

Etude par Photoémission
des
Excitations de Basse
Energie
et
Transitions de Phases
dans des Composés de
Basse Dimension

Travail de Thèse présenté à
l'Institut de Physique de l'Université de Neuchâtel
pour l'obtention du titre de
Docteur ès Sciences
par
Boris Dardel
1994

IMPRIMATUR POUR LA THÈSE

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de Monsieur Boris Dardel

UNIVERSITÉ DE NEUCHÂTEL

FACULTÉ DES SCIENCES

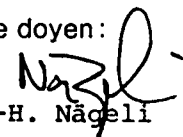
La Faculté des sciences de l'Université de Neuchâtel
sur le rapport des membres du jury,

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Neuchâtel, le 22 mars 1994

Le doyen :


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Unusual Photoemission Spectral Function of Quasi-One-Dimensional Metals

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(Received 14 August 1991)

We have carried out high-resolution photoemission experiments on two quasi-one-dimensional compounds: $K_{0.3}MoO_3$ and $(TaSe_4)_2I$. In both systems, a metal-insulator transition associated with a lattice distortion is reported. We show that the Fermi-step characteristic of a metallic phase is not observed above the Peierls temperature. As this Fermi step is always observed in higher-dimensional metals, we propose that this behavior results from the singular properties of one-dimensional systems and we suggest different mechanisms in order to explain this striking result.

PACS numbers: 71.45.Lr, 71.30.+h, 79.60.Cn

One-dimensional materials show many pathological features which are not present in higher dimensions such as the metallic-state instability [1]. Two alternative approaches have been developed to account for the unusual properties observed in such systems. The first one neglects the interaction between electrons and only considers the electron-phonon coupling. This leads to the well-known Fröhlich Hamiltonian [2], and spectacular properties are found such as the Kohn anomaly in the phonon dispersion, the phonon softening, and the formation of charge-density waves [3]. In the second approach, phonon effects are disregarded and the electronic correlations are investigated. The 1D interacting electron models qualitatively differ from those of 2D and 3D systems [4,5]. Exactly solvable approaches such as the Tomonaga-Luttinger models [6,7] show that all the degrees of freedom are collective (gapless plasmons), and that there are no elementary excitations corresponding to the quasiparticles found in normal Fermi liquids. Therefore, the momentum distribution function $n(k)$ does not exhibit a discontinuity at the Fermi momentum as it does in normal Fermi liquids, so that 1D metals are marginal Fermi liquids [8].

A normal metal is characterized by an incompletely filled electron band allowing electron-hole excitations of infinitesimal energy. Photoemission experiments reveal the metallic state by a step at the Fermi level with a width determined by the temperature broadening (Fermi function) and by the experimental resolution. However, previous photoemission studies of 1D metals [9–11] have reported an extremely low spectral intensity at the Fermi level (E_F), and no unambiguous existence of a metallic edge. The absence of this universal spectroscopic feature raises, if confirmed, very fundamental questions about our understanding of 1D metals and of the photoemission process. This issue can only be clarified by careful high-resolution measurements of the spectral function at E_F .

We have measured the two 1D compounds $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ which exhibit metal-insulator transitions

at 180 and 263 K, respectively. These transitions are associated with a lattice distortion and the formation of charge-density waves as evidenced by neutron and x-ray diffraction or electrical resistivity experiments [12–16]. Although these materials are certainly metallic above the Peierls temperature, they do not exhibit the typical Fermi edge in the photoemission spectral function. We suggest, therefore, that this striking observation is a characteristic property of 1D metals resulting from the singularities associated with this dimensionality, and we analyze the possible causes of this behavior.

$K_{0.3}MoO_3$ single crystals have been grown by electrolytical reduction from the fluxed melt at 550°C. $(TaSe_4)_2I$ single crystals have been prepared from stoichiometric mixture of the elements, by evaporation in closed quartz crucible between 510 and 480°C. Clean samples were prepared by cleavage in a vacuum of 1×10^{-10} torr. Our spectrometer, equipped with a helium-discharge lamp producing very narrow photon lines, has a total resolution better than 20 meV. The calibration of the energy was achieved by measuring the low-temperature Fermi edge on an adjacent Cu sample.

