Tunnelling spectroscopic study of the CDW energy gap in $TiSe_2$

1995 J. Phys.: Condens. Matter 7 2553

(http://iopscience.iop.org/0953-8984/7/13/006)

J. Phys.: Condens. Matter 7 (1995) 2553–2561. Printed in the UK

Tunnelling spectroscopic study of the CDW energy gap in $TiSe_2$

Y Miyahara, H Bando and H Ozaki

Department of Electrical Engineering, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169, Japan

Received 18 November 1994, in final form 4 January 1995

Abstract. The CDW energy gap structure of $TiSe_2$ has been observed by tunnelling spectroscopy and its temperature dependence obtained for $77\ K \leqslant T \leqslant 295\ K$. In addition to the energy gap associated with the CDW with $T_c = 201$ K, a narrower gap structure was observed to persist at higher temperature, which explains the negative temperature coefficient of the ρ–T curve above T_c.

1. Introduction

It is well known that one of the layered group-IVB transition-metal dichalcogenides, $TiSe_2$, undergoes a CDW phase transition at around 200 K. This phase transition is accompanied by the emergence of a $2a_0 \times 2a_0 \times 2c_0$ superlattice structure, and an anomalous peak is observed in the electrical resistivity–temperature curve near 160 K (Di Salvo *et al* 1976, Brown 1980). This phase transition has attracted special interest because of its unusual features. One is that $TiSe_2$ has no incommensurate phase and exhibits a commensurate superstructure directly from the high-temperature phase, and another feature is that the band structure of $TiSe_2$ has been considered to be semimetallic (Friend *et al* 1977, Zunger and Freeman 1978, Chen *et al* 1980, Margaritondo *et al* 1981). Therefore, several models (Wilson 1978, White and Lucovsky 1977, Hughes 1977), which are different from those for the group-VB materials, have been proposed for the mechanism of the phase transition. Most of these models rely on an energy band structure that is semimetallic.

Recently, however, a few authors questioned the semimetallic picture for this material, on the basis of their experimental data which implied that the value of the band overlap was much smaller than the accepted value of 0.2 eV or that there was a small band gap (Stoffel *et al* 1985, Anderson *et al* 1985b, Starnberg *et al* 1987, Coleman *et al* 1992). Thus, the electronic states above the transition temperature are expected to be investigated.

Furthermore, investigation of the CDW energy gap has not been carried out systematically, though it is important to characterize the CDW phase transition. Woo *et al* (1978) carried out infrared reflectivity measurements on $TiSe_2$ at 80 K, and derived a peak in the absorption coefficient at 0.4 eV. They attributed it to the CDW gap. Photoemission studies were carried out by several authors, and energy gap structures were observed near the Fermi level (Margaritondo *et al* 1981, Stoffel *et al* 1982, Anderson *et al* 1985a, Stoffel *et al* 1985). However, quantitative estimations of the gap were difficult because of those energy resolutions. Temperature dependences of the photoemission spectra were also observed by Anderson *et al* (1985a). However, the relationship of the spectra and the CDW gap was not

0953-8984/95/132553+09$19.50

made clear. Thus, a systematic investigation on the CDW energy gap in $TiSe_2$ is needed. Tunnelling spectroscopy is one of the most promising methods for this investigation.

In the present study, we have measured for the first time the temperature dependence of the CDW energy gap structure of $TiSe_2$ in the temperature range $77\,K \leqslant T \leqslant 295\,K$, by means of tunnelling spectroscopy.

2. Experiments

2.1. Crystal growth

Generally, in $TiSe_2$, the sample preparation conditions can lead to deviations from stoichiometry, and the resulting crystals tend to be rich in Ti. The non-stoichiometry causes variations of the physical properties such as the phase transition. Di Salvo *et al* (1976) made it clear that the high growth temperature leads to a large deviation from stoichiometry, and thus a suppression of the phase transition. Further, Taguchi (1981) pointed out that the iodine generally used as a chemical transport agent was incorporated in the crystals, and tended to suppress the phase transition. These effects are considered to be caused by the extrinsic carriers that originate from the excess Ti or iodine; therefore, the excess Ti or iodine must be minimized.

