Shimane Ika Daigaku Kiyo (Bull. Shimane Med. Univ.)
Vol. 5, pp. 1-8, December 1982

On the Electrical Resistivity of $TiSe_2$ near the Transition Temperature

($TiSe_2$/phase transition/electrical resistivity)

Isao TAGUCHI*

(Received October 18, 1982)

The lifetime of carriers in $TiSe_2$ is determined from the resistivity data by using the theories of excitonic insulators. The comparison with infrared measurements shows that the size of the discontinuity in the temperature-gradient of the resistivity at T_c is in accord with the theoretical prediction for excitonic insulators. The estimated transition-temperature for a perfect crystal of $TiSe_2$ nearly agrees with the onset of the strong short-range-order effect which is observed in the resistivity well above T_c. These results support the excitonic-insulator mechanism for the phase transition in $TiSe_2$.

1. INTRODUCTION

There have been extensive studies of the anomalous properties of the layered dichalcogenide $TiSe_2$. It exhibits a metallic behavior,[1,2] while diselenides of other metals of the same group-IVB as Ti are semiconductors. Energy-band-structure calculations[3] and photoemission studies[4] showed that $TiSe_2$ is a semimetal with holes around the Γ point in the Brillouin zone and electrons near the L points. The existence of the resistivity anomaly near 165 K was first reported by Benda.[5] Neutron diffraction[1] and electron diffraction[6-8] studies revealed that the anomaly is due to the formation of a commensurate superlattice ($2a_0 \times 2a_0 \times 2c_0$) below about 200 K. The superlattice formation is reminiscent of charge-density-wave (CDW) transitions in the group-VB dichalcogenides.[9] However, an incommensurate phase is lacking in $TiSe_2$ in contrast to the group-VB materials.

Several types of mechanisms have been proposed for the transition in $TiSe_2$. Di Salvo *et al.*[1] pointed out the possibility of Fermi-surface nesting and the existence of CDWs. Wilson and Mahajan[8] suggested an excitonic-insulator mechanism. Models based on an antiferroelectric phonon-driven instability and on a band Jahn-Teller effect were presented by White and Lucovsky[10] and by Hughes.[11] Liang *et al.*[12] reported infrared data on $TiSe_2$ which favor the phonon-driven instability. An investigation of transport properties of $Ti_{1-x}V_xSe_2$[13] also supported the mechanism. By contrast, an increase in the transition temperature of $Ti_{1-x}Hf_xSe_2$ with increasing x was detected by the present author,[14] which supports the excitonic-insulator mechanism. Further study of the Hall effect in $Ti_{1-x}Hf_xSe_2$[15] emphasizes the role of holes in the phase

* *Department of Physics*

transition in $TiSe_2$. Recently, the lattice instability has been discussed from the standpoint of the band Jahn-Teller mechanism by Yoshida and Motizuki.[16] They showed that the electron-phonon interaction must be taken into account under the nested condition of Fermi surfaces in order to explain the observed lattice distortion. It should be noted that their results would provide the possibility that $TiSe_2$ is an excitonic insulator with strong coupling of electrons and phonons. It is believed that in such a case the excitonic phase has a CDW associated with lattice distortion rather than a spin-density wave.[17] More recently, we have found that the resistivity anomaly in $TiSe_2$ is substantially suppressed at microwave frequencies if the crystal is of high quality.[18] This observation seems to demonstrate the CDW formation in $TiSe_2$.

The purpose of the present article is to investigate the transport properties of $TiSe_2$ from the viewpoint of the excitonic-insulator mechanism. An important characteristic in the physical properties of $TiSe_2$ is the abrupt change of the temperature gradient of the electrical resistivity near the transition temperature, T_c.[1,19] Figure 1 shows the temperature gradient of the resistivity (parallel to the layers) of an iodine-free single crystal of $TiSe_2$[19] as a function