Our He I ($h\nu = 21.2$ eV) ultraviolet photoemission spectra (UPS) of $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ are in good agreement with previous measurements [17,18], but our resolution allows us to study the vicinity of the Fermi level with more accuracy. In Fig. 1 we have reported the first 500-meV range below the Fermi level for the two one-dimensional compounds and, for comparison, we have also plotted characteristic spectra of higher-dimensional metals. The photoemission spectra of $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ have been measured at 190 and 300 K, respectively, just above the Peierls temperature (T_P) of these two compounds (180 and 263 K). Surprisingly, although the samples are in their metallic phase, no evidence of a Fermi step can be detected. This behavior strongly contrasts with the situation observed for higher dimensionality as illustrated on the spectra of $TaSe_2$, a 2D metal, and of rhodium metal. In these 2D and 3D metals, the Fermi

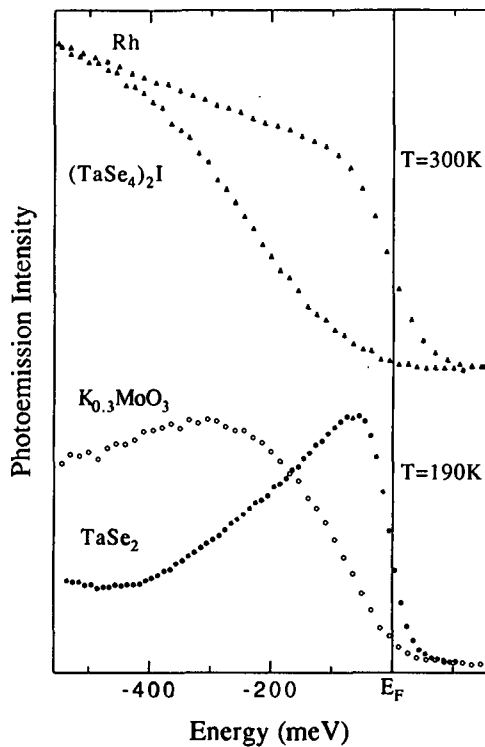


FIG. 1. UPS photoemission spectra of the $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ measured at a temperature just above the Peierls transition. For comparison, the spectra of 2D (1T-TaSe₂) and 3D (Rh) metals are reported at the same temperatures. All spectra are normalized at their maximum intensity.

discontinuity is clearly observed and as the energy resolution is better than 20 meV, the width at E_F is essentially due to the thermal broadening. As we shall report elsewhere [19], in both 1D compounds, a temperature dependence of the spectrum is observed. Below the transition temperature, the spectra are shifted to higher binding energies reflecting the progressive gap opening; above T_P , no evidence of a metallic signature up to 300 K is obtained. In order to estimate the limit of a detectable Fermi step, we simulate the experimental spectra by spectral functions with different values at the Fermi level $\rho(E_F)$. We then multiply them by the Fermi function ($T=190$ K) and convolute them with a Gaussian (20 meV FWHM) to account for the temperature and resolution broadenings. In Fig. 2, a careful inspection of the different curves shows that a Fermi step can be detected for $\rho(E_F)$ larger than about 10% of the maximum $[\rho(E)_{max}]$.

This study is the first detailed measurement and analysis of the vicinity of E_F in 1D metals. Previous photoemission experiments with a lower resolution have shown that the intensity near E_F is very low in many 1D metallic compounds [9-11]. Recent studies on conducting polymers [20,21] contain indications of intensity near E_F but the resolution is too low and the thermal broadening at room temperature too high to allow a detailed analysis of the spectral shape at E_F . Furthermore, higher-dimensional interactions can be invoked to explain

