Mott Phase at the Surface of 1T-$TaSe_2$ Observed by Scanning Tunneling Microscopy

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In this Letter we report the observation, by scanning tunneling microscopy, of a Mott metal to insulator transition at the surface of 1T-$TaSe_2$. Our spectroscopic data compare considerably well with previous angle-resolved photoemission spectroscopy measurements and confirm the presence of a large hysteresis related to a first order process. The local character of the tunneling spectroscopy technique allows a direct visualization of the surface symmetry and provides spectroscopic measurements on the defect-free region of the sample. It follows that the electronic localization is driven purely by the enhancement of the charge density wave amplitude which drives a bandwidth controlled metal-insulator transition.

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Since the prediction of the Mott insulating phase and the discovery of correlated insulators, model systems exemplifying the complex physics behind such a topic have been regularly searched [1]. It would be desirable to tune and reduce the electronic bandwidth (W) until the on-site Coulomb repulsion (U) becomes the prevailing force. In these conditions, the electron gas becomes unstable and the charges localize in a correlated Mott phase. Hydrostatic pressure is an ideal perturbation that modifies W, but it is not compatible with many experimental techniques. Besides, solid solutions with modified lattice parameters can be prepared by isoelectronic substitution [2]. This method has been successfully applied in many materials but faces problems as stoichiometry and disorder. Recently, it has been shown that charge density wave (CDW) compounds may comprise excellent systems to investigate the bandwidth control metal-insulator transition [3,4]. Here the CDW amplitude changes with temperature, eventually tuning the transfer interaction through the critical value. A typical example is provided by the layered 1T-$TaSe_2$, in which a Mott transition at the surface has been recently reported [5]. The spectral density measured by angle-resolved photoelectron spectroscopy (ARPES) compares well with the predictions of dynamical-mean-field theory and establishes a comprehensive picture of the electronic localization. Currently, these appealing results have not been confirmed by any other experimental technique. None of the many scanning tunneling spectroscopy (STS) or ARPES investigations observed the occurrence of a surface phase transition. On the contrary, most of the early works concluded that the spectroscopic data can be explained entirely by the strong CDW modulation [6,7]. Later on, two distinct surfaces, one insulating and the other metallic, have been indeed observed at room temperature and on different specimens. Most likely, the reduced coordination of the topmost Se atoms [8] favors a surface enhancement of the CDW. However, the data suggest that sample quality deeply affects the properties of the topmost layers, modifying the critical temperature or even suppressing the correlation effects [9].

In this Letter we present STS measurements that confirm the occurrence of a first order process at the surface of 1T-$TaSe_2$. The data are consistent with the ARPES results [5] and suggest that below 250 K the electrons of the topmost layers localize in a Mott phase. We visualize the surface symmetry by means of scanneling tunneling microscopy (STM), and we measure the local density of the states (LDOS) via STS. Our results compare reasonably well with previous STM [6,10] works but highlight the presence of an electronic transition that does not break the symmetry of the CDW.

The 1T-$TaSe_2$ is a layered transition metal chalcogenide that crystallizes in the CdI_2-type structure [11]. A strong CDW develops below 475 K, holding a commensurate superlattice of $\sqrt{13} \times \sqrt{13}$ symmetry [12]. In real space, the periodic distortion corresponds to the formation of metal clusters with two shells of six atoms and a centered thirteenth Ta atom. This strong perturbation splits the conduction band in three manifolds. Two of them are completely filled while the third one, which is only half filled, is susceptible to electronic localization [3,13]. Below 475 K the electronic and structural properties of the bulk are stable, leading to metallic conductivity down to 4 K [14]. Nonetheless, at 260 K the surface displays a first order transition towards an insulating phase which is correctly described as a Mott insulator. The spectral function derived by ARPES shows a lower Hubbard band peaking at 260 meV and a suppressed density of the states near the chemical potential [5]. Moreover, the transition holds a large hysteresis, similar to the one observed in the 1T-TaS_2 [15].

