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Electron Localization Probed by Temperature-dependent Tunneling Spectroscopy in 1T-TaS_2

Ju-Jin Kim

Department of Physics, Chonbuk National University, Chonju 560-756

Håkan Olin

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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In order to present a clear picture of the density of states at both sides of the Fermi level (E_F) in 1T-TaS_2 near the nearly commensurate to commensurate transition ($\sim$ 187 K) and at low temperatures, we have done a temperature-dependent tunneling spectroscopy study using a scanning tunneling microscope. We observed an abrupt transition from a charge-density-wave induced depletion to an opening of a deep pseudo gap near the E_F of the nearly commensurate to commensurate transition within $\sim$ 1 K. The measured pseudo gap turned out to be deep enough to form localized states at E_F. In contrast to an inverse photoelectron spectroscopy study, our tunneling results indicate the gap structures of two Hubbard subbands resulting from band splitting of the Ta 5d band due to the electron correlation effect.

The transition metal dichalcogenides have received much attention as a typical group of materials that form charge density waves (CDWs) [1–2]. Among the transition metal dichacogenides, 1T-TaS_2 shows very peculiar physical properties which include a dramatic change in resistivity and Hall data at the nearly commensurate (NC) to commensurate (C) CDW transition temperature and an insulating behavior of resistivity at low temperatures [1–4]. It is known that the occurrence of Mott localization at the NC-C transition temperature [5,6] and disorder-driven Anderson localization [2,4] may play a crucial role in the low-temperature transport properties. A spectral peak at 150 $\sim$ 200 meV, which is considered to be due to the lower Hubbard band, has been observed by several groups [3,4] using photoelectron spectroscopy (PES), although there has still been no observation of the upper Hubbard band [7]. Recently, Dardel *et al.* [4] observed the abrupt collapse of the Fermi surface at the NC-C transition. Also, by using high-resolution PES, they determined that the Fermi level lay in a deep, temperature dependent pseudo gap. These observations give a clue for explaining the existing conflicts between the well-known transport properties and the previous PES data.

After Coleman *et al.* [8] first observed the CDW image in real space with scanning tunneling microscopy (STM), extensive works have been done to image the CDW directly in real space with respect to the atomic lattice in various layered dichalcogenides [9–10]. Spectroscopic techniques using the STM [9] and conventional macroscopic tunneling method [11] have also been applied to the layered materials to observe the CDW gap. However, the tunneling spectra obtained by using STM and conventional macroscopic tunneling techniques so far have given no explanation for the existing conflicts in the nature of 1T-TaS_2 and are also quite different from the existing PES results [9,11,12].

The effect of the phase transition near the NC-C transition in the unoccupied band was also investigated by Classen *et al.* using inverse photoelectron spectroscopy (IPES) [7]. There was no indication of a change of the electronic structure in the unoccupied band at the NC-C transition, contrary to the results for the occupied band. Hence, they concluded that the localization gap opens entirely in the occupied band and that the Fermi level is pinned close to the lowest unoccupied band. However, since the IPES technique has relatively low energy resolution, the real nature of the unoccupied band might not yet be clear.

Tunneling spectroscopy is a high-resolution method for investigating changes in the density of states (DOS) near E_F. Noutomi *et al.* [12] have studied the temperature dependent CDW gap structure of 1T-TaS_2 by using the tunneling junction method. They could only observe an