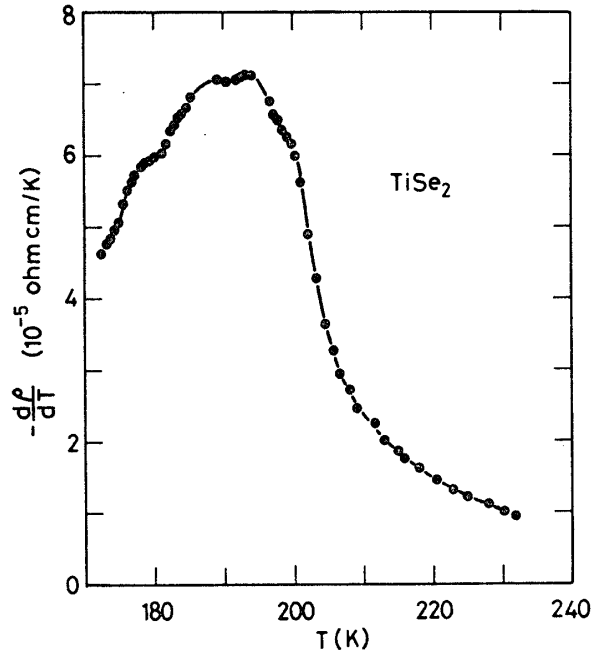

Fig. 1. Temperature gradient of the electrical resistivity of a $TiSe_2$ single crystal of high quality as a function of temperature. The crystal is free from iodine because it was grown by a selenium vapor transport method (ref. 19).

of temperature. The temperature gradient clearly shows a break near 200 K. Di Salvo *et al.*[1] found that the superlattice appears at a temperature which corresponds to the break in the temperature gradient. This rapid change of the resistivity is compared with theories of excitonic insulators.[20,21]

The electrical resistivity of excitonic insulators containing normal impurities was calculated by Zittartz.[20] The calculations were extended to the case of

unequal masses of elctrons and holes, $m_e \neq m_h$, by Ebisawa and Fukuyama.[21] According to these authors, the theory of excitonic insulators is analogous to that of superconductors containing magnetic impurities. In excitonic insulators, normal impurities have pair-breaking effects: if the impurity potential is repulsive for electrons (holes), it is attractive for holes (electrons). The theories predict that the electrical conductivity σ/σ_n decreases linearly when temperature is lowered near T_c, and that its gradient with respect to temperature is discontinuous at T_c. We shall suggest that the curve in Fig. 1 reflects this discontinuous change. The lifetime of carriers is determined from resistivity data by use of the theories. The result is compared with infrared measurements.[12,22] The theories also allow us to estimate the transition temperature for a prefect compound of $TiSe_2$ where carriers have the infinite-lifetimes.

The present approach relies on the theories which assume a two-band model and disregard coupling of the electron system to phonons. Of course, the problem of the excitonic phase in $TiSe_2$ must be examined by a more complete theory which takes account of the real band structure and the electron-phonon coupling. The present analysis is, nevertheless, attempted in order to obtain information on the possibility of the excitonic phase in $TiSe_2$ because it is an exceptional compound concerning the superlattice development among group-IV and-V dichalcogenides, and the origin of the phase transition has been somewhat controversial.

2. ELECTRICAL RESISTIVITY NEAR THE TRANSITION TEMPERATURE

The proposed excitonic-insulator mechanism for the transition in $TiSe_2$ is akin to the large scale electron-hole nesting present in Cr. In $TiSe_2$, there are one hole-pocket and three electron-pockets per zone, and the electron pocket at L and the hole pocket at Γ are near nesting.[3] The spanning vector from Γ to L could give the $a_0^*/2$ superlattice and $c_0^*/2$ repeat perpendicular to the layers. Experimental results of neutron scattering[1] suggest that the transition involves three co-existing CDWs whose wave vectors link Γ to L. Each wave vector of them is perpendicular to those of the other two CDWs.

In the following analysis, we assume that the amplitude of the three CDWs are independent; this would be the case if the part of the Fermi surface utilized by one CDW was not affected by the energy gaps of the other two CDWs. Then the problem may be treated using the two-band model: only one valence-band maximum and one conduction-band minimum are essential to the formation of excitons.

