Thouless, and R. C. Jones, Phys. Rev. Lett. 36, 1217 (1976).

[4] See J. Samuel Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Philadelphia, Pa., 1966), p. 116 ff.; J. M. Kincaid and E. G. D. Cohen, Phys. Rep. 22C, 60 (1975).

# Electron-Hole Scattering and the Electrical Resistivity of the Semimetal $TiS_2$†

Carl A. Kukkonen and Pierre F. Maldague
*Department of Physics, Purdue University, West Lafayette, Indiana 47907*

(Received 18 June 1976)

We present the first complete theory of the effect of collisions between charge carriers on the electrical resistivity of a simple degenerate semimetal. We find that (i) electron-hole scattering can explain the anomalous $T^2$ resistivity of *stoichiometric* $TiS_2$, (ii) electron-electron and hole-hole scattering do not contribute to $\rho$, and (iii) the theory of electron-hole scattering predicts that the resistivity of *nonstoichiometric* $TiS_2$ should fall significantly below $T^2$ at high temperatures.

In a recent Letter Thompson[1] reported that the $a$-axis, temperature-dependent electrical resistivity, $\rho(T)-\rho(0)$, of the layered semimetallic compound $TiS_2$ was proportional to $T^2$ from at least 10 to 400 K. Thompson suggested that this remarkable behavior was due to "general" electron-electron scattering which encompasses electron-electron (e-e), hole-hole (h-h), and electron-hole (e-h) processes. In this Letter we present the first complete theory of the effect of collisions between charge carriers on the electrical resistivity of a simple degenerate semimetal. In $TiS_2$ the electron and hole densities are sufficiently small and the carrier pockets (assumed spherical) are sufficiently isolated that all e-e, h-h, and e-h scatterings conserve momentum. Therefore e-e and h-h processes do not contribute to $\rho$. For e-h scattering momentum conservation does not imply current conservation; and we find that this mechanism can explain the observed $T^2$ resistivity. Furthermore, the theory of e-h scattering suggests additional experiments to confirm the validity of this explanation.

Specifically our theory predicts that a compensated (stoichiometric) semimetal has a $T^2$ term in the resistivity [Eq. (8)] for all $T$, as has been found in $TiS_2$. An extension of the theory predicts that the resistivity of an uncompensated (nonstoichiometric) semimetal, e.g., $Ti_{1+x}S_2$, should fall significantly below $T^2$ at high $T$, eventually going linearly with temperature as a result of phonon scattering. The particular behavior we predict for $Ti_{1+x}S_2$ is shown in Fig. 1, where we plot the temperature-dependent resistivity versus $T^2$ for different values of $x$. For *stoichiometric* $TiS_2$, $x=0$, the solid curve including e-h and impurity scattering is pure $T^2$ and the dashed curve including some phonon scattering shows only a slight deviation. Both are consistent with the data of Thompson. For *nonstoichiometric* $TiS_2$ our predictions are quite different. At low $T$, $\rho$ is also proportional to $T^2$, but with a coefficient that decreases with $x$. At higher $T$, however, the curves fall far below $T^2$. The solid curves become constant at high $T$, while the dashed curve

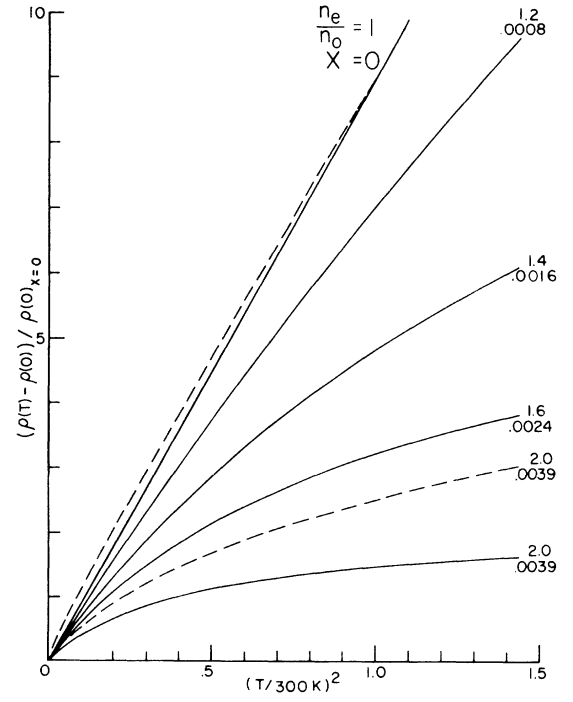

FIG. 1. Theoretical temperature-dependent electrical resistivity of $Ti_{1+x}S_2$ for different values of $x$. The solid curves include electron-hole and impurity scattering. The dashed curves illustrate the changes that occur when phonon scattering is included.