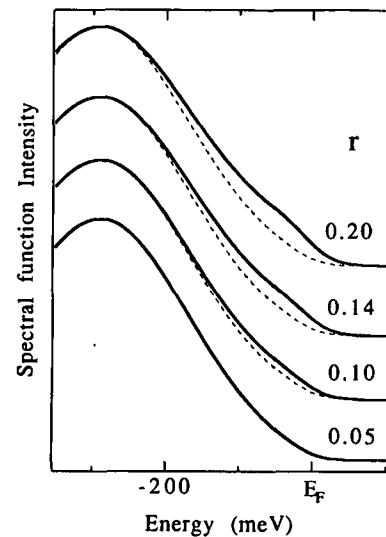


FIG. 2. Calculated spectral functions for several values of the spectral function at the Fermi level (a Gaussian shape was chosen for $\rho(E)$: $\rho(E) = \{\exp[-(E - E_0)/\Delta]^2 + A\}/(1 + A)$ for different values of A). The effects of temperature and resolution are investigated as a function of $r = \rho(E_F)/\rho(E)_{max}$. For $r > 0.1$, the Fermi step is apparent in the spectrum. The dashed line represents the case $r = 0.05$.

a finite spectral function at E_F [20]. To the best of our knowledge, there is no indisputable evidence of a metallic edge in any 1D metal. As the formation of a Peierls distortion is favored by a high density of states at E_F [$N(E_F)$] and a strong electron-phonon coupling, we think that a low $N(E_F)$ is unlikely; then the density of excitations (photoemission spectral function) differs from the quasiparticle density of states as a consequence of electron-electron and electron-phonon interactions.

Let us recall some generalities concerning the peculiar thermodynamic properties of one-dimensional systems. In mean-field theory, fluctuations are ignored and the system exhibits a second-order transition at T_P^{MF} (mean-field Peierls temperature) to a low-temperature insulating state. Introduction of fluctuations strongly modifies this picture. As stated in a theorem of statistical physics [22], the fluctuations in purely 1D systems begin at $T=0$ K and suppress the transition. Thus the order parameter (the energy gap) fluctuates in time and space below T_P^{MF} . These fluctuations are reflected in the density of excitations near the Fermi level where the band gap is expected to open [23]. Near T_P^{MF} , the density of excitations is similar to that of the metallic state, but for $T < T_P^{MF}$, a pseudogap appears as a result of the fluctuations between the metallic and insulating states and leads to a strong reduction of the spectral intensity near the Fermi level. The temperature dependence of the density of excitations shows that a sharp evolution takes place at about a quarter of the mean-field temperature [23]. From the gap value of $K_{0.3}MoO_3$ deduced from optical [24] and resistivity [25] measurements, T_P^{MF} can be estimated to be be-

tween 450 and 300 K. Then a pseudogap should be observed in the photoemission spectrum above the transition temperature (180 K) that could explain the very low intensity at E_F . Similar arguments apply to $(\text{TaSe}_4)_2\text{I}$.

However, in this approach there is no phase transition and the model must be extended to account for the well-characterized thermodynamic transitions observed in real materials. In fact, the "1D" compounds are highly anisotropic tridimensional systems since a weak interchain coupling always exists. This transverse coupling results in a reduction of the fluctuations and then in a transition at finite temperature (the Peierls temperature T_P), which is reduced with respect to the mean-field value ($T_P \ll T_P^{\text{MF}}$). To discuss the influence on the density of excitations, Rice and Strässler have developed a simplified model [26]: They investigate the fluctuation effects as a function of the interchain coupling by calculating the electronic Green function to the first order in the electron-phonon coupling. Their analysis shows that the fluctuations induce the formation above T_P of a pseudogap reminiscent of the actual gap in the low-temperature insulating phase. Such a pseudogap was observed at room temperature in $\text{K}_{0.3}\text{MoO}_3$ and $(\text{TaSe}_4)_2\text{I}$ by optical measurements [24,27]. These fluctuation effects are also reflected on the thermodynamical properties; for example, the magnetic susceptibility exhibits a jump at T_P , and it slowly increases when temperature is raised to 300 K, which has been attributed to fluctuations [28]. A reduction of the density of excitations near E_F is then predicted and depends on the transverse coupling: For strong coupling, the density of excitations is weakly modified (strong 3D effects) whereas, in the weak-coupling range, the pseudogap is more pronounced and the metallic signature is strongly reduced. With this formalism, a temperature-dependent evolution of the spectral intensity at E_F is expected and a metallic behavior should be observed near T_P^{MF} . As our room-temperature measurements do not exhibit an increase in the spectral intensity at E_F , one has to look for additional mechanisms contributing to the reduction of the spectral function.