Single crystals of 1T-$TaSe_2$ were grown by the usual iodine transport technique and were characterized by Laue

diffraction and resistivity measurement. The sample surface was prepared by cleavage in vacuum. The measurements were performed in an UHV system composed of a preparation chamber connected to the measurements chamber where the STM stage (Omicron Vakuumphysik GmbH model LT-STM) is installed. The base pressure was low 10^{-10} mBar and low 10^{-11} mBar in the preparation chamber and in the microscope chamber, respectively. The sample temperature was controlled by a liquid nitrogen bath and a heater in contact with the sample stage. The temperature was measured by a silicon diode clamped on the STM stage. The piezoelectric scanner was calibrated by measuring a Si(111) 7×7 reconstructed surface. Chemically etched tungsten tips were used after a cleaning procedure by field emission discharge against a metal electrode. A set of 20×20 nm^2 STM images were collected at different temperatures, with a constant tunneling current of 0.1 nA and sample bias of 1 V. Several cycles of measurements were carried out cooling the sample to 80 K and heating it up to room temperature. Before every acquisition, the cryostat had been carefully stabilized to the desired temperature, so to minimize the thermal drift. Tunneling spectra were collected during the image scanning on a regular 80×80 points grid covering the entire scanning area. Each differential conductance spectrum corresponds to the average result over all the 6400 spectra for each image.

From the line shape of the curves reported in Fig. 1, one can clearly observe a phase transition occurring between 250 and 200 K. Two new features reported as A and B in Fig. 1 appear below 250 K. The signal decreases considerably in proximity of the zero bias, indicating a strong depletion of electronic states near the Fermi level. This process can be reversed within one temperature cycle,

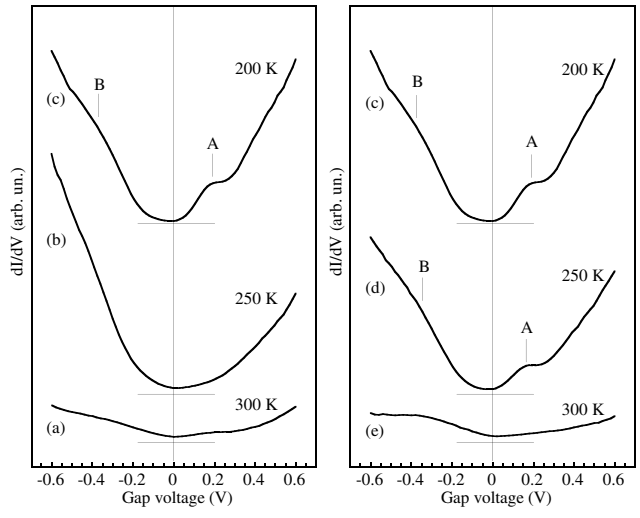

FIG. 1. Differential tunneling conductivity, $\frac{\partial I}{\partial V}$, as a function of temperature. Cooling series: curves (a)–(c); heating series: curves (c)–(e). The sample-tip distance was chosen in order to have a tunneling current of 0.1 nA for a bias voltage of 1 V.