We tried two sample preparation methods. One is the usual chemical vapour transport with iodine, and the other is direct synthesis from the constituent elements without iodine. We obtained relatively large and good crystals by the latter method. Consequently, we employed iodine-free samples for the following measurements. In this method, stoichiometric amounts of the elements (purities Ti: 99.99%, Se: 99.999%) were weighed and sealed into the quartz ampoule (10 mm diameter $\times$ 200 mm length) under vacuum (6×10^{-6} Torr) with excess Se of about 5 mg per cm^3 of ampoule volume. Then the ampoule was heated to 700 °C for 120 hours. The typical size of the resulting crystals was 5 mm $\times$ 5 mm, and 10–100 μm thick—thinner than those prepared by using iodine. The crystal surfaces exhibited metallic lustre, and seemed cleaner than the crystals developed using iodine. Therefore, we did not cleave the crystal surfaces for the tunnelling measurements.

2.2. ρ–T measurements

To estimate the sample quality and the critical temperature of the phase transition, we measured the temperature dependence of the electrical resistivity perpendicular to the c axis (temperature range 77 K–300 K) by using the Van der Pauw technique. The electrical contacts were formed by indium soldering.

2.3. Tunnelling spectroscopy measurements

Tunnelling spectroscopy measurements were carried out in the metal/insulator/sample structure. The tunnel junctions were fabricated by the following method. Al was evaporated onto a clean glass substrate and it was heated to 150 °C for 30 minutes in an O_2 atmosphere of 50 Torr to oxidize the Al surface. Then it was left in the chamber for 12 hours at room temperature. The Al_2O_3 surface, thus prepared, was pressed onto the $TiSe_2$ sample surface to form the tunnel junction as shown in figure 1. In this planar contact method, the condition of the junction can be varied by varying the applied force. To avoid the effects of the series resistance, such as lead resistance and the contact resistance, on the tunnelling

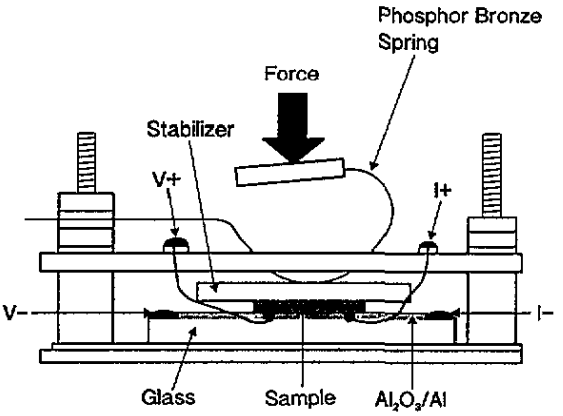

Figure 1. The geometry of the tunnel unit.

characteristics, we employed the four-terminal method with separate terminals for measuring the bias voltage and the current. Ohmic contacts were formed by indium soldering similarly to in the ρ–T measurements. We confirmed that the series resistance was negligibly small ($\leqslant 0.1\,\Omega$) compared with the tunnel junction resistance ($\sim 100\,\Omega$). The measurements were carried out in the temperature range 77 K–295 K. Temperature was controlled by a heater, and the temperature fluctuation during the measurements was within 1 K. We used the standard modulation technique with a modulation bias of 1 mV to obtain the differential conductance $\mathrm{d}I/\mathrm{d}V$ but sometimes also carried out numerical differentiations of the I–V characteristics.

3. Results

3.1. ρ–T measurements

The temperature dependence of the electrical resistivity measured perpendicular to the c axis is shown in figure 2. According to the definition of Di Salvo *et al* (1976), we find that the critical temperature is 201 K by analysing the discontinuity in the $\mathrm{d}\rho/\mathrm{d}T$–$T$ curve as shown in the inset of figure 2. The value of $\rho_{\max}/\rho(300\ \mathrm{K})$, which is considered to show the degree of stoichiometry, is 3.14. It is known that the amount by which this resistivity ratio exceeds 3 is a measure of the stoichiometry with respect to the phase transition. The temperature of the resistivity peak is 155 K, and is lower than that in the crystals grown by using iodine. This is in agreement with Taguchi's result (Taguchi *et al* 1981). Judging from the above results, we have confirmed that our samples have a good enough quality for the study of the phase transition.