One-dimensional interacting electron systems are marginal Fermi liquids and a peculiar spectroscopic behavior is expected. Unfortunately, to our knowledge, the effect of 1D correlations on the photoemission spectral function has not been theoretically investigated yet. Nevertheless, this point has been studied for higher dimensions. In particular, electronic correlations in 3D systems are known to modify the spectral function near E_F . For example, in heavy-fermion materials like some cerium-based compounds, the quasiparticle density of states exhibits a narrow peak near E_F as revealed by the large value of the specific-heat coefficient [29]. Although this high density of states is deduced from specific-heat or magnetism measurements, a very low intensity near E_F is found in the photoemission spectra [30]. The spectral function $\rho(E_F)$ and the quasiparticle density of states $N(E_F)$ at the Fer-

mi level are related by the renormalization factor Z through the relation $\rho(E_F) = ZN(E_F)$. Therefore, the lower the renormalization factor, the lower the spectral function at E_F . This factor Z is also the discontinuity amplitude in the momentum-distribution function of $4f$ states at Fermi momentum in such systems. In 1D metals the discontinuity disappears [8] and the singular limit ($Z \rightarrow 0$) must be considered. In this limit, the representation of excitations in terms of quasiparticles is no longer valid: The state of electrons on the Fermi surface becomes unstable with respect to the emission of electron-hole pairs. A classical example of infrared catastrophe is encountered in the edge singularity of x-ray-absorption spectroscopy and results in a vanishing spectral weight at the edge [31]. Then, we expect the infrared catastrophe in the 1D system to induce a strong reduction of the photoemission spectrum at E_F . This conjecture is corroborated by a calculation in the Luttinger model which predicts that the density of excitations vanishes at E_F [32].

Final-state effects resulting from the photoemission technique itself can also be invoked. In the photon absorption, high-energy phonons (of the order of the Debye energy) corresponding to quasimolecular modes can be excited. As a consequence, satellites corresponding to final states with a few phonons lead to a transfer of weight from the Fermi energy to higher binding energies. A similar mechanism has been previously proposed to account for the low density of excitations near 1D organic metals like TTF-TCNQ [10,11]. Because of the narrowness of the conduction band in this material, the hole left behind can be considered as localized in the characteristic excitation time ($\sim 10^{-16}$ s) and various vibration modes can be excited according to the Franck-Condon principle. In such approaches, the low intensity near E_F is only a consequence of a localized character of the hole left behind and could also be encountered in higher dimensions.

To summarize, high-resolution photoemission shows that the spectral function of quasi-one-dimensional compounds in their metallic phase does not exhibit a Fermi edge. We cannot exclude a very low intensity at E_F but such spectra strongly suggest that the photoemission spectral function significantly differs from the quasiparticle density of states. We have reviewed several unusual mechanisms which can be invoked to explain this striking behavior: the large fluctuation effects, the interacting electron properties, and the excitations of high-energy phonons in the photoemission processes. At this stage, it is difficult to discriminate between these different mechanisms. We will attempt to investigate the relative effects of electron-phonon coupling and electronic correlations by studying 1D metals which do not present a Peierls transition. Then, low-temperature high-resolution UPS measurements could unambiguously characterize the metallic 1D state. From a theoretical point of view, little is known concerning the spectroscopic properties of a mar-

ginal Fermi liquid. This problem is fundamental not only for 1D systems but also for high- T_c superconductors since a description of their metallic phase in terms of a marginal Fermi liquid has recently been proposed [33].

We thank Professor C. Schlenker for kindly providing us with the crystal of $K_{0.3}MoO_3$ and Professor J. P. Pouget, Y. Pétroff, and D. Baeriswyl for helpful discussions. This work was supported by the Fonds National Suisse de la Recherche Scientifique.

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Temperature-dependent pseudogap and electron localization in 1T-TaS₂

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(Received 21 October 1991)

Photoelectron spectroscopy reveals a striking correspondence between charge-density-wave-related phase transitions and modifications of the electronic structure in 1T-TaS₂. 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.