although different critical temperatures are found for the cooling [Fig. 1(a)] and heating [Fig. 1(b)] procedure. Such a large hysteresis is in agreement with the previous ARPES results and confirms the first order character of the transition [5]. It is well established that the first derivative of the tunneling current over the tip-sample voltage $\frac{\partial I}{\partial V}$ follows the LDOS [16]. Indeed, it is possible to write $\frac{\partial I}{\partial V} \propto \rho(R, V)T(V)$, where $\rho(R, V)$ is the LDOS at the tip position and $T(V)$ is a factor which takes account of the transmission probability through the barrier. Following a commonly accepted procedure $T(V)$ is estimated by the total conductivity $\frac{I}{V}$ [17]. Figure 2 shows the normalized conductivity curves, $\frac{\partial I}{\partial V} / \frac{I}{V}$, obtained from data reported in Fig. 1. The 200 K curve, where the electronic transition is complete, compares quite well with ARPES [5] and confirms the appearance of two pronounced peaks in the low temperature phase. The normalization process reduces the steep increase of the $I(V)$ allowing a better localization of the new features induced by the surface electronic transition. Moreover, normalized spectra allow one to rule out the possibility that the observed features were due to the bias dependent transmission probability. On the other hand, these peaks cannot be ascribed to the presence of the charge density wave alone; otherwise they would be also visible at room temperature. On the contrary, we associate them to the lower (B) and upper (A) Hubbard bands taking place together with the electron localization. The normalization procedure proposed by Altfeder *et al.* [18] was tested as well (not shown) giving comparable results. The energy position of peak B (0.23 eV) is in excellent agreement with the value found by photoemission spectroscopy (0.26 eV) [5]. In addition, the use of the scanning tunneling spectroscopy allows one also to probe the empty electronic states. The position of peak A (0.15 eV) gives $U = 0.38$ eV. The U value (given by the difference between the A and B positions) is a measure of the electron correlation energy. The U value obtained by STS is quite different from the 0.52 eV value obtained by simply reflecting around E_F the measure of the filled states obtained by photoelectron spectroscopy [5]. This new U value could be used for more precise theoretical calculations. Surprisingly, the energetic positions of the two bands are not symmetric with respect to the Fermi level. Even if we cannot exclude the presence of artifacts introduced by the tip DOS, this result may suggest that the electron-hole symmetry is no longer valid when band structure effects are taken into account. We argue that the observed electronic transition is driven purely by the enhancement of the CDW amplitude and cannot be related to surface reconstruction or commensurability. As a matter of fact, the CDW structure at 80 K is identical to the one at 300 K so that no breaking of the lattice symmetry occurs during the phase transition. This is clearly evinced in Fig. 3, where two 15×15 nm^2 STM images of the sample surface are shown (constant tunneling current of 2 nA and a

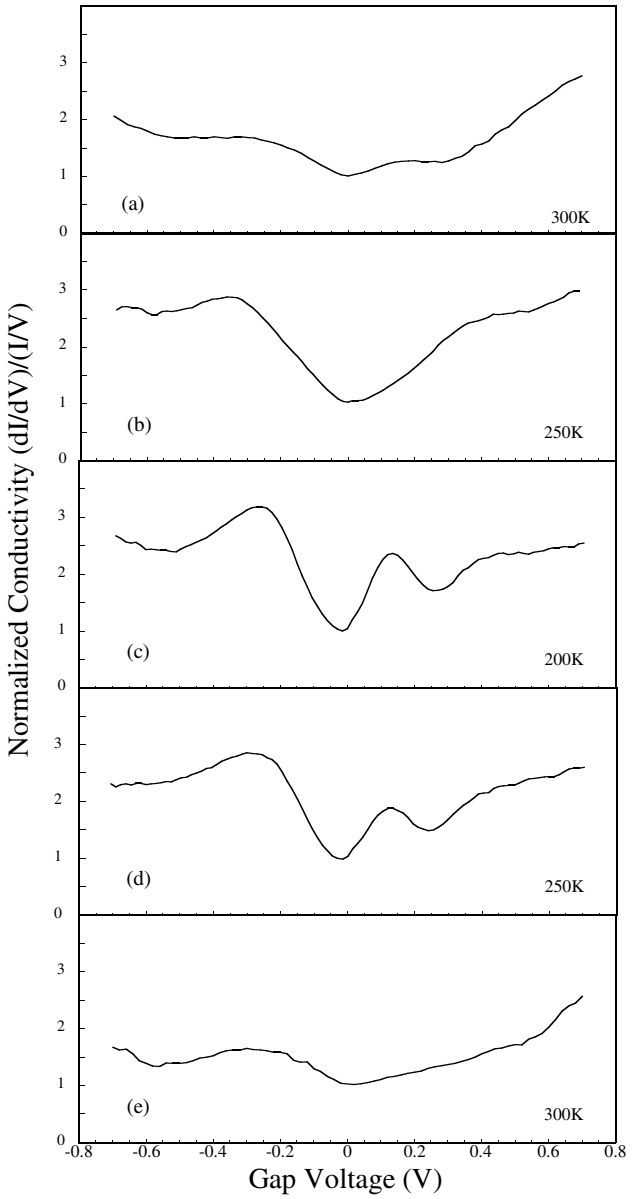

FIG. 2. Normalized differential tunneling conductivity, $\frac{\partial I}{\partial V} / \frac{I}{V}$, spectra as a function of temperature. Cooling series: curves (a)–(c); heating series: curves (c)–(e). The sample-tip distance was chosen in order to have a tunneling current of 0.1 nA for a bias voltage of 1 V.