According to Zittartz,[20] and to Ebisawa and Fukuyama,[21] near T_c the electrical conductivity σ of the excitonic insulator in the semimetallic region is expressed as

$$\sigma/\sigma_n = 1 - A(T_c)\Delta^2, \tag{1}$$

where σ_n is the electrical conductivity in the normal state and Δ is the order

parameter. The coefficient $A(T_c)$ is written as

$$A(T_c)=\frac{\beta_c}{2}\int_0^\infty dx\ \mathrm{sech}^2\frac{\beta_c x}{2}\ \frac{rx^2+s\Gamma^2}{(x^2+\Gamma^2)^2}, \tag{2}$$

where $\beta_c=1/K_B T_c$. The coefficients r and s, and constant Γ are defined by the following equations: (setting $\hbar=1$)

$$\Gamma=(\Gamma_e+\Gamma_h)/2=1/\tau, \tag{3}$$

$$r=M/\mu-2(M/2\mu-1)^{-1}, \tag{4}$$

$$s=4\mu/M+M/\mu-4, \tag{5}$$

where Γ_e is the inverse lifetime of electrons and Γ_h is that of holes, and M is the total mass and μ the reduced mass:

$$M=m_e+m_h, \qquad \mu^{-1}=m_e^{-1}+m_h^{-1}. \tag{6}$$

If we introduce the effective-mass ratio $m^*=m_e/m_h$, the mass ratio M/μ becomes

$$M/\mu=(m^*+1)^2/m^*. \tag{7}$$

Then, we find that r and s are functions of m^*. Near T_c the square of the order parameter is proportional to T_c-T;[23]

$$\Delta^2=S(T_c)\,(1-t), \tag{8}$$

where

$$S(T_c)=\frac{2\pi^2}{\beta_c^2}\ \frac{(m^*+1)^2}{m^*} \times\frac{1-(\beta_c\Gamma/2\pi)\sum_{n=0}^{\infty}\left(n+\frac{1}{2}+\beta_c\Gamma/2\pi\right)^{-2}}{\sum_{n=0}^{\infty}[(n+\frac{1}{2})/(n+\frac{1}{2}+\beta_c\Gamma/2\pi)^4]}, \tag{9}$$

and $t=T/T_c$. Combining eqs. (1) and (8), we obtain

$$\sigma/\sigma_n=1-A\,(T_c)\,S\,(T_c)\,(1-t). \tag{10}$$

The temperature gradient of the electrical resistivity ρ can, therefore, be written as

$$\frac{d}{dt}\left(\frac{\rho}{\rho_n}\right)=-\frac{A(T_c)S(T_c)}{[1-A(T_c)S(T_c)(1-t)]^2}, \qquad t\lesssim 1, \tag{11}$$

$$=-A(T_c)S(T_c), \qquad t=1. \tag{12}$$

Equations (2) and (9) can be calculated numerically if the values of m^* and $\beta_c\Gamma$ are fixed. Figure 2 represents the product of $A(T_c)$ and $S(T_c)$ as a