1T-TaS₂ 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 bands¹¹ and, at low temperature, disorder,^{12,13} play a major role in determining the properties of 1T-TaS₂. Photoelectron spectroscopy (PES) investigations¹⁴⁻¹⁷ have provided experimental support to a model¹¹ that predicts the occurrence of a Mott localization¹⁸ 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 $k_B T$ 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 1T-TaS₂, 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 1T-polytypic phase is obtained by the addition of SnS₂ (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 4f 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 $\pm 5^\circ$.

Figure 1 shows PES spectra of the top 1.5 eV of the 1T-TaS₂ 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

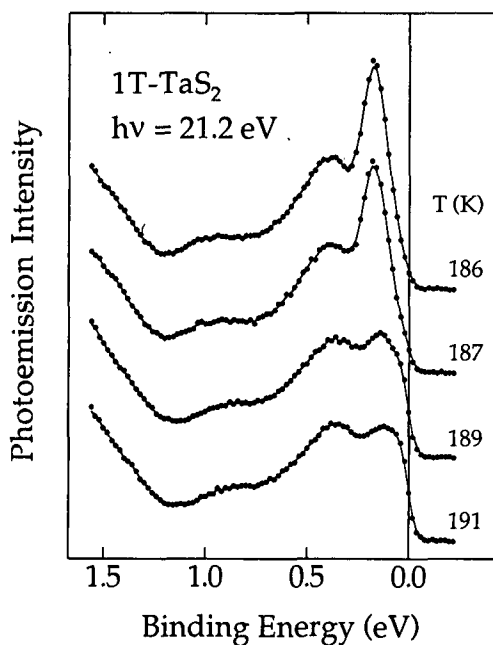


FIG. 1. Photoelectron spectra of 1T-TaS₂ at the quasi-commensurate-commensurate CDW transition, on cooling. Temperature differences are accurate to ± 0.5 K. Binding energies are referred to the Fermi level. The solid lines are guides to the eye.

phase. The structures visible in the 191 K spectrum are absent from the band-structure calculations of undistorted 1T-TaS₂, and we did not observe them in the incommensurate phase, above 355 K.²³ Smith, Kevan, and Di Salvo¹⁵ 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 energy¹⁷ and intensity²³ 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-TaS₂ 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 incom-

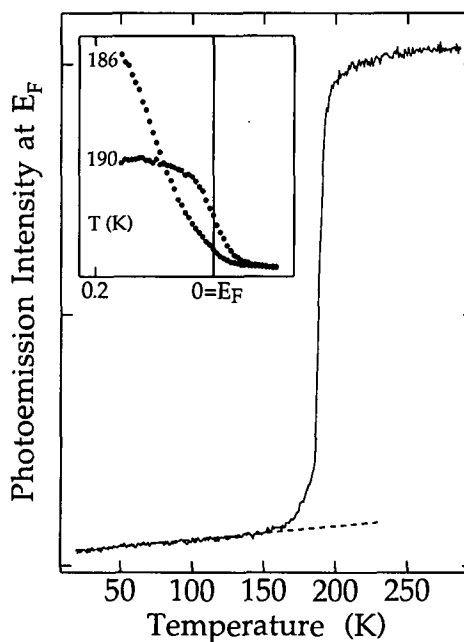


FIG. 2. Temperature dependence of the photoemission intensity at E_F ; the bottom ticks on the vertical axes mark the intensity zero. Inset: Photoelectron spectra of 1T-TaS₂ taken immediately above and below the quasicommensurate-commensurate CDW transition in a region close to the Fermi level. Binding energies are in eV.

plete, 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 spectroscopy²¹ and Hall effect⁴ 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 suggestion¹¹ 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

