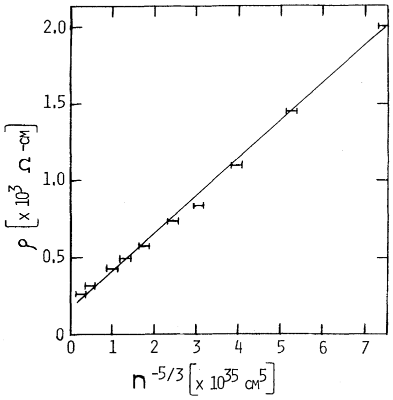

FIG. 3. The electrical resistivity versus $n^{-5/3}$. The carrier concentration is calculated on the assumption that each supernumerary titanium atom in Ti_xS_2 donates four electrons to the conduction band.

K) $\underset{\sim}{\propto} n^{-5/3}$. The coefficient of T^2 for TiS_2 can be calculated from the slope of this line and is found to be 2.0×10^{-8} Ω cm/K^2, in agreement with the slope of the curve of ρ versus T^2. The curvature of the curve of ρ versus n^{-y} is fairly insensitive to the value of the exponent and depends on the accuracy in the measurement of the carrier concentration from the Hall effect. From an analysis of the experimental data I take $\frac{5}{3} \leqslant |y| \leqslant 2$.

In addition to the proportionalities of ρ to T^2 and $n^{-5/3}$, the magnitude of ρ is also consistent with electron-electron scattering. If there is a high probability that a resistive, electron-electron scattering event will occur, then $\rho \propto m^2 n^{-5/3} \times T^2$ according to Ref. 2. For TiS_2, $m^2 n^{-5/3}$ is three to five orders of magnitude larger than in classical metals and the Lawrence-Wilkins result predicts an electron-electron resistivity at 300 K of 1.5×10^{-4} Ω cm, within one order of magnitude of the measured value at room temperature. This agreement is judged satisfactory. The large value of $m^2 n^{-5/3}$ for TiS_2 is equivalent to there being a small Fermi energy or a low degeneracy temperature. For TiS_2 the degeneracy temperature is approximately 1500 K so that even at 400 K finite-temperature corrections to the T^2 dependence should be small. Electron-electron scattering then predicts the magnitude of the resistivity and its functional form over the measured temperature range.

At the same time the phonon contribution to the resistivity is suppressed by the small Fermi momentum. In a metal, conservation of energy and momentum requires that $k_D < 2k_F$ (k_D is the Debye radius) or the Bloch equation[18] for the lattice resistivity of normal processes will overestimate the resistivity by a factor of $(2k_F/k_D)^4$.[19] The summation over phonon wave vector for the Bloch equation would include phonons of such large momentum that the scattered electron would not remain on the Fermi surface. In TiS_2, $k_D = 5k_F$ and a large correction would be expected. Suppression of the phonon resistivity favors the domination of the electron-electron scattering mechanism.

An exact mechanism for the scattering in TiS_2 and the extent to which this mechanism is unique are not presently clear. One speculative possibility is that TiS_2 with resistance ratios between 9 and 11 is a material with an incipient charge-density wave (CDW).[20] Such CDW's have been observed in other layered compounds[17, 21, 22] and, in particular, transitions have been seen in $TiSe_2$ and $TiTe_2$.[23] In addition, diffuse scattering suggestive of the precursor to CDW's has been seen in the electron diffraction from TiS_2.[24] These results support the speculation that electron-electron scattering in TiS_2 may be enhanced by fluctuations into the CDW state ("paraphasons").

I conclude that the combined transport and magnetic measurements yield substantial evidence for electron-electron scattering in TiS_2 from 10 to 400 K. I *define* a general electron-electron scattering event to be one in which the Pauli principle must be satisfied twice, once for each interacting electron, so that $\rho \propto T^2$. The determination of the specific scattering mechanism (intervalley electron-electron, electron-hole, electron-paraphason-electron, etc.) awaits comparative calculations on the mechanisms and experimental determinations of the Fermi surface. The resolution of the mechanism problem may unambiguously answer questions surrounding the origin of the semimetallic properties of TiS_2 and may improve our understanding of transport properties in the presence of charge-density wave distortions.

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Resistivity and Mössbauer Measurements for Solid Xe-Fe Mixtures[*]

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Resistivity measurements of frozen mixtures of Xe and Fe versus concentration and temperature exhibit various conduction regions including a nonconducting-to-conducting transition at ~30 at.% Fe. Mössbauer-effect measurements reveal no changes in isomer shift or hyperfine magnetic field with concentration above ~14 at.% Fe. However, the change in shape of the Mössbauer spectra suggests that a transition from a paramagnetic relaxing phase to a magnetically ordered phase occurs at ~30 at.% Fe.

Since Mott[1] proposed the occurrence of metal-nonmetal transitions, a number of these transitions have been investigated.[2] Recently transitions have been observed in frozen mixtures of rare gases and metals.[3-6] Sharp, discontinuous transitions of resistivity as a function of concentration have been reported for Ar-Na[3] and Ar-Cu.[4] Also a sharp transition was suggested by the optical measurements on Xe-Hg.[5] By contrast, Kr-Rb and Xe-Cs systems[6] did not show sudden changes in their optical properties, while resistivity measurements indicated gradual metal-nonmetal transitions.

We report a study of a system in which the metallic constituent is a magnetic transition metal. In this study we monitor the resistivity and ^{57}Fe Mössbauer-effect parameters of Xe-Fe as a function of iron concentration. A gradual transition from a nonconducting to a conducting phase was observed around 30 at.% Fe. Neither the Mössbauer isomer shift nor the hyperfine field of ^{57}Fe (H_i) showed an observable change on passing through the transition.

Samples were prepared in a vacuum of better than 10^{-7} Torr by allowing Fe vapor and Xe gas to condense on the 7-K surface of either a sapphire or beryllium substrate. Iron was evaporated from an alumina crucible held in a tantalum heater that was temperature regulated to better than ± 2°C. By weighing the crucible before and after an evaporation, and by using the furnace efficiency (the ratio of Fe deposited on the substrate to Fe evaporated), the amount of Fe in the sample could be determined. The furnace efficiency was determined in a separate experiment by weighing the Fe deposited on a substrate held at room temperature. It was assumed that the sticking coefficient for Fe was the same at 7 K as at 300 K. From the amount of Fe deposited and from the attenuation of the 14.4-keV γ ray of ^{57}Co, the amount of Xe deposited was determined. The error in the amount of iron in