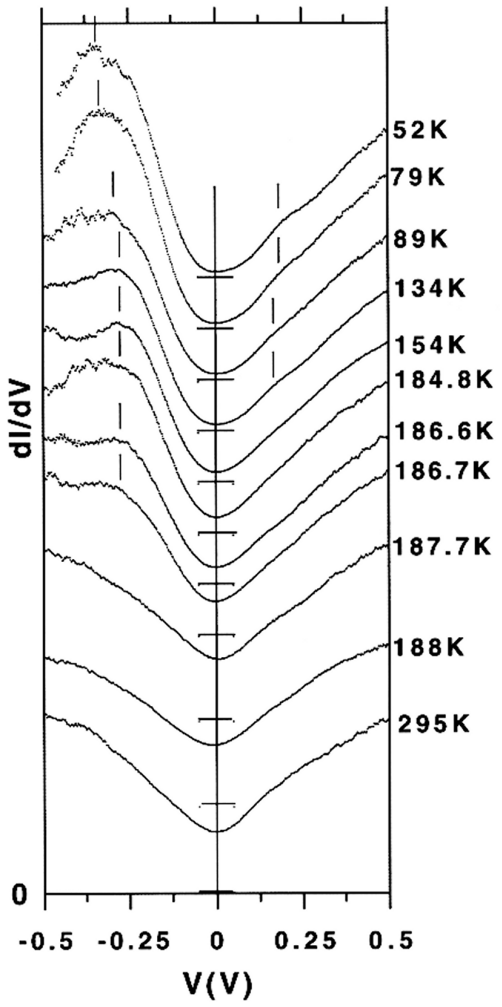

Fig. 1. Tunneling spectra at different temperatures. The bias voltage was 0.3 V, and the tunnel current was 0.75 nA. The small horizontal bars represent the zeros for the individual dI/dV curves.

energy gap of about 0.4 eV in the NC phase, and a gradually increasing gap, up to 1.0 eV, while lowering the temperature. Particularly, they did not observe any change in the tunneling spectra near E_F at the NC-C transition, contradictory to results of the PES experiment. Because it might be difficult to make a stable insulating barrier on the fragile surface of this layered material, if one can make a more reliable tunneling barrier, the tunneling method should give valuable information about the unusual phase transition in this system due to its high resolution capability near E_F.

To clarify the picture of the DOS at both sides of E_F in $1T$-TaS_2 around the NC-C transition, we used temperature-dependent tunneling spectroscopy employing STM. In contrast to the PES technique, tunneling spectroscopy simultaneously gives high resolution information about the DOS both in the occupied and the unoccupied bands. We observed an abrupt transition from CDW-induced depletion to an opening of a deep pseudo gap near E_F within 1 K of the NC-C transition temperature. The measured pseudo gap was deep enough to form localized states at E_F.

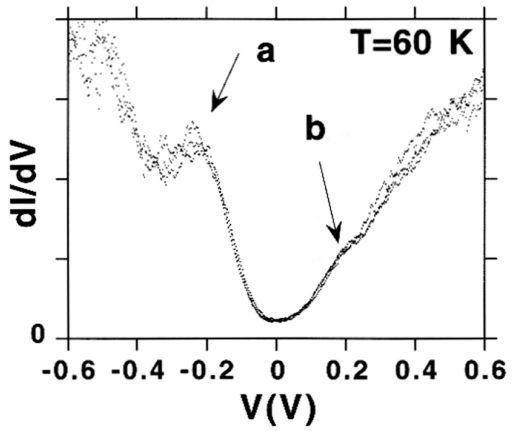

Fig. 2. Typical tunneling spectra in the C phase at 60 K. The bias voltage was 0.3 V, and the tunnel current was 0.5 nA. The zero point of dI/dV is the V-axis.

Single crystals of $1T$-TaS_2 were grown by the usual iodine transport method [2]. We used a commercial variable temperature-dependent ultrahigh vacuum STM (Omicron Vakuumphysik GmbH) equipped with a He flow cryostat [13]. The temperature was controlled by counter resistive heating. Under equilibrium conditions, the temperature stability was better than 0.1 K. The sample was cleaved in air. The experiments were made below 8×10^{-11} mbar. The dI/dV curves for the negative and the positive sides of the bias voltage reflect the local density of states below and above the Fermi level, respectively. Electrochemically etched W tips were used.