3.2. Tunnelling spectroscopy measurements

The tunnelling spectrum measured at 81 K in the low-temperature phase is shown in figure 3. A couple of knee structures are observed at around ± 0.4 eV in the I–V curve and, correspondingly, a gap structure appears in the $\mathrm{d}I/\mathrm{d}V$–V curve. This structure is almost symmetrical, and peaks like those in a superconductor are observed at the gap edges. The intensities of these peaks depend on the condition of the tunnel junction. When the applied bias voltage exceeds the gap-edge bias voltage, the tunnelling current tends to

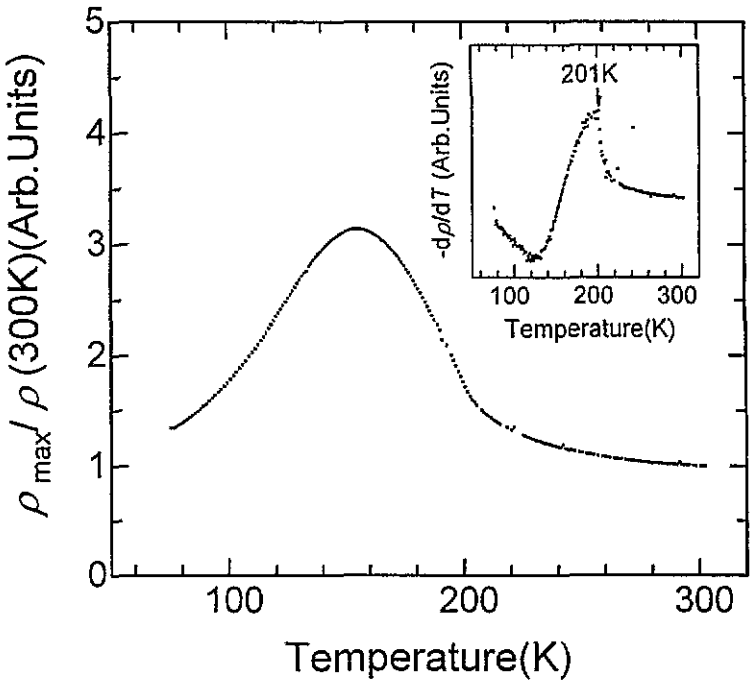

Figure 2. The temperature dependence of the normalized resistivity of $TiSe_2$. The inset shows $d\rho/dT$–T for the same sample.

become unstable; therefore, we limited the bias voltage to a value just above the gap-edge bias voltage. This instability is considered to be due to the disturbance of the CDW states caused by the tunnelling injection or ejection of electrons in CDW states. Further, the hump structures inside the gap are sensitive to the condition of the tunnel junction. Except for these features, the general shape of the tunnelling spectrum was reproducible. The tunnelling measurements were carried out separately in the higher- and in the lower-temperature region in order to establish the tunnel junction suited to each temperature range. Figures 4(*a*) and (*b*) show the temperature dependences of the tunnelling spectra in the lower- and higher-temperature regions, respectively. In these figures, the curves are shifted vertically for clarity but the scale is common to all the curves. The profiles of the dI/dV–V curves including the gap width and the gap depth systematically depend on the temperature. The curves have a flat region inside the gap below 150 K. This flat region becomes narrower with increasing temperature, and above 160 K the curve has a parabolic shape. As the temperature increases, the dip of the curve becomes shallower, and the curve becomes more or less flat at high temperatures. Figure 4(*c*) displays in detail the curves in figure 4(*b*) for temperatures of 256 K, 272 K and 295 K. As seen in the figure, the pseudo-gap structure is found to remain at 256 K, but it seems to have vanished at 295 K.

Owing to the shape and its temperature dependence, we conclude that the gap structure reflects the pseudo-gap associated with the CDW transition.

For the actual CDW states, the dI/dV–V curve is difficult to characterize on the basis of one energy gap value, because the curve will depend on the degree of obliteration of the Fermi surface, the variation of the gap and so on. However, if there is a well defined average energy gap, there will appear a bias range where dI/dV increases from the low in-gap value to the high out-of-gap value in the dI/dV–V characteristics. From this viewpoint,

