Temperature-dependent scanning tunneling spectroscopy of $1T$-TaS_2

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We have studied temperature-dependent tunneling spectroscopy of $1T$-TaS_2 from room temperature down to about 40 K. The spectra indicated an abrupt transition from the charge-density-wave-induced broad depletion to an opening of a deep pseudogap within 1 K of the nearly commensurate to commensurate transition temperature. The measured pseudogap was deep enough to form localized states at the Fermi level. In contrast to an inverse photoelectron spectroscopy study, our tunneling results indicate gap structures of two Hubbard subbands resulting from the band splitting of the Ta $5d$ band due to the electron correlation effect. We have also found an abrupt increase of thermoelectric voltage developing between the tip and sample at the transition temperature. [S0163-1829(96)05327-1]

$1T$-TaS_2 has unique physical properties among transition-metal dichalcogenides. Among these properties there are a complex charge-density-wave (CDW) phase diagram and an abrupt change of physical properties at the nearly commensurate (NC) to commensurate (C) CDW transition which occurs at $\sim$190 K.[1,2] Recent studies using temperature-dependent high-resolution photoelectron spectroscopy (PES) (Refs. 3 and 4) revealed the detailed nature of the density of states (DOS) near the Fermi level (E_F) in this material. In particular, the existence of a deep pseudogap in the occupied band was observed, which gives us a clue to understanding the unusual transport properties near the transition temperature as well as at lower temperatures. The abrupt change of physical properties at the NC-C transition has been interpreted as a Mott transition by Fazekas and Tosatti.[5] A recent site-specific scanning tunneling spectroscopy study on this material at 77 K also showed a significant charge transfer on the CDW crest induced by electron localization.[6] Hence this system would provide us with a unique opportunity to study a temperature-driven metal-insulator transition.

The effect of the phase transition near the NC-C transition in the unoccupied band was investigated by Claessen *et al.*[7] using inverse photoelectron spectroscopy (IPES). There was no indication of a change of the electronic structure in the unoccupied band at the NC-C transition, like the one in the occupied band. Hence it was 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 a relatively low energy resolution, the real nature of the unoccupied band might not yet be clear.

Tunneling spectroscopy is a high-resolution method to investigate changes of the DOS near E_F. Previous tunneling studies[8–10] on transition-metal dichalcogenides have been rather limited to the observation of a simple CDW gap. These temperature-independent studies give no explanation for the unusual properties at the NC-C transition at lower temperatures. Noutomi *et al.*[11] studied the temperature-dependent CDW gap structure of $1T$-TaS_2 using the tunneling junction method. They could only observe an 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 of tunneling spectra near E_F at the NC-C transition contradictory to the PES experiment. It might be difficult to create a stable insulating barrier on the fragile surface of this layered material. If one can create a more reliable tunneling barrier, the tunneling method should provide 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 have used temperature-dependent tunneling spectroscopy employing a scanning tunneling microscope (STM). In contrast to the PES technique, tunneling spectroscopy simultaneously gives high-resolution information about the DOS both in the occupied and unoccupied bands. We observed an abrupt transition from the CDW-induced depletion to an opening of a deep pseudogap near E_F within 1 K of the NC-C transition temperature. The measured pseudogap was deep enough to form localized states at E_F. We also found an abrupt increase of thermoelectric voltage developing between tip and sample at the transition temperature, indicating a metal-insulator transition.

Single crystals of $1T$-TaS_2 were grown by the usual iodine transport method.[2] We used a commercial variable temperature ultrahigh-vacuum STM (Omicron Vakuumphysik GmbH) equipped with a He flow cryostat. The temperature was controlled by counter-resistive heating. In our STM the sample is cooled separately while the microscopic stage, including the tip, remains at a constant temperature close to room temperature.[12] 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 sign of the applied bias voltages corresponds to sample voltage, so that the dI/dV curves for the negative and

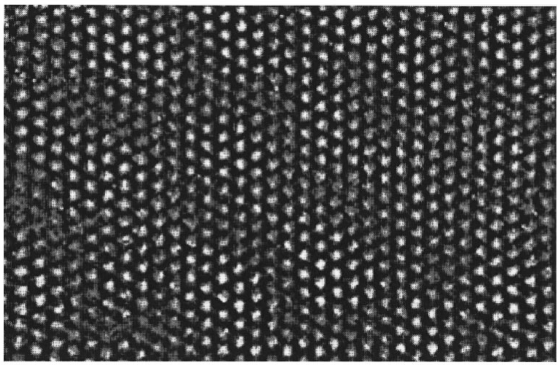

FIG. 1. STM image of $1T$-TaS_2 at room temperature. The sample bias voltage was 10 mV and the tunnel current was 0.3 nA. The domain size is approximately 80–85 Å at room temperature. The scan size was about 350×220 Å^2.