The STM image showed a the typical hexagonal $\sqrt{13}\times\sqrt{13}$ CDW superlattice with a period of $\sim$ 12 Å. Domain structures with periods 80-85 Å also existed, indicating that the sample is in the NC phase. To get reliable and reproducible tunneling spectra, we first located a flat and defect-free region of the sample and then the measured tunneling spectra at about every 18 Å (11 × 11 array) over a 200 Å × 200 Å area. To increase the signal-to-noise ratio, we averaged the spectra over this area for each temperature. In this way, we could get very reproducible tunneling spectra at a local area of the sample surface. Typical bias voltages and tunnel currents for tunneling spectroscopy were +0.3 V and 0.5 nA, respectively. The STM images showed a clear $\sqrt{13}\times\sqrt{13}$ CDW structure over the whole measured temperature range.

Temperature-dependent tunneling spectra near the NC-C transition are shown in Fig. 1. At high temperatures, that is, above 187.7 K, the measured tunneling spectra show a broad opening of the CDW gap. The

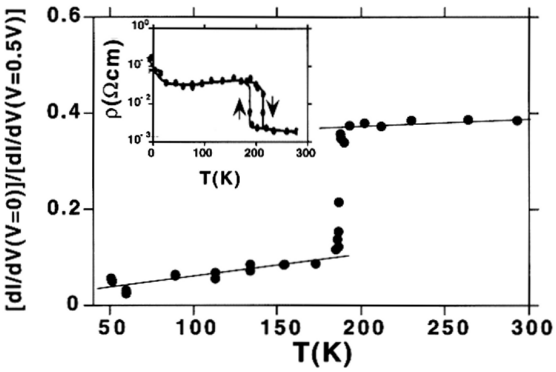

Fig. 3. Temperature dependence of the normalized zero-bias conductance, $[dI/dV(V{=}0\text{ V})]/[dI/dV(V{=}0.5\text{ V})]$, which is a rough measure of the DOS at E_F. the inset is the temperature-dependent resistivity of the $1T$-TaS_2 single crystal used in this experiment.

CDW-driven band splitting structures of the Ta $5d$ band in the occupied band, which are commonly found in high resolution PES measurements [3,4] is not clear in our tunneling spectra. However, our spectra are closer to the ones obtained by the macroscopic tunneling junction method in the NC phase [11,12]. In contrast to the angle-resolved PES technique, STM tunneling spectra represent spectra averaged over the Fermi surface ones with appropriate weights and are more closely related to the angle integrated-photoelectron spectra [14]. Hence, we believe that the absence of detailed structures in our NC tunneling spectra might reflect this.

Decreasing the temperature below 300 K, the CDW-induced depletion of the DOS near E_F changed very little. However, between 187.7 K and 186.6 K, the tunneling spectra changed abruptly, and simultaneously a prominent peak structure appeared at ~ -0.25 V in the occupied band. We also noticed that the DOS at E_F dropped drastically, which represented an opening of a deep pseudo gap structure. Note that there is still a finite DOS at E_F after the transition. However, no appreciable gap structure was observed in the unoccupied band at this temperature, except an abrupt drop of DOS at E_F.

At temperatures below the abrupt transition, the general shapes of the tunneling spectra were not changed although there was a gradual increase of the peak at ~ -0.25 V. However, by further decreasing the temperature, a small, but clear, gap structure in the unoccupied band appeared at ~ 0.20 V, and the gap structure in the occupied band widened slightly, as shown in Fig. 1. Figure 2 shows the tunneling spectra at 60 K, which demonstrate the high reproducibility of the tunneling spectra at each location. The tunneling spectra clearly reveal the presence of two reproducible characteristic peak structures at V$\approx$ –250 $\sim$ –300 mV (peak a in Fig. 2) and +200 mV (peak b in Fig. 2). From our tunneling spectra, the overall size of the pseudo gap structure is estimated to be 0.45 - 0.5 eV, which is consistent with an optical measurement at 80 K by Baker *et al.* [15]. The optical measurement showed a broad gap of 0.5 eV having a considerable depletion of the DOS.