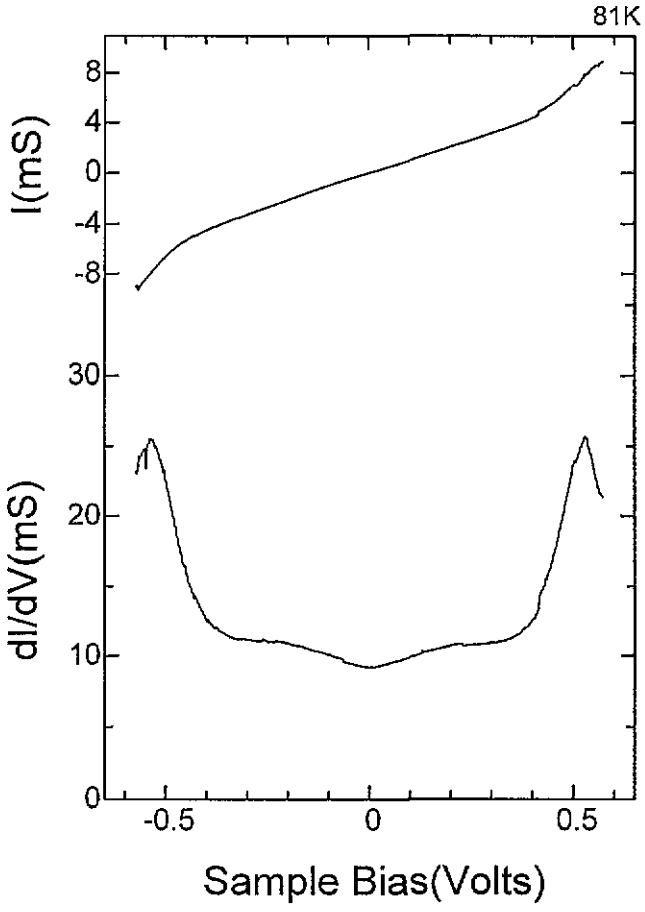

Figure 3. The tunnelling spectrum of $TiSe_2$ at 77 K.

we define an average CDW gap as the separation of the bias voltages at which the dI/dV–V curve takes the maximum slopes for each bias polarity, and this is used in this paper from now on.

Figure 5 shows the temperature dependence of the CDW gap, thus defined, in $TiSe_2$ derived from figure 4.

Another method of determination of the gap, often employed, is to measure the separation of the peaks for each bias porality in the dI/dV–V curve. The gap values determined by this method are about 0.1 eV larger than those shown in figure 5 for the whole the temperature range, and the overall behaviour of the temperature dependence is quite similar to that in figure 5. When the gap structure is broadened in the weak-coupling model, the estimation of the gap using the maximum slopes is known to be a fairly good approximation, while that using the peaks gives an overestimation.

As is shown in figure 5, the CDW gap width increases monotonically with decreasing temperature, and it approaches 1 eV at liquid nitrogen temperature.

Furthermore, these data demonstrate the important fact that the gap structure definitely exists even above T_c determined from the ρ–T measurement. This verifies clearly that a fluctuation of CDW remains above T_c as pointed out by several authors (Di Salvo *et al* 1976, Caillé *et al* 1983, Anderson *et al* 1985a, b).