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.

Figure 1 is a typical STM image of $1T$-TaS_2 obtained at room temperature in the normal STM mode. This image shows the hexagonal $\sqrt{13}\times\sqrt{13}$ CDW superlattice with a period of ~12 Å. Domain structures with a period of 80–85 Å are clearly seen in this picture, indicating that the sample is in the NC phase. Wu and Lieber observed that the average domain size increases continuously as the temperature approaches the NC-C transition temperature.[13] To obtain reliable and reproducible tunneling spectra, we first located a flat and defect-free region of the sample, such as the one in Fig. 1, and then measured tunneling spectra at about every 18 Å (11×11 array) over a 200×200-Å^2 area. To increase the signal-to-noise ratio, we averaged the spectra over this area for each temperature. In this way, we could obtain 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 measured tunneling spectra showed high reproducibility, with a tunneling resistance above 50 MΩ. The STM images showed a clear $\sqrt{13}\times\sqrt{13}$ CDW structure over the whole measured temperature range.

A resistivity measurement of our sample shows that the NC-C phase transition occurs around 187 K during cooling, and that the unbounded increase of resistivity starts below 50 K. Temperature-dependent tunneling spectra near the NC-C transition are shown in Fig. 2. At high temperatures, that is above 187.7 K, the measured tunneling spectra show a broad

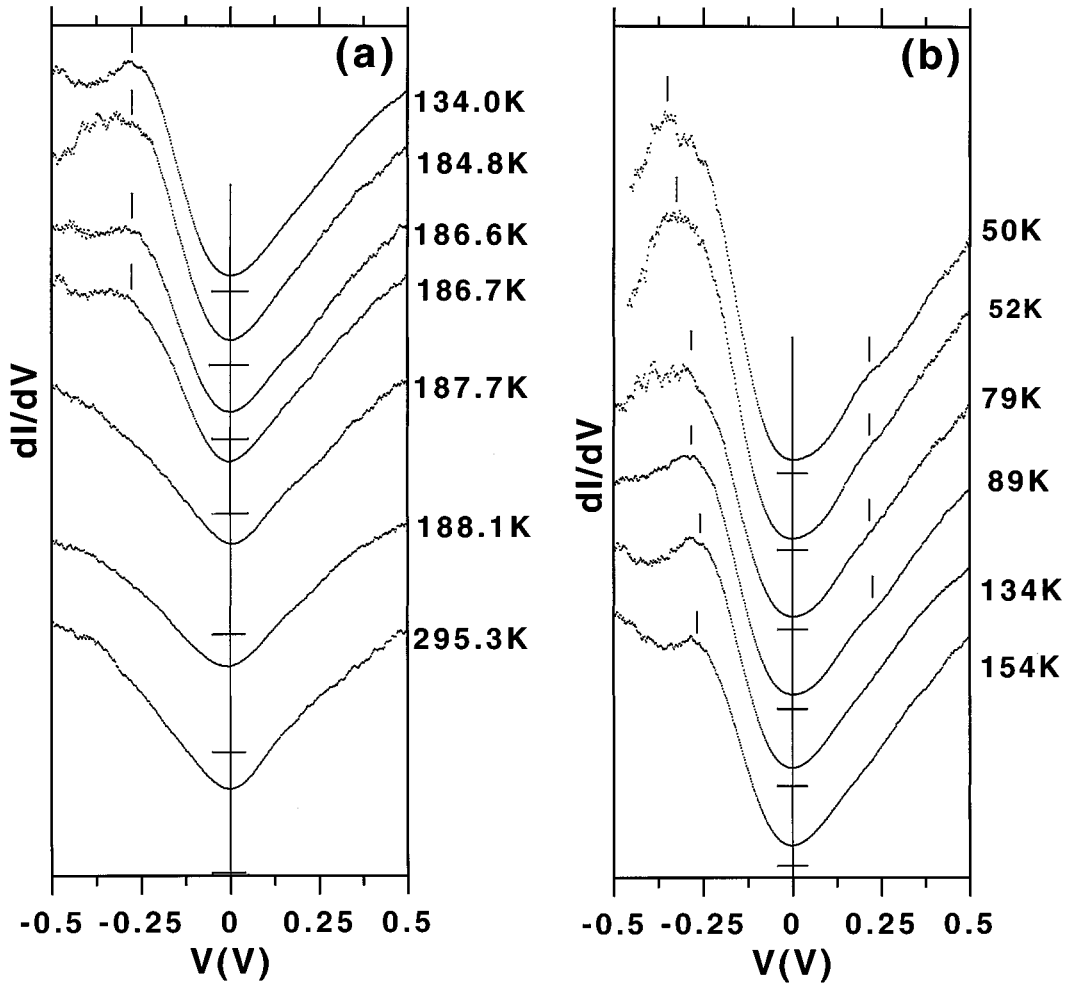

FIG. 2. Tunneling spectra at different temperatures near the NC-C transition (a) and at low temperatures (b). The bias voltage was 0.3 V and the tunnel current was 0.5 nA. The small horizontal bars represent the zeros for the individual dI/dV curves.