becomes linear in $T$ due to phonon scattering. The fact that e-h scattering is required to explain the unusual stoichiometric data is itself surprising, but our off-stoichiometry predictions are an extraordinary and, we believe, unique signature of e-h scattering. Consequently the results of experiments on nonstoichiometric samples will provide a crucial test of our theory, which, if confirmed, would yield additional strong evidence for the existence of holes in $TiS_2$.

Our results for the resistivity are derived from exact solutions of the coupled electron-hole Boltzmann equations, found using the method of Højgaard-Jensen, Smith, and Wilkins.[2] Because the inclusion of impurity and phonon-scattering complicates the theory, exact results are not generally available; but an accurate (10%) approximate solution is obtained. Rather than reporting the details of that calculation, we choose to emphasize the physics of electron-hole scattering by writing simple, coupled, electron and hole kinetic equations in the relaxation-time approximation that, with a proper choice of parameters, reproduce exactly our more complicated analysis.

Baber[3] first showed that e-h scattering leads to a $T^2$ resistivity in transition metals. Appel[4] presented, without derivation, an expression for the total conductivity of an e-h system, which though similar to ours, leads to the erroneous conclusion that the resistivity of a compensated system no longer has a $T^2$ term at high temperature.

Our theory strictly applies to any degenerate e-h system with spherical carrier pockets in which collisions between charge carriers conserve momentum; although we consider only $TiS_2$, many of the features are quite general and should be of interest to those concerned with transport in elemental semimetals, transition metals, and the new "unusual" metals such as the layered compounds, $(SN)_x$ and tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ).[5]

$TiS_2$ has a hexagonal Brillouin zone. Although existing band structure calculations[6] predict that it is a semiconductor, experiments[1] indicate that it is a semimetal. Following the recent suggestion of Freeman and Zunger,[7] we assume a pocket of holes at $\Gamma$ and electron pockets at the $M$ points. This structure is shown in Fig. 2. $TiS_2$ is a layered compound, but with a small anisotropy ratio, $\rho_c/\rho_a < 10$. Since detailed Fermi surface data are not available, we assume the simple case of spherical carrier pockets.[5] For stoichiometric $TiS_2$, the density of electrons and holes are equal so that $n_e = n_h = n_0 = 2\times 10^{20}$ cm$^{-3}$.[8]

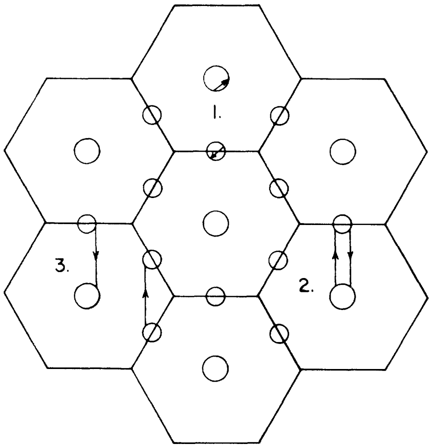

FIG. 2. Reciprocal lattice of $TiS_2$ viewed along the $c$ axis. The large circles denote pockets of holes and the small circles pockets of electrons. The three different types of electron-hole scattering are indicated.

To illustrate the importance of momentum conservation, we consider first e-e scattering. The current carried by the electrons is given by

$$\vec{J}_e = (-e/m_e)\sum n_i \vec{p}_i \equiv (-e/\Omega m_e)\vec{P}_e, \qquad (1)$$

