RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 3 15 JANUARY 1992-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Temperature-dependent pseudogap and electron localization in 1*T*-TaS_2

B. Dardel, M. Grioni, D. Malterre, P. Weibel, and Y. Baer
Institut de Physique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

F. Lévy
Laboratoire de Physique Appliquée, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland
(Received 21 October 1991)

Photoelectron spectroscopy reveals a striking correspondence between charge-density-wave-related phase transitions and modifications of the electronic structure in 1*T*-TaS_2. High-energy-resolution spectra indicate that the collapse of the Fermi surface is abrupt at the quasicommensurate-commensurate transition (~185 K) and that, below this critical temperature, the Fermi level lies in a deep, temperature-dependent pseudogap. These results strongly suggest successive localizations due to electron correlations and disorder, and resolve an outstanding contradiction between transport data and previous spectroscopic results with lower resolution.

1*T*-TaS_2 exhibits unique physical properties that are the consequence of its quasi-two-dimensional (2D) character, and of an unusually complex charge-density-wave (CDW) phase diagram.[1-9] The most striking observations concern the resistivity which undergoes a sudden tenfold increase in coincidence with the first-order phase transition ($T \sim 185$ K) from the *quasicommensurate* (QC) to the commensurate (*C*) CDW structure, followed by a metalliclike decrease and, below ~60 K, by a steep rise.[10] This anomalous behavior indicates that important modifications of the electronic structure, with the disappearance of a large portion of the Fermi surface, take place at the QC-*C* transition, but their origin is not obvious since CDWs alone are not expected to produce such dramatic effects in a 2D solid.

It is now clear, however, that electronic correlations within the CDW distorted bands[11] and, at low temperature, disorder,[12,13] play a major role in determining the properties of 1*T*-TaS_2. Photoelectron spectroscopy (PES) investigations[14-17] have provided experimental support to a model[11] that predicts the occurrence of a Mott localization[18] at the QC-*C* transition. A sharp spectral feature, centered at ~200 meV below the Fermi level (E_F) in the commensurate CDW phase, has been interpreted as representing the lower Hubbard subband, and from its binding energy a Mott-Hubbard gap of 125–200 meV has been inferred.[14,17] However, this conclusion sharply contrasts with the known transport properties of the material, which exhibit a much smaller energy scale. As an example, the analysis of the low-temperature electrical resistivity yields an activation energy of about 1 meV.[3,10]

In order to clarify this discrepancy, an investigation of the electronic structure within few k_BT of E_F is of capital importance. This information can be obtained by high-resolution PES, which has already proved to be a powerful tool to investigate low-lying excitations and phase transitions in solids.[19] In this paper we show that the high-resolution results are crucial for the understanding of the electronic properties of 1*T*-TaS_2, and that they provide, for the first time, a direct picture of what is thought to be a very general mechanism of conduction in disordered impurity bands.[18,20]

Single crystalline samples have been prepared from the elements by reversible chemical reaction with iodine as a transport agent, between 950 °C (hot zone) and 900 °C (cold zone). The 1*T*-polytipic phase is obtained by the addition of SnS_2 (less than 0.5% weight) and by rapid cooling from the growth temperature. The temperature dependence of the resistivity, measured with a standard four-wire technique, was in good agreement with published data. The sample was mounted on a He flow cryostat, and the temperature was measured by a Rh-Fe calibrated resistor. Clean surfaces were prepared by cleavage in a vacuum of 1×10^{-10} torr. X-ray photoelectron spectra of the Ta 4*f* core lines, obtained with monochromatized Al K_α radiation in the different CDW phases, were found to agree with published data.[21,22] Photoelectrons were collected at near normal emission with an energy resolution of 15 meV and an angular resolution of $\pm 5°$.