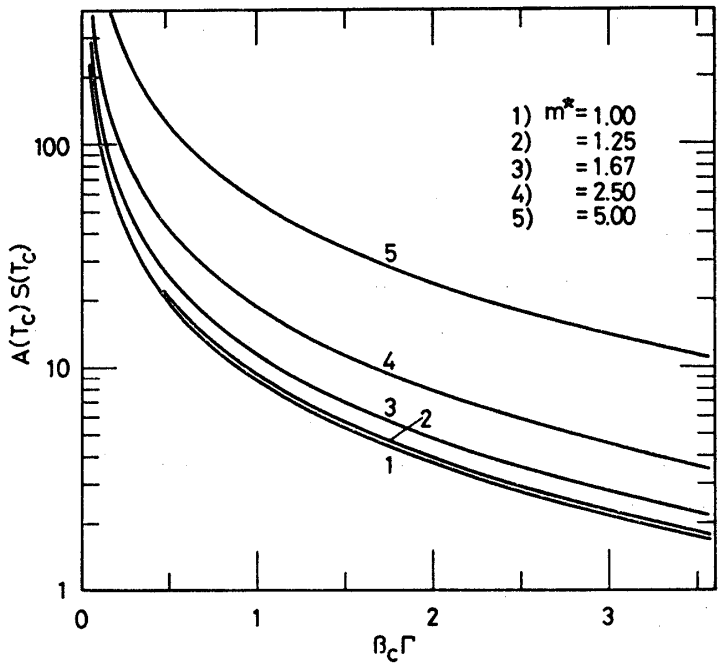

Fig. 2. Results of numerical calculations of $A(T_c)S(T_c)$ as a function of $\beta_c\Gamma$.

function of $\beta_c\Gamma$ for various values of m^*.

The magnitude of the jump at T_c in the slope of the normalized resistivity is analyzed. We examine the resistivity data on $TiSe_2$ single crystals by Di Salvo *et al.*[1,2] because infrared data[22] are available on the crystals. The crystals have $T_c \simeq 202$ K and $d\rho/dT \simeq -5.0\times10^{-5}$ Ωcm/K at T_c. The value of ρ_n is chosen to be 6.6×10^{-4} Ωcm by extraporating the ρ vs T curve linearly from high temperatures ($T>450$ K) to 202 K. (see Fig. 1 in ref. 2) Using eq. (12) with these values, we find $A(T_c)S(T_c)\simeq 15$. The effective-mass ratio m^* in the plane of the layers was estimated to be 2.5 from the infrared study of $TiSe_2$.[12] Heavy mass appears to be common to d-like electrons in dichalcogenides of group-IVB transition metals.[24] Figure 2 shows that for $m^*=2.5$ this value of $A(T_c)S(T_c)$ corresponds to the lifetime of carriers of $\tau\simeq 3.2\times10^{-14}$ sec at 200 K.

We compare the determined lifetime of carriers with infrared studies. Wilson *et al.*[22] obtained $\tau\simeq 2.78\times10^{-14}$ sec at 200 K by analyzing the infrared spectra of the $TiSe_2$ single crystals on the basis of a dominant carrier model. Liang *et al.*[12] reported $\tau\simeq 0.43\times10^{-14}$ sec at 214 K and 7.6×10^{-14} sec at 189 K. The lifetime of carriers tends to increase at lower temperatures. The

latter study also showed that the same scattering mechanism is operative at d. c. and at optical frequencies over a wide range of temperature.[12] Thus, there seems to be reasonable agreement between the lifetimes derived from the resistivity data and from the infrared data. Because of the crudeness of the theoretical model, a final conclusion cannot be drawn at the present stage, but it seems highly likely that the rapid change of the resistivity near T_c is caused by the onset of the excitonic phase. In addition, when we make more detailed comparison on a sounder basis, the presence of extra carriers must also be considered. These carriers result from structural defects[22] and suppress T_c by decreasing the number of holes. The appearance of the peak in the resistivity near 165 K appears to be due to the increase in the mobility of such extra carriers. It would be necessary to examine the contribution of extra carriers in order to explain the dependence of the Hall effect in $TiSe_2$ on temperature.[15]

3. TRANSITION TEMPERATURE

In the excitonic insulator, normal impurities have pair-breaking effects as in the case of magnetic impurities in superconductors.[20,23] Near T_c the excitonic insulator is in the gapless state because of the smallness of the order parameter. The transition temperature of the excitonic insulator is determined by the following equation :[23]

$$ln\frac{T_{c0}}{T_c}=\psi\left(\frac{1}{2}+\frac{\beta_c\Gamma}{2\pi}\right)-\psi\left(\frac{1}{2}\right), \tag{13}$$

where $\psi(x)$ is the digamma function and T_{c0} is the transition temperature of a pure material (i. e. $\Gamma=0$). The results of numerical calculations of T_{c0}/T_c