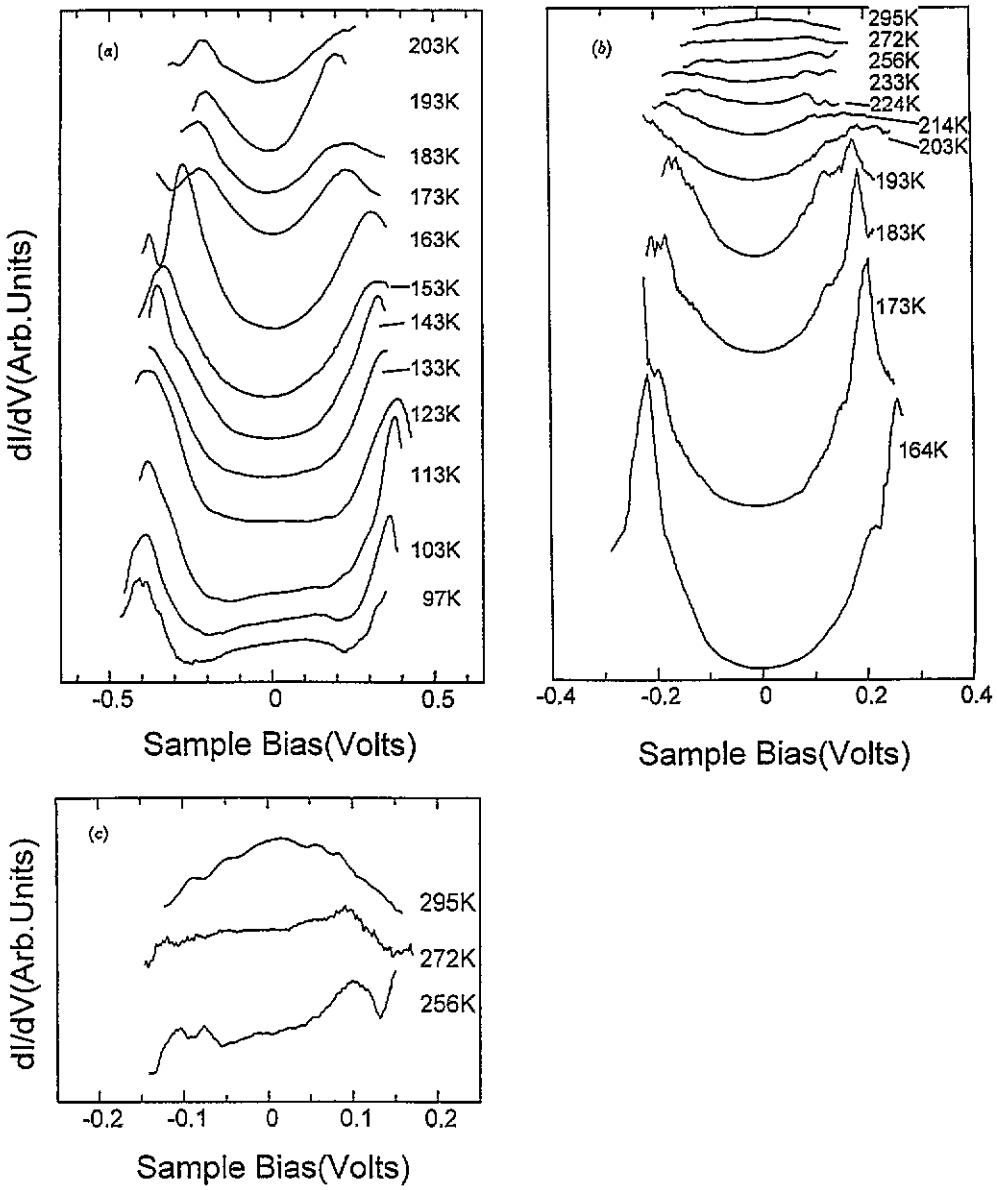

Figure 4. Tunnelling spectra of $TiSe_2$ at various temperatures. (*a*) (97 K $\leqslant T \leqslant$ 203 K) and (*b*) (164 K $\leqslant T \leqslant$ 295 K) show measurements for the different runs. (*c*) shows the dI/dV–V curves at 256 K, 272 K and 295 K in detail.

4. Discussion

Information about the CDW gap including the temperature dependence is important in discussing the CDW phase transition. We have measured for the first time the temperature dependence of the CDW energy gap of $TiSe_2$ by means of tunnelling spectroscopy for the temperature range 77 K $\leqslant T \leqslant$ 295 K. There have been some experimental evaluations of the CDW gap from optical and the photoemission measurements, but most of the studies

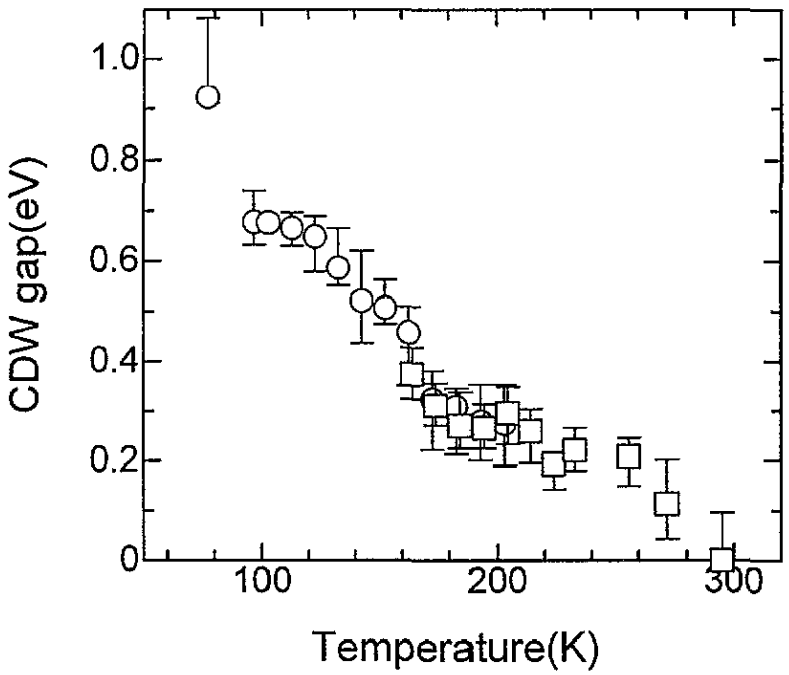

Figure 5. The temperature dependence of the CDW gap derived from figure 4. ○, from figure 4(*a*); and □, from figure 4(*b*).

were made at a particular temperature.