Figure 1 shows PES spectra of the top 1.5 eV of the 1*T*-TaS_2 valence band, taken around the QC-*C* CDW transition temperature. The 191 K spectrum is typical of the quasicommensurate phase, while the 186 K one is characteristic of the low-temperature, commensurate

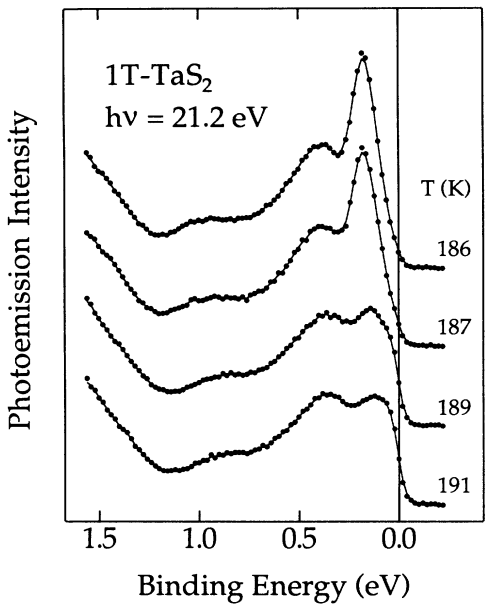

FIG. 1. Photoelectron spectra of $1T$-TaS_2 at the quasicommensurate-commensurate CDW transition, on cooling. Temperature differences are accurate to ± 0.5 K. Binding energies are referred to the Fermi level. The solid lines are guides to the eye.

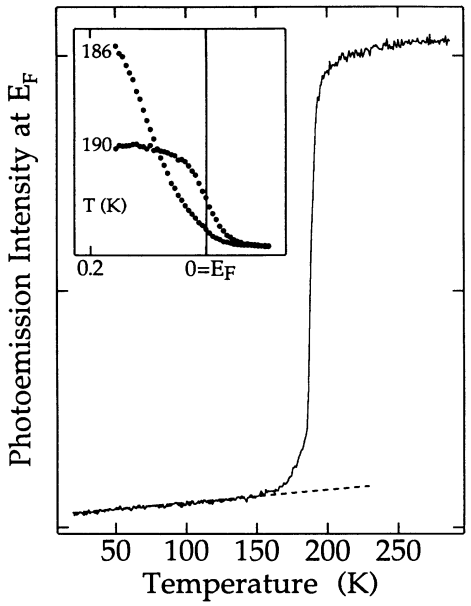

FIG. 2. Temperature dependence of the photoemission intensity at E_F; the bottom ticks on the vertical axes mark the intensity zero. Inset: Photoelectron spectra of $1T$-TaS_2 taken immediately above and below the quasicommensurate-commensurate CDW transition in a region close to the Fermi level. Binding energies are in eV.

phase. The structures visible in the 191 K spectrum are absent from the band-structure calculations of undistorted $1T$-TaS_2, and we did not observe them in the incommensurate phase, above 355 K.[23] Smith, Kevan, and Di Salvo[15] have shown that they result from the periodic CDW modulation that splits the Ta d band in three subbands, the topmost one straddling the Fermi level and containing 1 electron per unit cell (thirteen Ta atoms). The three subbands, separated by gaps in the C phase, overlap in the QC phase, as a consequence of the limited size of the commensurate domains in this phase.[9] On the low-temperature side of the transition, exemplified by the spectrum at 186 K, the shallowest peak undergoes a dramatic evolution, doubling in intensity and shifting away from the Fermi level to a final binding energy of 180 meV, within 2–3 K. Remarkably, both the peak's binding energy[17] and intensity[23] reproduce the discontinuity observed in the resistivity at the same temperature. The spectra of Fig. 1 leave little doubt as to the importance of the changes that occur in the electronic structure in coincidence with the QC-C transition. Just from the analysis of these curves, one could conclude that at the QC-C transition $1T$-TaS_2 completely loses its metallic character and becomes a semiconductor with a gap of the order of ~ 0.1 eV. However, the picture that emerges from careful measurements near the Fermi level is more subtle, and, as we shall show, it is consistent with resistivity data.

The temperature dependence of the photoemission intensity at E_F is shown in Fig. 2. We observe a sudden drop at the transition temperature which correlates with the jump in the resistivity. This fact, and analogous observations at different emission angles, suggest that, even if our sampling of the Brillouin zone is necessarily incomplete, the measured variations reflect variations in the density of states (DOS) at the Fermi level, $N(E_F)$. Figure 2 proves that the collapse of the Fermi surface occurs within a few degrees (see also the inset). The qualitatively different information that emerges from our high-resolution investigation is that $N(E_F)$ remains finite below the transition. This observation provides a direct evidence of the fact that the Mott transition does not completely open a gap in the density of states, but only a *pseudogap,* in line with the original prediction of a zero Mott-Hubbard gap formulated by Fazekas and Tosatti.[11]