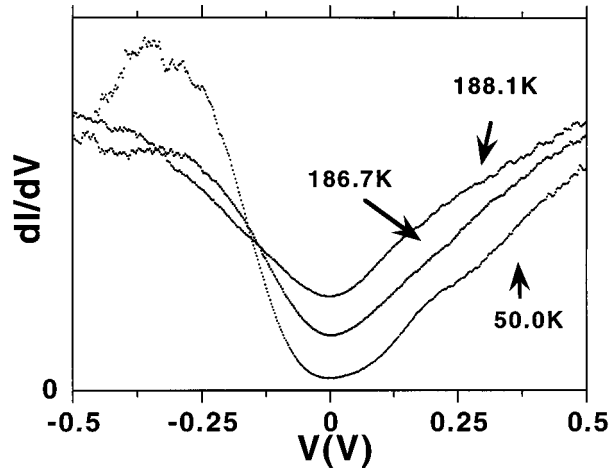

FIG. 3. Typical tunneling spectra in the NC phase (188.1 K), during transition (186.7 K), and in the *C* phase (50.0 K). The bias voltage was 0.3 V and tunnel current was 0.5 nA. The curves are not shifted, meaning that the zero point of dI/dV is the V axis.

opening of the CDW gap. The CDW-driven band-splitting structures of the Ta $5d$ band in the occupied band, which is 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.[10,11] In contrast to the angle-resolved PES technique, STM tunneling spectra represent the averaged ones with appropriate weights over the Fermi surface, and are more closely related to 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 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 represents an opening of a deep pseudogap 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 for an abrupt drop of the DOS at E_F.

At temperatures below the abrupt transition, the general shape of the tunneling spectra was 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. 2(b). This gap structure in the unoccupied band has been interpreted as the upper Hubbard band, and has been observed at 77 K in a previous tunneling experiment.[6] From our tunneling spectra the overall size of the pseudogap structure is estimated to be 0.45–0.5 eV, which is consistent with an optical measurement at 80 K by Barker, Ditzenberger and DiSalvo.[15] The optical measurement showed a broad gap of ~ 0.5 eV, having a considerable depletion of the DOS.

To show the change of the tunneling spectra more clearly, we plot the tunneling spectra at three particular temperatures, 188.1 K (NC phase), 186.7 K (during the transition), and 50 K (*C* phase) in Fig. 3. When comparing the spectra of the NC phase with those of the *C* phase, one finds that the broad CDW-driven depletion of the DOS near E_F changed significantly after the transition. The overall shape has also been changed completely.

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 a 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 submanifolds separated by energy gaps of 0.1 and 0.2 eV.[17] The Fermi level stays in the middle of the narrow uppermost band, which cannot be seen in our tunneling spectra in the *C* phase. This may of course reflect the negligence of the electron correlation effect in 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 at 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 difficult at this point to address any quantitative comment. However, our tunneling results are, as noted above, consistent with the optical measurement by Barker, Ditzenberger, and DiSalvo.[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 E_F in our tunneling spectra below the NC-*C* transition, rather than the pinning of E_F as suggested by the IPES study.

Our tunneling spectra clearly show that the Mott transition does not completely open a gap but rather a pseudogap structure at E_F.[18] The Fermi level lies at the touching point of the two Hubbard band edges, resulting in a pseudogap structure. In this pseudogap a small DOS still remains at E_F.[18] It is also more natural to consider the change of the unoccupied band during the transition in terms of Anderson localization in the pseudogap between the overlapping Hubbard subbands to explain the low-temperature transport data.[4]

Figure 4(a) 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 the decrease of the