where $\vec{p}_i = m_e \vec{v}_i$ is the physical momentum of an electron in state $i$, $n_i$ is the distribution function, and $\Omega$ is the volume of the sample. The current is proportional to the total momentum $\vec{P}_e$ in the electron system. The wave vector of the $i$th electron is $\vec{q}_i = \vec{K}_i + \vec{p}_i$ where $\vec{K}_i$ is the vector from the origin to the center of the pocket containing the $i$th electron. In an e-e collision, wave vector is conserved which implies that $\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{q}_4 + \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector (including $\vec{G} = 0$). In terms of momenta, this reads $\vec{p}_1 + \vec{p}_2 = \vec{p}_3 + \vec{p}_4 + \vec{Q}$, where $\vec{Q} = \vec{K}_3 + \vec{K}_4 - \vec{K}_1 - \vec{K}_2 + \vec{G}$. A process in which $\vec{Q} = 0$ conserves momentum and therefore cannot affect the current. In $TiS_2$ the smallest nonzero $|\vec{Q}| = 1.1$ Å$^{-1}$ is greater than the maximum momentum transfer $4p_F = 0.50$ Å$^{-1}$; therefore, momentum nonconserving e-e processes do not occur at all. We conclude that e-e scattering does not contribute to the electrical resistivity of $TiS_2$.[9] The same conclusion applies to h-h scattering.

We now turn our attention to e-h scattering. The current carried by the e-h system is simply written in terms of the total electron and hole momenta as

$$\vec{J} = (-e/\Omega)(\vec{P}_e/m_e - \vec{P}_h/m_h). \qquad (2)$$

It is more physical to rewrite this expression in terms of the total and relative momenta defined by

$$\vec{P} = \vec{P}_e + \vec{P}_n, \qquad \vec{\mathcal{P}} = \mu(\vec{P}_e/n_e m_e - \vec{P}_h/n_h m_h) = \Omega\mu(\vec{V}_e - \vec{V}_h), \tag{3}$$

where $1/\mu = 1/n_e m_e + 1/n_h m_h$ and $\vec{V}_e - \vec{V}_h$ is the relative velocity of the electrons and holes. Thus the current becomes

$$\vec{J} = \frac{-e}{\Omega}\left[\left(\frac{n_e - n_h}{n_e m_e + n_h m_h}\right)\vec{P} + \left(\frac{1}{m_e} + \frac{1}{m_h}\right)\vec{\mathcal{P}}\right]. \tag{4}$$

In general $\vec{J}$ depends on both the total and relative momenta. Using the same reasoning as for e-e scattering, we see that e-h scattering also conserves the total momentum in $TiS_2$. However, the the relative momentum is degraded by e-h scattering. For a stoichiometric sample, $\vec{J}$ is independent of $\vec{P}$ and there is a finite conductivity due to e-h scattering alone. In contrast a nonstoichiometric system with only e-h scattering has an infinite conductivity; impurities and phonons must be introduced to relax the total momentum. This fundamental difference between a compensated and uncompensated system leads to surprising consequences.

Consider an electron-hole system in an external field $\vec{E}$ with e-h, impurity, and phonon scattering. In the steady state the total rate of the change $\vec{P}_e$ is zero, i.e., $d\vec{P}_e/dt|_{\text{total}} = d\vec{P}_e/dt|_{\vec{E}} + d\vec{P}_e/dt|_{\text{eh}} + d\vec{P}_e/dt|_{\text{ip}} = 0$, where the change due to $\vec{E}$ is $d\vec{P}_e/dt|_{\vec{E}} = -n_e\Omega\vec{E}$. Impurities and phonons relax $\vec{P}_e$ toward zero; $d\vec{P}_e/dt|_{\text{ip}} = -\vec{P}_e/\tau_{\text{ip}}$, where $1/\tau_{\text{ip}} = 1/\tau_{\text{imp}} + 1/\tau_{\text{phon}}$. A new feature of this calculation is the recognition that electron-hole scattering relaxes the *relative* velocity or *relative* momentum to zero;

$$d\vec{\mathcal{P}}/dt|_{\text{eh}} = -\vec{\mathcal{P}}/\tau_{\text{eh}} = d\vec{P}_e/dt|_{\text{eh}} = -d\vec{P}_h/dt|_{\text{eh}}. \tag{5}$$