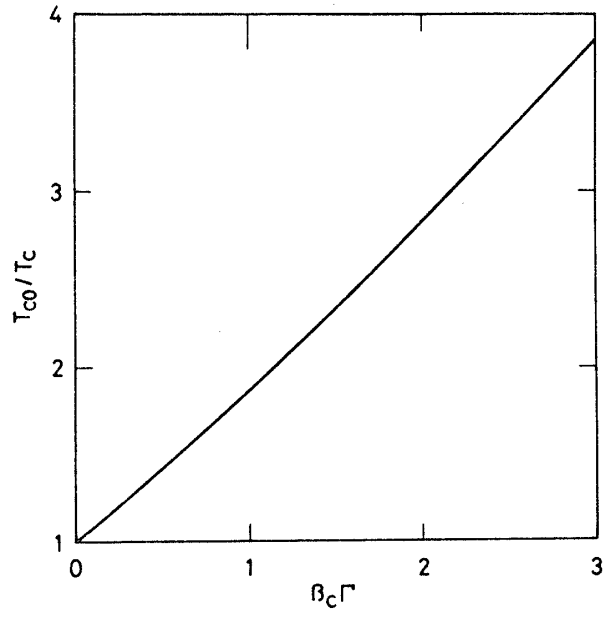

Fig. 3. Numerical solution for the transition temperature of the excitonic insulator containing normal impurities as a function of the inverse lifetime of carriers.

are represented in Fig. 3 as a function of $\beta_c\Gamma$. From Fig. 3 we obtain $T_{c0}\simeq$ 410 K for the value of $\beta_c\Gamma$ determined in the preceding section.

Strong short-range-order effects have been observed in $TiSe_2$. When temperature decreases, the resistivity starts to rise at about 450 K,[2] which is about 250 K higher than the onset temperature of the long-range-order condensation. In electron diffraction patterns, the diffuse $2a_0$ streaking is observed well above T_c.[7,8] A polaron model was proposed by Wilson,[25] where the precursor effects were related to exciton self-trapping. By contrast, the value of T_{c0} estimated above fairly agrees with the temperature, $T\simeq$450 K, where the resistivity begins to increase over the linear extraporation from higher temperatures. This result shows that the short-range-order effects could be connected with fluctuations in the order parameter. Although the transition temperature is suppressed by impurity scattering, it may be possible that spontaneous creations and annihilations of electron-hole pairs are repeated when $T_c<T\leq T_{c0}$.

4. CONCLUSIONS

The dependence of the electrical resistivity of $TiSe_2$ on temperature has been analyzed from the viewpoint of the excitonic-insulator mechanism. On the basis of the theories of excitonic insulators, the lifetime of carriers has been derived from the magnitude of the rapid change in the temperature gradient of the resistivity near T_c. The determined lifetime is consistent with the infrared results. The transition temperature of a perfect compound of $TiSe_2$ (i. e. with carriers having the infinite-lifetime) has been estimated to be$\sim$410 K. This estimation suggests that the short-range-order effects observed in $TiSe_2$ are correlated with fluctuations in the order parameter. These results support the possibility of the excitonic-insulator mechanism for the origin of the phase transition in $TiSe_2$. In order to make further comparison between theory and experiment, it is clearly necessary to establish a theoretical model which is more realistic and includes the electron-phonon coupling.

REFERENCES

1) Di Salvo, F. J., Moncton, D. E., and Waszczak, J. V. (1976) Electronic properties and superlattice formation in the semimetal $TiSe_2$. *Phys. Rev. B* **14**, 4321–4328
2) Di Salvo, F. J. and Waszczak, J. V. (1978) Transport properties and the phase transition in $Ti_{1-x}M_xSe_2$ (M=Ta or V). *Phys. Rev. B* **17**, 3801–3807
3) Zunger, A. and Freeman, A. J. (1978) Band structure and lattice instability of $TiSe_2$. *Phys. Rev. B* **17**, 1839–1842
4) Traum, M. M., Margaritondo, G., Smith, N. V., Rowe, J. E., and Di Salvo, F. J. (1978) $TiSe_2$: Semiconductor, semimetal, or excitonic insulator. *Phy. Rev. B* **17**, 1836–1838
5) Benda, J. A. (1974) Optical, electrical-transport, and heat-capacity studies of the solid solutions $Ti_xTa_{1-x}S_2$, $Zr_xTa_{1-x}S_2$, and $Ti_xNb_{1-x}Se_2$. *Phys. Rev. B* **10**, 1409–1420
6) Williams, P. M. (1976) Phase transitions and charge density waves in the layered transition metal dichalcogenides. In : Crystallography and Crystal Chemistry of Materials with Layered Structures. pp. 51–92, Reidel, Dordrecht
7) Woo, K. C., Brown, F. C., McMillan, W. L., Miller, R. J., Schaffman, M. J., and Sears, M. P. (1976) Superlattice formation in titanium diselenide. *Phys. Rev. B* **14**, 3242–3247