It is well known that the values of $2\Delta_{CDW}/k_BT_c$, for the layered-compound transition-metal dichalcogenides are usually much larger than the value of 3.5 expected for a weak-coupling, long-coherence-length model (Wang *et al* 1991). For the CDW states in these materials, a short-coherence-length model proposed by McMillan (1977) is required. In the present study, the energy gap approaches 1 eV at liquid nitrogen temperature. If we use this value as a measure of $\Delta(0)$, $2\Delta(0)/k_BT_c = 57$. Woo *et al* (1978) obtained a CDW gap in $TiSe_2$ of 0.4 eV at 80 K from infrared reflectivity measurement. Our result is considerably larger. We can find an additional structure at around ± 0.2 eV in the dI/dV–V curve in figure 3, and there is a possibility that this structure is connected with Woo's optical result. There is a report that the intensity of the CDW in 1T-TaS_2 is somewhat larger in the surface layer than in the bulk (Cantini *et al* 1980). If this is the case also with $TiSe_2$, there is another possibility—that a part of the difference comes from the surface effect because the tunnelling measurement mainly 'observes' the density of states near the surface.

There have been photoemission studies of $TiSe_2$ (Margaritondo *et al* 1981, Stoffel *et al* 1982, Stoffel *et al* 1985, Anderson *et al* 1985a, b). In these studies, reductions of the densities of states were observed immediately below the Fermi level at lower temperature, and they were assigned to the CDW gap. They are qualitatively in agreement with our results, though it is rather difficult to estimate the gap value from the photoemission data. The photoemission measurement gives information only below the Fermi level, and as the energy resolution is insufficient for us to derive the energy gap value quantitatively.

Figure 5 shows that there is a sudden change in the temperature dependence of the gap structure at around 160 K. This temperature corresponds to the change in the profile of the tunnelling dI/dV–V curves in figures 4(*a*) and (*b*); that is, below this temperature the

curves have a flat bottom while above this temperature they have a parabolic shape. As shown in figure 5, the gap increases rapidly with decreasing temperature below 160 K. It is to be noted that the gap approaches zero near 201 K—that is the critical temperature, when the temperature dependence below 160 K is extrapolated to the higher temperature. This implies that the energy gap structure below 160 K is due to the CDW that originates at $T_c = 201$ K.

Figures 4 and 5 show that the gap structure exists even above T_c (201 K). This indicates that the fluctuations of the CDW above T_c play an important role in the CDW phase transition of $TiSe_2$ (McMillan 1977). This is manifested in the anomalous behaviour of ρ–T characteristics above T_c that has not been pointed out previously.

The peak in the ρ–T curve has been explained as follows (Di Salvo *et al* 1976). $TiSe_2$ in the normal phase has a semimetallic band structure; thus, the electrical conduction is metallic. However, in the low-temperature phase, the density of states near the Fermi level decreases due to the CDW phase transition (forming the CDW gap), and the decrease in the number of carriers causes the increase in the electrical resistivity. Nevertheless, the Fermi surface is not lost completely—a fragment of it remains even at the lowest temperature. Therefore, with further decrease in the temperature, the reduction of the thermal scattering of carriers causes the decrease in the electrical resistivity and, thus, forms a peak. If this is the case with the above model, the ρ–T characteristics should have a metallic behaviour above T_c. In the above model the fluctuations were not considered above T_c, and thus the samples were purely in the normal phase above T_c.