Making the same analysis for the total hole momentum and writing $\vec{P}_e$ and $\vec{P}_h$ in terms of $\vec{P}$ and $\vec{\mathcal{P}}$, we find the coupled kinetic equations

$$\begin{aligned} 0 &= -en_e\Omega\vec{E} - \vec{\mathcal{P}}/\tau_{\text{eh}} - [\vec{\mathcal{P}} + (\mu/n_h m_h)\vec{P}]/\tau_{\text{ip}}, \\ 0 &= en_h\Omega\vec{E} + \vec{\mathcal{P}}/\tau_{\text{eh}} - [-\vec{\mathcal{P}} + (\mu/n_e m_e)\vec{P}]/\tau_{\text{ip}}, \end{aligned} \tag{6}$$

where we have assumed that $\tau_{\text{ip}}$ was the same for electrons and holes. Solving we obtain the following expression for the conductivity:

$$\sigma = e^2\mu\left[\frac{(n_e - n_h)^2}{n_e n_h m_e m_h}\tau_{\text{ip}} + \left(\frac{1}{m_e} + \frac{1}{m_h}\right)^2\left(\frac{1}{1/\tau_{\text{eh}} + 1/\tau_{\text{ip}}}\right)\right], \tag{7}$$

where the first term derives from $\vec{P}$ and second from $\vec{\mathcal{P}}$. The relaxation rates obtained from our Boltzmann equation analysis are given in Eqs. (9) and (10). We note that $1/\tau_{\text{imp}}$ is a constant independent of temperature; $1/\tau_{\text{phon}}$ is given by a Bloch-Grüneisen function, thus varying as $T^5$ for low $T$ and linearly at high $T$; $1/\tau_{\text{eh}}$ is proportional to $T^2$ at all temperatures.

*On stoichiometry,* the term deriving from $\vec{P}$ disappears and the resistivity reduces to

$$\rho = \frac{1}{\sigma} = \frac{1}{ne^2}\left(\frac{1/\tau_{\text{eh}} + 1/\tau_{\text{ip}}}{1/m_e + 1/m_h}\right). \tag{8}$$

At low temperatures, phonons may be ignored and $\rho = A + CT^2$. At high $T$, phonons contribute a linear term and $\rho = A + BT + CT^2$. For sufficiently small $B/C$, the $T^2$ term dominates for all $T$ as observed in $TiS_2$. For other materials with a large $B/C$, $\rho$ will look phononlike at intermediate temperatures. We note, however, that the $T^2$ term is present for all $T$ and eventually dominates.

*Off stoichiometry,* the first term in Eq. (7) no longer vanishes and this dramatically changes the high-temperature limit where the second term becomes negligible compared with the first and $\rho = A' + B'T$, which has no $T^2$ term at all. This surprising result may be understood by recalling that e-h scattering, which predominates at very high $T$, tends to make the relative velocity equal to zero. When this occurs, both electrons and holes are carried at the drift velocity; and the current, proportional to the net charge $-e(n_e - n_h)$, is degraded only by impurity and phonon scattering.

Our theory completely specifies the resistivity in terms of the electron-hole interaction, the electron-phonon coupling constant $\lambda$, and $1/\tau_{\text{imp}}$. Unfortunately the interaction between $d$ electrons and $p$ holes is not known and therefore we simply assume a constant (in $q$) e-h scattering rate $W$ which we take to be the same for all three types of e-h scattering shown in Fig. 1. This yields

$$\frac{1}{\tau_{\text{eh}}} = \frac{n_h m_e}{\mu}\frac{(k_B T)^2 W}{\pi^2\hbar^6} \times \left(\frac{m_e m_h^2\alpha^3}{3} + \frac{m_e^2 m_h(3\alpha - 1)}{4}\right), \tag{9}$$

where $\alpha = 1$ $(p_F/k_F)$ for $p_F/k_F$ greater (less) than 1; $k_F$ is the Fermi wave vector for holes. A crude estimate of $W$ is given by $W \approx (2\pi/\hbar)V_{TF}^2$, where $V_{TF}$ is the $q = 0$ Thomas-Fermi interaction, known to be too weak for electron-electron scattering in the alkali metals.[10]

*For stoichiometric* $TiS_2$, this yields a resistivity too small by a factor of 16; and we must choose the interaction four times stronger than $V_{\rm TF}$ to fit the observed $T^2$ term.