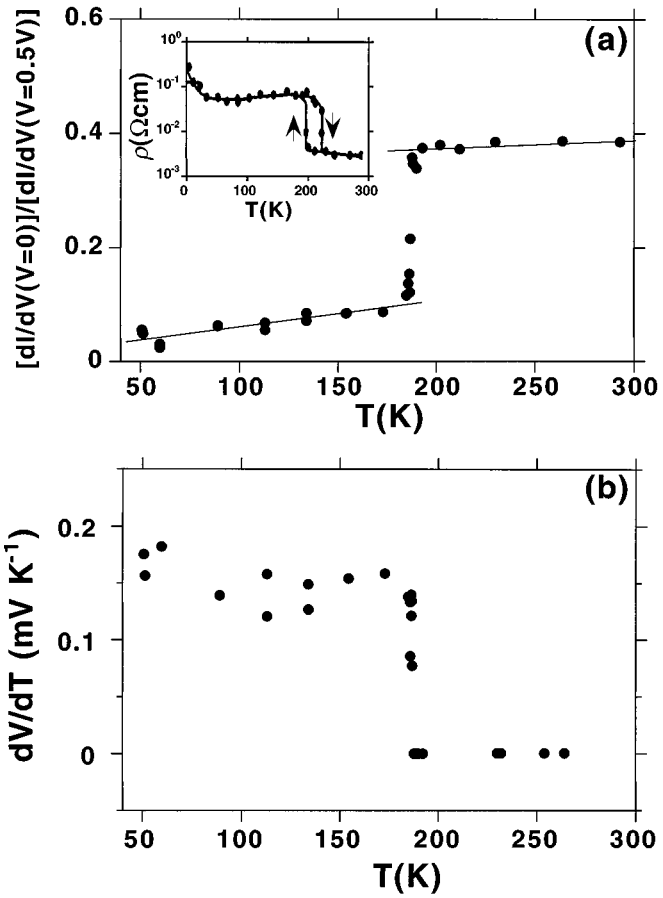

FIG. 4. (a) Temperature dependence of the normalized zero-bias conductance, $[dI/dV(V=0\ \mathrm{V})]/[dI/dV(V=0.5\ \mathrm{V})]$, which is a rough measure of the DOS at E_F. Inset: Temperature dependent resistivity of the $1T$-TaS_2 single crystal used in this experiment. (b) The measured thermoelectric voltage divided by the temperature difference between the STM tip and the sample.

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 pseudogap is deep enough, that is below Mott's criterion for Anderson localization, the DOS should be localized, and the conduction at low temperature is caused by thermally activated hopping. At higher temperature, carriers would be excited to the mobility edge E_C.[18] Mott's criterion reads $g=N(E_F)/N(E_F)_{\mathrm{free}}\approx 0.3$, where $N(E_F)_{\mathrm{free}}$ is the free-electron value of $N(E_F)$. If we assume that the value of $N(E_F)_{\mathrm{free}}$ 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. 4(a). According to this the g value is smaller than ~ 0.23 below the NC-C transition, and 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 and 60 K can be explained by the excitation of carriers to the mobility edge, in line with Mott's idea, and the unbounded increase of resistivity below 50 K is explained as the thermally activated hopping processes. The hopping leads to a variable-range hopping conductivity $\sigma(T)\propto\exp[-(T_0/T)^{\nu}]$ at low temperatures. For a noninteracting electron system, $\nu=\frac{1}{4}$ in three dimensions, and $\nu=\frac{1}{3}$ in two dimensions.[18]

During the tunneling measurement, we have also measured the thermoelectric voltage developing between the tip and sample by a tunneling thermometry technique.[19] In our STM unit the sample is cooled separately, while the microscopic stage, including the tip, remains close to room temperature. This enables us to measure the thermoelectric voltage of the sample induced by the large thermal gradient between the tip and the cool sample. Assuming that the temperature of the tip remains constant during the measurement, the thermoelectric voltage for a certain temperature gradient (dV/dT) should be related to the thermopower for the couple consisting of the tip and sample.[20] Near the transition temperature, we found an abrupt change of the thermopower from a very small value to $\sim 150\ \mu$V/K, as shown in Fig. 4(b). If the thermopower of the W tip remains constant and small during the transition, a large change of thermopower at the NC-C transition would mainly originate from the sample. Our results are quite consistent with the existing conventional thermoelectric power measurement made by Tani *et al.*[21] Considering the typical value of the thermopower for metals, 1–10 μV/K, and for semiconductors, 100 μV–1 mV/K, we interpret our large increase of thermopower as a transition from the metallic state to the semiconducting state, that is carrier excitation from E_F to the mobility edge E_c, between at least 50 and 180 K. A large drop of thermopower below 20 K has also been observed,[20] suggesting that the conduction is accomplished by the variable-range hopping process in the localized states near E_F at low temperatures.

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 pseudogap at E_F below the NC-C transition temperature due to a Mott transition. The measured pseudogap turned out to be deep enough to form localized states at E_F. We have also found an abrupt increase of thermoelectric voltage developing between the W tip and the sample at the transition temperature, which indicates a metal-insulator transition. In contrast to the IPES study, our tunneling results show pseudogap structures of two Hubbard subbands resulting from the band splitting of the Ta $5d$ band due to electron correlation effect.

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