sample bias voltage of 25 mV), collected at 80 K [Fig. 3(a)] and 300 K [Fig. 3(b)], respectively. Both images display a strong modulation due to the $\sqrt{13} \times \sqrt{13}$ charge density wave superlattice [6]. The measured superlattice cell parameter is about 1.27 nm which correlates well with 1.245 nm obtained by x-ray diffraction [13]. The local CDW amplitude is defined as the valence charge of the several Ta site with respect to the nominal value Ta^{4+}. It can be quantified by means of the Mössbauer effect [19], which showed the occurrence of $\simeq 0.5$ electrons transfer from the outer shell of the star towards the inner shell and

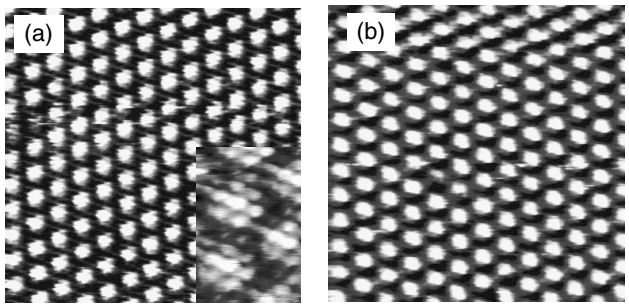

FIG. 3. STM images of the 1T-$TaSe_2$ surface at 80 K (a) and 300 K (b) ($I = 2$ nA, $V = 25$ mV). The strong CDW modulation induces bright and dark areas that follow the commensurate periodicity of a $\sqrt{13} \times \sqrt{13}$ superstructure. In the inset of (a) is shown an atomically resolved image collected at 80 K.

the center of the Ta clusters. The temperature induced variation of the CDW is too small to be observed by the contrast of the STM images. To support the occurrence of temperature dependent CDW amplitude, we present in Fig. 4 the Ta $4f^{7/2}$ core level peak measured by ultraviolet photoemission spectroscopy (UPS) at 300 and 70 K. The data have been collected on a freshly cleaved sample by means of a spectrometer with overall resolution of 250 meV. A charge transfer of 0.5 electrons diminishes the binding energy of core holes excited in the inner shell whereas increasing the binding energy of core holes excited in the outer one [20]. As a consequence the splitting between the two spectral components is proportional to the CDW amplitude [21]. The spectra in Fig. 4 are composed indeed of two distinct components, each one related to a different shell of the metal clusters. Their energetic separation, which increases by 40 meV (5%) in the low temperature phase [22], furnishes a direct proof of the CDW

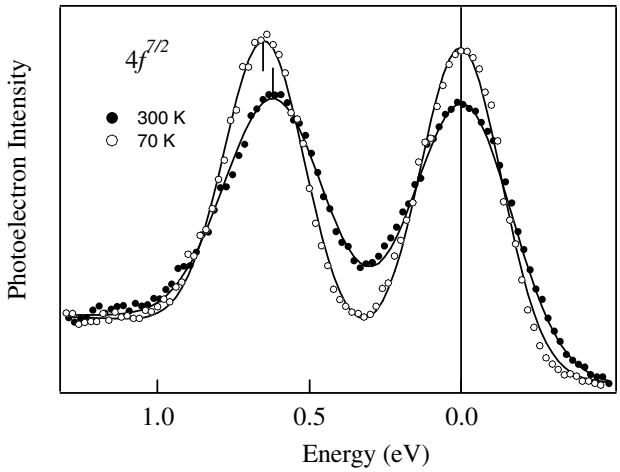

FIG. 4. UPS spectra of the core levels acquired at 300 K (filled circles) and at 70 K (open circles) (photon energy of 80 eV). The zero of the energy scale has been set to the position of the first peak while two short lines mark the relative position of the second component.

enhancement. A clear scenario follows from the reported data; the stronger CDW reduces the conduction bandwidth, driving a first order Mott transition. This weak perturbation can induce the observed dramatic change in the electronic surface structure for two reasons: (i) the system is near the transition point so even a small perturbation can trigger the electronic transition; (ii) the bandwidth does not vary linearly with respect to the CDW amplitude; hence a small increase of the splitting (5%) can result in a larger reduction of W. Previous STS measurements on 1T-$TaSe_2$ were interpreted in the framework of a CDW induced modification of the electronic band structure. Here a different model is proposed. To explain the different results it is worth noting that previous measurements were done on samples cleaved in air. This sample preparation procedure could induce defects at the surface hindering the real surface electronic structure. Moreover, the previous experiment did not explore in a systematic way the temperature range of the surface Mott localization.