For $1/\tau_{\rm phon}$ we use

$$1/\tau_{\rm phon} = (2\pi/\hbar)\lambda k_{\rm B}T[4(T/\theta_R)^4 J_5(\theta_R/T)], \qquad (10)$$

where $\theta_R = 2p_{\rm F}v_{\rm sound}$ and $J_5$ is a Debye integral. Since our theory predicts that $\rho = A + BT + CT^2$ for stoichiometric $\rm TiS_2$ at high $T$ and the linear term is not evident experimentally, we conclude that the electron-phonon coupling constant is rather small ($\lambda \lesssim 0.05$), which we do not fully understand. $1/\tau_{\rm imp}$ is now determined by the observed resistivity ratio of 10. [Our e-h analysis of experiment[8] shows that $1/\tau_{\rm ip}$ is not the same for electrons and holes as assumed in Eq. (6) and that a straightforward generalization is required.]

*Nonstoichiometric* $\rm TiS_2$ is obtained by intercalating additional Ti atoms, which are each assumed to give up four electrons. Calculating the electron and hole densities as functions of $x$ in $\rm Ti_{1+x}S_2$, we find that all the holes are filled when $n_e = 5.4n_0$ or $x = 0.015$. Using the same parameters as for stoichiometric $\rm TiS_2$ and assuming further that $1/\tau_{\rm ip}$ scales as the density of states, we are able to calculate the temperature-dependent resistivity of $\rm Ti_{1+x}S_2$ for different values of $x$. We exhibit curves for $\lambda_e = \lambda_h = 0$ and 0.05 in Fig. 1, which has been discussed earlier.

In conclusion, we emphasize that the general features of our off-stoichiometry predictions are independent of our crude approximation to the e-h interaction; and, therefore, these experiments will provide a severe test of the theory. Obviously more work on the interaction is needed, but the additional effort will be justified only if experiments confirm that e-h scattering is the dominant mechanism. Thompson informs us that systematic measurements on nonstoichiometric samples are now underway and his preliminary results are in qualitative agreement with our predictions.

The authors thank A. H. Thompson for generously sharing his knowledge of $\rm TiS_2$.

---

†Work supported by National Science Foundation Grant No. GH41884 and Material Research Laboratory Program No. GH33574A3.

[1] A. H. Thompson, Phys. Rev. Lett. 35, 1786 (1975).

[2] H. Højgaard-Jensen, Henrik Smith, and John W. Wilkins, Phys. Rev. 185, 323 (1969).

[3] W. G. Baber, Proc. Roy. Soc. London, Ser. A 158, 383 (1937).

[4] Joachim Appel, Philos. Mag. 8, 1071 (1963).

[5] In one dimension, $\rho_{\rm eh} \propto T$. Cylindrical surfaces can give $\rho_{\rm eh} \propto T^2 \ln T$.

[6] H. W. Myron and A. J. Freeman, Phys. Rev. B 9, 481 (1974).

[7] A. J. Freeman and Alex Zunger, Bull. Am Phys. Soc. 21, 261 (1975).

[8] Our analysis of experiment using an e-h model shows that the heat capacity, Hall effect, and plasma frequency [J. A. Benda, Phys. Rev. B 10, 1409 (1974)] are consistent with $m_e = m_h = 0.8m$, $n_0 = 2\times10^{20}/\rm cm^3$, and $(\tau_{\rm ip}{}^{\rm el}/\tau_{\rm ip}{}^{\rm holes}) = 3.4$ at 300 K.

[9] A nonspherical Fermi surface can allow a nonzero contribution due to e-e scattering.

[10] Carl A. Kukkonen and Henrik Smith, Phys. Rev. B 8, 4601 (1973), and Ph.D. thesis, Cornell University, 1975 (unpublished).

---

## COMMENTS

# Charm Spectroscopy via Electron-Positron Annihilation*

A. De Rûjula, Howard Georgi,† and S. L. Glashow
*Lyman Laboratory, Harvard University, Cambridge, Massachusetts 02138*

(Received 8 July 1976)

Electron-positron annihilation should be a rich source of charmed hadrons. The search for invariant-mass peaks together with the measurement of recoil-mass spectra is a technique that recently has borne fruit at SPEAR. We show how this technique may reveal the existence of the charmed baryons and of the excited states of the charmed mesons.

Charmed hadrons should be abundant in debris of $e^-e^+$ annihilation above the charm threshold.[1] A good candidate for the lightest charmed particle $D^0$ was found at SPEAR[2] at 1.865 GeV decaying into $K^-\pi^+$ and $K^-\pi^-\pi^+\pi^+$, presumably a $J^P = 0^-$ $S$-wave $c\bar{u}$ meson. Its isotopic partner $D^+$ must