According to Fig. 2 the density of states in the pseudogap varies with temperature. The observed linear decrease of the photoemission intensity at E_F between ~ 150 K and the experimental limit of 20 K, is accompanied by an increase of $\sim 15\%$ in the intensity of the peak at 180 meV, and by a corresponding width reduction.[23] We suggest that these observations are the consequence of the continuous growth of the CDW amplitude in the commensurate phase. This interpretation is also supported by previous x-ray photoemission spectroscopy[21] and Hall effect[4] measurements. It is based on the assumption that a larger CDW results in a further reduction of the hybridization in the subband, entailing a bandwidth reduction and the observed smaller overlap at E_F. The decrease with decreasing temperature of the spectral intensity at E_F is evident from the comparison of spectra collected at 145 and 20 K (Fig. 3). In line with a previous suggestion[11] we have superimposed on the spectra parabolic lines centered at E_F. In order to simulate the experimental resolution, these parabola, which differ by a constant, have been multiplied by the appropriate Fermi-Dirac

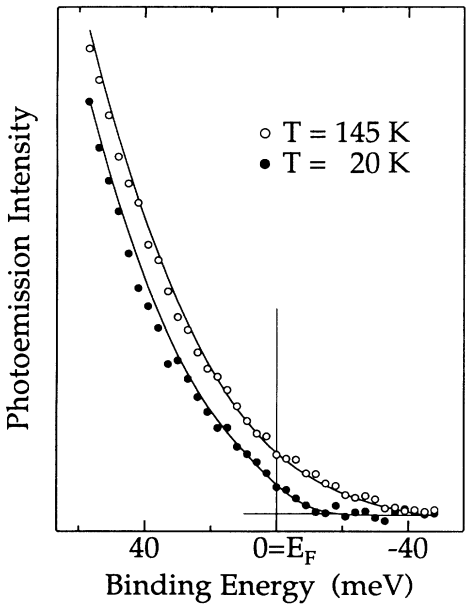

FIG. 3. Close-up around the Fermi level of the photoelectron spectra of $1T$-TaS_2 at 145 K (open dots) and at 20 K (solid dots). The solid lines represent parabolic lines centered at E_F, multiplied by the appropriate Fermi-Dirac functions and broadened to account for the experimental resolution (15 meV). The two parabola differ by a constant.

function and convoluted with a Gaussian line shape (full width at half maximum is 15 meV). The broadening of the metallic edge reflects the temperature dependence of the Fermi-Dirac function. From the good fit we conclude that the energy width of the step at E_F in the raw spectra is perfectly compatible with the experimental conditions (temperature, resolution), and that the two spectra essentially differ by their value at E_F. We must stress that the high-energy resolution is capital to obtain a faithful image of the DOS.

The most interesting information provided by the curves of Figs. 2 and 3 is that $N(E_F)$ remains finite much below the QC-C transition. Therefore, although the center of mass of the lower Hubbard subband is actually quite far from E_F, the transport properties of the material are entirely governed by the presence of electronic states near E_F. It remains to be determined whether these states can contribute as extended states to the transport properties, or whether localization, due to the random field of impurities and defects, prevails. The possibility of a disorder driven localization in the pseudogap between overlapping Hubbard subbands has been considered for $1T$-TaS_2 by Fazekas and Tosatti, and on a quite general basis by Mott[18] and Thouless.[20] The fractional power-law dependence of the logarithm of the resistivity indicates that below $\sim$20 K electrons are localized and conduction occurs by variable range hopping (VRH).[12,13] The extended tails observed in our PES spectra certainly confirm the importance of disorder on the low-temperature side of the transition. Moreover, the good fit obtained in Fig. 3 with parabolic line shapes suggests, on the basis of previous experimental[13] and theoretical work,[11,24] that conduction in the VRH limit might have a 3D character.

The PES spectra are also useful to determine the onset of localization. Mott has derived a criterion for the occurrence of an Anderson transition in a pseudogap, based on the ratio g between $N(E_F)$ and the free-electron value $N(E_F)_{\text{free}}$, such that localization occurs for values of g smaller than $\sim$0.25. $1T$-TaS_2 is metallic above the QC-C transition; if we assume that the value of $N(E_F)$ just above the critical temperature is representative of $N(E_F)_{\text{free}}$, we must conclude from Fig. 2 that localization already occurs somewhere below the steep edge, around 180 K. This is not in contradiction with the metallicklike character of the resistivity between 180 and 60 K. In fact, on the nonmetallic side of the transition, and at sufficiently high temperature, electrons excited from E_F to the mobility edge can contribute to band conduction. The situation is similar to that observed, e.g., in cerium sulphide,[25] where an Anderson localization occurs as a function of excess Ce content. A rough estimate of the energy difference between the Fermi level and the mobility edge can be obtained from the temperature at which the minimum of resistivity occurs: For $1T$-TaS_2 this gives approximately 5 meV.