From our tunneling measurements and the existing PES results [3,4], we can derive a qualitative picture of the DOS near E_F. According to the band calculation by Matteiss [16], the undistorted $1T$-TaS_2, that is, without the CDW formation, has a half- filled Ta d_z^2 band with a width of about 2.5 eV. This leads to a good metallic character. However, the incorporation of the CDW modulation drastically distorts the electronic band structure. The d_z^2 band collapses into three sub-manifolds separated by energy gaps of 0.1 and 0.2 eV [17]. The Fermi level stays in the middle of the narrow uppermost band. This may, of course, reflect the omission of the electron correlation effect from the band calculation. Considering this correlation effect, the narrow uppermost band is susceptible to splitting into two independent bands. We believe that these two bands correspond to the two peak structures on both sides of the Fermi level in our tunneling spectra. Comparing our tunneling results with the existing PES spectra of Manzke *et al.* [3] and Dardel *et al.* [4], the sharp peak structure in the occupied band can be interpreted as representing the lower Hubbard band. Since there has been no theoretical study, as far as we know, of the band structure with both CDW and electron-correlation effects considered, it is, at this point, difficult to address any quantitative comment. However, our tunneling results are, as noted above, consistent with the optical measurement by Baker *et al.* [15]. Considering the lower Hubbard band to be located at ~ 0.25 eV, we can regard the peak structure in the unoccupied band as the upper Hubbard band. Then, our tunneling spectra give experimental evidence that the splitting of the narrow uppermost CDW-derived band is due to electron correlation effects. This corresponds to an opening of gap structures at the E_F in our tunneling spectra below the NC-C transition, rather than the pinning of the E_F as suggested by the IPES study.

A resistivity measurement of our sample [inset of Fig. 3] shows that the NC-C phase transition occurs around 187 K during cooling. Figiure 3 shows the temperature dependence of the normalized zero-bias conductance, $[dI/dV(V{=}0\text{ V})]/[dI/dV(V{=}0.5\text{ V})]$, which is a rough measure of the thermally smeared DOS at the Fermi level, $N(E_F)$. This entirely governs the electron-transport properties. $N(E_F)$ drops abruptly around 187 K, at the same temperature where the discontinuity of resistivity takes place. This shows that the abrupt tenfold increase of resistivity at the NC-C transition is caused by the drop of $N(E_F)$, and not by a decrease of mobility. This sudden drop of carrier density at the NC-C transition is difficult to explain in any way except to invoke a metal-insulator transition. Apparently, the DOS remains finite below the transition and decreases very

slowly with decreasing temperature. If the pseudo gap is deep enough, that is, below Mott's criterion for Anderson localization, the DOS should be localized, and the conduction at low temperature should be caused by thermally activated hopping. At higher temperatures, carriers should be excited to the mobility edge, E_c [18]. Mott's criterion reads $g = N(E_F)/N(E_F)_{free} \approx 0.3$, where $N(E_F)_{free}$ is the free-electron value of $N(E_F)$. If we assume that the value of $N(E_F)_{free}$ is equivalent to $N(E_F)$ before the transition, although it might be underestimated due to the existing CDW depletion, we can roughly estimate the g-value from the data in Fig. 3. According to this the g-value is smaller than ~ 0.23 below the NC-C transition; our tunneling data lead us to suggest that the remaining $N(E_F)$ should be localized below the NC-C transition. The very weak metallic character between 180 K and 60 K can be explained by excitation of carriers to the mobility edge, in line with Mott's idea, and the unbounded increase in the resistivity below 50 K is due to the thermally activated hopping processes. The hopping leads to a variable-range hopping conductivity $\sigma(T) \propto \exp(-T_o/T)^{\nu}$ at low temperatures. For a non-interacting electron system, ν=1/4 in 3-dimensions and ν=1/3 in 2-dimensions [18].

In summary, we used temperature-dependent tunneling spectroscopy to clarify the real nature of the DOS in 1T-TaS_2 near the NC-C transition. The tunneling spectra showed an abrupt appearance of a pseudo gap at E_F below the NC-C transition temperature due to a Mott transition. The measured pseudo gap turned out to be deep enough to form localized states at the E_F. In contrast to the IPES study, our tunneling results show pseudo gap structures of two Hubbard subbands resulting from the band splitting of the Ta 5d band due to the electron-correlation effect.

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