In conclusion, we show by STS the occurrence of a Mott phase at the surface of 1T-$TaSe_2$. Our spectroscopic data compare considerably well with previous ARPES measurements and confirm the presence of a large hysteresis related to a first order process. Moreover, we verify that the surface symmetry is identical in the metallic and insulating phases. It follows that the electronic localization is driven purely by the enhancement of the CDW amplitude which drives a bandwidth controlled metal-insulator transition. The existence of a magnetic ordering at low temperature cannot be excluded. In most cases, the Mott phase displays an antiferromagnetic ground state. However, the triangular lattice of the 1T-$TaSe_2$ is a frustrated geometry that does not favor antiferromagnetism. Further experiments should be done in order to clarify this issue.

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[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[2] J. A. Wilson, in *The Metallic and Nonmetallic States of Matter*, edited by P. P. Edwards and C. N. Rao (Taylor and Francis, London, 1985).
[3] P. Fazekas and E. Tosatti, Philos. Mag. B **39**, 229 (1979).
[4] N. V. Smith, S. D. Kevan, and F. J. DiSalvo, J. Phys. C **18**, 3175 (1985).
[5] L. Perfetti, A. Georges, S. Flores, S. Bierman, S. Mitrovic, H. Berger, Y. Tomm, H. Höchst, and M. Grioni, Phys. Rev. Lett. **90**, 166401 (2003).
[6] B. Giambattista, C. G. Slough, W. W. McNairy, and R. V. Coleman, Phys. Rev. B **41**, 10 082 (1990).
[7] Ju-Jin Kim, W. Yamaguchi, T. Hasegawa, and K. Kitazawa, Phys. Rev. B **50**, 4958 (1994).
[8] A. Spijkerman, J. L. de Boer, A. Meetsma, G. A. Wiegers, and S. van Smaalen, Phys. Rev. B **56**, 13 757 (1997).
[9] O. Shiino, T. Endo, W. Yamaguchi, H. Sugawara, K. Kitazawa and T. Hasegawa, Appl. Phys. A **66**, S175 (1998).
[10] G. Raina, K. Sattler, U. Müller, N. Venkateswaran, and J. Xhie, J. Vac. Sci. Technol. B **9**, 1039 (1991).
[11] R. N. G. Wychoff, in *Crystal Structures* (Wiley, New York, 1964).
[12] R. Brouwer and F. Jellinek, Physica (Amsterdam) **99B**, 51 (1980).
[13] M. Y. Whangbo and E. Canadel, J. Am. Chem. Soc. **114**, 9587 (1992).
[14] F. J. DiSalvo, R. G. Maines, J. V. Waszczak, and R. E. Schwall, Solid State Commun. **14**, 497 (1974).
[15] A. H. Thompson, F. R. Gamble, and J. F. Revelli, Solid State Commun. **9**, 981 (1971).
[16] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
[17] J. A. Stroscio and R. M. Feenstra, in *Scanning Tunneling Microscopy*, edited by J. A. Stroscio and W. J. Kaiser (Academic Press, New York, 1993).
[18] I. B. Altfeder, X. Liang, T. Yamada, D. M. Chen, and V. Narayanamurti, Phys. Rev. Lett. **92**, 226404 (2004).
[19] M. Eibschutz, Phys. Rev. B **45**, 10 914 (1992).
[20] H. P. Hughes and J. A. Scarfe, Phys. Rev. Lett. **74**, 3069 (1995).
[21] A. Ino, T. Mizokawa, A. Fujimori, K. Tamasaku, H. Eisaki, S. Uchida, T. Kimura, T. Sasagawa, and K. Kishio, Phys. Rev. Lett. **79**, 2101 (1997).
[22] H. P. Hughes and R. A. Pollak, Philos. Mag. **34**, 1025 (1976).