In conclusion, our photoemission data confirm that the QC-C CDW transition in $1T$-TaS_2 is accompanied by an abrupt decrease of the density of states at the Fermi energy, in agreement with a model predicting a Mott transition. The high resolution of our spectra allows us to extend the analysis to the range of the low-energy excitations which are directly linked to transport properties. In contrast to previous photoemission investigations which suggested a 200-meV gap, incompatible with resistivity data, we provide a direct demonstration of the existence of a finite density of states at E_F in the commensurate phase, which proves that $1T$-TaS_2 would retain a weak metallic character if disorder did not induce an Anderson localization.

We thank P. Flückiger for performing the resistivity measurements and Y. Pétroff and C. H. Marbuzet for stimulating suggestions. This work was supported by the Fonds National Suisse de la Recherche Scientifique.

[1]P. M. Williams, in *Physics and Chemistry of Materials with Layered Structures*, edited by F. Lévy (Reidel, Dordrecht, 1976), p. 51.

[2]J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).

[3]P. D. Hambourger and F. J. Di Salvo, Physica B **99**, 173 (1980).

[4]R. Inada, Y. Onuki, and S. Tanuma, Phys. Lett. **69A**, 453 (1979).

[5]M. D. Nunez-Regueiro, J. M. Lopez-Castillo, and C. Ayache, Phys. Rev. Lett. **55**, 1931 (1985).

[6]R. Brouwer and F. Jellinek, Physica B **99**, 51 (1980).

[7]R. V. Coleman, B. Drake, P. K. Hansma, and G. Slough, Phys. Rev. Lett. **55**, 394 (1985).

[8]X.-L. Wu, P. Zhou, and C. M. Lieber, Phys. Rev. Lett. **61**, 2604 (1988).

[9]B. Burk, R. E. Thomson, A. Zettl, and J. Clarke, Phys. Rev. Lett. **66**, 3040 (1991).

[10]A. H. Thompson, F. R. Gamble, and J. F. Revelli, Solid State Commun. **9**, 981 (1971).

[11]P. Fazekas and E. Tosatti, Philos. Mag. B **39**, 229 (1979); Physica B **99**, 183 (1980).

[12]F. J. Di Salvo and J. E. Graebner, Solid State Commun. **23**, 825 (1977).

[13]N. Kobayashi and Y. Muto, Solid State Commun. **30**, 337 (1979).

[14]R. A. Pollak, D. E. Eastman, F. J. Himpsel, P. Heimann, and B. Reihl, Phys. Rev. B **24**, 7435 (1981).

[15]N. V. Smith, S. D. Kevan, and F. J. Di Salvo, J. Phys. C **18**, 3175 (1985).

[16]R. Manzke, O. Anderson, and M. Skibowski, J. Phys. C **21**, 2399 (1988).

[17]R. Manzke, T. Buslaps, B. Pfalzgraf, M. Skibowski, and O. Anderson, Europhys. Lett. **8**, 195 (1989).

[18]N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974), p. 44ff.

[19]M. Grioni, D. Malterre, B. Dardel, J.-M. Imer, Y. Baer. J. Muller, J. L. Jorda, and Y. Petroff, Phys. Rev. B **43**, 1216 (1991), and references therein.

[20]D. J. Thouless, J. Phys. (Paris) Colloq. **37**, C4-349 (1976).

[21]H. P. Hughes and R. A. Pollak, Philos. Mag. **34**, 1025 (1976).

[22]G. K. Wertheim, F. J. Di Salvo, and S. Chiang, Phys. Rev. B **13**, 5476 (1976).

[23]B. Dardel, M. Grioni, D. Malterre, P. Weibel, Y. Baer, and F. Lévy (unpublished).

[24]E. M. Hamilton, Philos. Mag. **26**, 1043 (1971).

[25]M. Cutler and N. F. Mott, Phys. Rev. **181**, 1336 (1969).