In contrast, experiments show a negative temperature coefficient (so-called semiconducting behaviour) in the ρ–T curve even around room temperature, which is inconsistent with the view of a rigid semimetallic band structure. This behaviour is pronounced in the higher-quality sample, which has a larger value of $\rho_{max}/\rho(300\,K)$ (Di Salvo *et al* 1976). Therefore, the negative temperature coefficient above T_c is an intrinsic property, and the metallic behaviour above T_c, observed in the lower-quality sample, is extrinsic and due to the excess carriers originating from the imperfections, such as the non-stoichiometry. The negative temperature coefficient above T_c is explained as follows. At high temperature the $TiSe_2$ is in the normal phase with semimetallic character. As the temperature decreases, the fluctuation of the CDW increases and a pseudo-gap opens and grows at the Fermi level. With the growth of the pseudo-gap, the density of states at the Fermi level decreases and this causes the increase in the electrical resistivity.

Thus, around room temperature, the electronic states are semimetallic in the sense that there is a density of states at the Fermi level, but the electronic states at the Fermi level are in the pseudo-gap due to the fluctuations of the CDW, and are quite different from those in the semimetal predicted by the band calculation for the normal states. Thus the negative temperature coefficient in the ρ–T characteristics above T_c implies the importance of the fluctuations of the CDW in $TiSe_2$, and it is in agreement with the fact that diffusive superlattice spots were observed in the electron diffraction and the x-ray diffraction patterns above T_c (Woo *et al* 1976). The importance of the fluctuations above T_c, which was suggested by some authors previously, has thus been demonstrrated convincingly in this study.

5. Conclusion

The temperature dependence of the CDW energy gap of $TiSe_2$ has been observed via the tunnelling spectroscopy. In addition to the energy gap structure associated with the CDW which originates at $T_c = 201$ K, a narrower gap structure has been observed to persist

at higher temperature. The existence of this pseudo-gap due to the fluctuations of the CDW corresponds to the diffusive satellite spots obtained in the x-ray and the electron diffraction measurements, and it explains the negative temperature coefficient of the ρ–T curve above T_c.

Acknowledgments

We thank K Sano for assistance in the whole experiment, and we also thank M Tohda for assistance in the sample preparation. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture.

References

Anderson O, Karschnick G, Manzke R and Skibowski M 1985a *Solid State Commun.* **53** 339
Anderson O, Manzke R and Skibowski M 1985b *Phys. Rev. Lett.* **55** 2188
Brown F C 1980 *Physica* B **99** 264
Caillé A, Lepine Y, Jerico M H and Simpson A M 1983 *Phys. Rev.* B **28** 5454
Cantini P, Boato G and Colella R 1980 *Physica* B **99** 59
Chen C H, Fabian W, Brown F C, Woo K C, Davies B, DeLong B and Thompson A H 1980 *Phys. Rev.* B **21** 615
Coleman R V, Dai Zhenxi, McNairy W W, Slough C G and Wang Chen 1992 *Surface Properies of Layered Structures* ed G Benedek (Dordrecht: Kluwer Academic) p 88
Di Salvo F J, Moncton D E and Waszczak J V 1976 *Phys. Rev.* B **14** 4321
Friend R H, Jérome D, Liang W Y, Mickkelsen J C and Yoffe A D 1977 *J. Phys. C: Solid State Phys.* **10** L705
Hughes H P 1977 *J. Phys C: Solid State Phys.* **10** L319
Margaritondo G, Bertoni C M, Weaver J H, Lévy F, Stoffel N G and Katnani A D 1981 *Phys. Rev.* B **23** 3765
McMillan W L 1977 *Phys. Rev.* B **16** 643
Starnberg H I, Johnson M T, Friend R H, Hughes H P and Lévy F 1987 *J. Phys. C: Solid State Phys.* **20** 1483
Stoffel N G, Kevan S D and Smith N V 1985 *Phys. Rev* B **31** 8049
Stoffel N G, Lévy F, Bertoni C M and Margaritondo G 1982 *Solid State Commun.* **41** 53
Taguchi I, Asai M, Watanabe Y and Oka M 1981 *Physica* B **105** 146
Wang C, Slough C G, Coleman R V 1991 *J. Vac. Sci. Technol.* B **9** 1048
White R M and Lucovsky G 1977 *Phil. Mag.* B **39** 133
Wilson J A 1978 *Phys. Status Solidi* b **86** 11
Woo K C, Brown F C, McMillan W L, Miller R J, Schaffman M J and Sears M P 1976 *Phys. Rev.* B **14** 3242
Woo K C, Brown F C and Silsbee R H 1978 *Solid State Commun.* **28** 341
Zunger A and Freeman A J 1978 *Phys. Rev* B **17** 1839