8) Wilson, J. A. and Mahajan, S. (1977) The anomalous behaviour of $TiSe_2$ and the excitonic insulator mechanism. *Commun. Phys.* **2**, 23–29
9) Wilson, J. A., Di Salvo, F. J., and Mahajan, S. (1975) Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides. *Adv. Phys.* **24**, 117–201
10) White, R. M. and Lucovsky, G. (1977) Suppression of antiferroelectricity in $TiSe_2$ by excess carriers. *Nuovo Cimento B* **38**, 280–289
11) Hughes, H. P. (1977) Structural distortion in $TiSe_2$ and related materials-a possible Jahn-Teller effect? *J. Phys. C* **10**, L319–L323
12) Liang, W. Y., Lucovsky, G., Mikkelsen, J. C., and Friend, R. H. (1979) Infra-red studies of $TiSe_2$: IR phonons and free carriers. *Philos. Mag. B* **39**, 133–146
13) Levy, F. (1979) Electrical resistivity and Hall effect in $TiSe_2$ containing vanadium impurities. *J. Phys. C* **12**, 3725–3732
14) Taguchi, I. (1979) Electrical resistivity and the phase transition temperatures of $Ti_{1-x}Hf_xSe_2$ mixed crystals. *Solid State Commun.* **32**, 679–681
15) Taguchi, I. (1981) Electrical resistivity and Hall effect in the mixed system $Ti_{1-x}Hf_xSe_2$. *J. Phys. C* **14**, 3221–3229
16) Yoshida, Y. and Motizuki, K. (1980) Electron lattice interaction and lattice instability of 1T-$TiSe_2$. *J. Phys. Soc. Jpn.* **49**, 898–905
17) Halperin, B. I. and Rice, T. M. (1968) The excitonic state at the semiconductor-semimetal transition. In : Solid State Phys. 21, pp. 115–192, Academic Press, New York
18) Taguchi, I. and Asai, M. (1981) Suppression of the resistivity anomaly in $TiSe_2$ at microwave frequencies. *Solid State Commun.* **40**, 187–189
19) Taguchi, I., Asai, M., Watanabe, Y., and Oka, M. (1980) Transport properties of iodine-free $TiSe_2$. Proc. 4th Yamada Conf. Physics and Chemistry of Layered Materials, Sendai, 1980; (1981) *Physica B* **105**, 146–150
20) Zittartz, J. (1968) Transport properties of the "excitonic insulator" : electrical conductivity. *Phys. Rev.* **165**, 605–611
21) Ebisawa, H. and Fukuyama, H. (1969) Hall effect in excitonc insulator. *Prog. Theor. Phys.* **42**, 512–522
22) Wilson, J. A., Barker, A. S., Di Salvo, F. J., and Ditzenberger, J. A. (1978) Infrared properties of the semimetal $TiSe_2$. *Phys. Rev. B* **18**, 2866–2875
23) Zittartz, J. (1967) Theory of the excitonic insulator in the presence of normal impurities. *Phys. Rev.* **164**, 575–582
24) Isomäki, H., von Boehm, J., and Krusius, P. (1979) Band structure of group IVA transition-metal dichalcogenides. *J. Phys. C* **12**, 3239–3252
25) Wilson, J. A. (1978) Proc. Int. Conf. Lattice Dynamics, Paris, 1977, p. 211, Flammarion, Paris