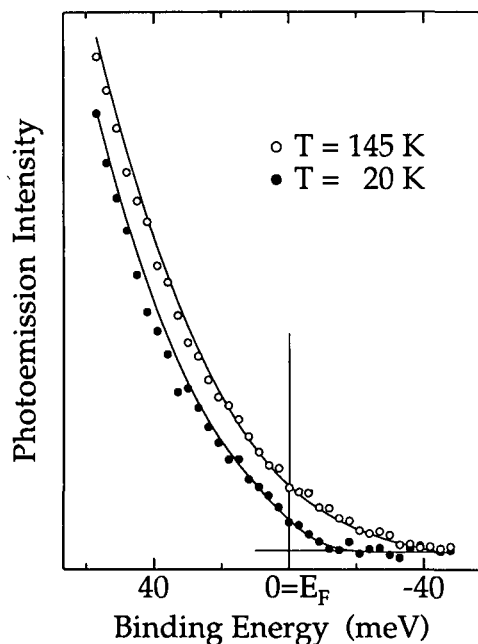


FIG. 3. Close-up around the Fermi level of the photoelectron spectra of 1T-TaS₂ at 145 K (open dots) and at 20 K (solid dots). The solid lines represent parabolic lines centered at E_F , multiplied by the appropriate Fermi-Dirac functions and broadened to account for the experimental resolution (15 meV). 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-TaS₂ by Fazekas and Tosatti, and on a quite general basis by

Mott¹⁸ and Thouless.²⁰ The fractional power-law dependence of the logarithm of the resistivity indicates that below ~ 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 experimental¹³ 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 ~ 0.25 . 1T-TaS₂ 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 metalliclike 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-TaS₂ this gives approximately 5 meV.

In conclusion, our photoemission data confirm that the QC-C CDW transition in 1T-TaS₂ 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-TaS₂ 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. Pétrouff and C. H. Marbuzet for stimulating suggestions. This work was supported by the Fonds National Suisse de la Recherche Scientifique.

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Temperature Dependence of the Spectral Function through the Peierls Transition in Quasi-One-Dimensional Compounds.

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(received 3 April 1992; accepted 12 June 1992)

PACS. 71.45L – Charge-density-wave systems.

PACS. 71.30 – Metal-insulator transitions.

PACS. 79.60 – Photoemission and photoelectron spectra.

Abstract. – High-resolution photoemission measurements have been carried out on blue-bronze materials ($K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$). In these quasi-one-dimensional systems, a metal-insulator transition at 180 K is associated with a lattice distortion, the formation of a charge density wave and the opening of an energy gap. In contrast to naive expectations, a modification of the spectral function over an energy range one order of magnitude larger than the energy gap is observed through the transition. This behaviour suggests that unusual mechanisms associated with the 1D character strongly modify the photoemission spectra.

In the recent past, many works have been devoted to the study of quasi-one-dimensional materials. From a theoretical point of view, the one-dimensionality is responsible for many properties which qualitatively differ from higher dimensionalities. Firstly, as demonstrated by Peierls [1], the metallic state is unstable with respect to a lattice distortion which yields the formation of an insulating state. Secondly, a statistical physics theorem establishes that with short-range interactions, a 1D system cannot present a thermodynamic transition at finite temperature owing to the very large fluctuations associated with the 1D character [2]. Thirdly, the electronic correlations are known to be very unusual [3, 4]; the simple model of Landau-Fermi liquid which generally accounts for the excitations in 2 and 3D materials is no longer valid in 1D systems where an infrared catastrophe leads to the Luttinger liquid pathology [5, 6]. In real 1D materials, electronic transitions are actually observed which suggest that transverse interactions play a significant role. Nevertheless, in systems where these interactions are weak, the main characteristic features of one-dimensionality remain [4].

The molybdenum blue bronzes ($K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$) belong to this class of materials. They are metallic oxides with a crystalline structure formed by slabs of MoO_6 clusters separated by alkali atoms. This atomic distribution clearly shows a preferential direction, and leads to anisotropic physical properties, such as the electrical conductivity [7, 8]. Moreover, these systems exhibit a metal-insulator transition at 180 K as shown in many experimental studies [9-11]. In particular, the Peierls gap in the electronic density of states has been estimated between $(100 \div 150)$ meV from optical measurements [12]. This electronic transition can be understood in the framework of the Fröhlich model which shows that the electron-phonon coupling actually leads to a lattice distortion and the formation of a charge density wave in the low-temperature insulating phase. A mean-field treatment of the Fröhlich Hamiltonian predicts a modification of the spectral function similar to that encountered in the BCS theory of superconductors [13]. In going from the metallic to the semiconducting phases, a transfer of spectral weight from the vicinity of Fermi level to lower energy is expected. This transfer reflects the opening of the Peierls gap and its evolution with temperature should present a BCS shape.

Recent photoemission studies on superconductors [14] and heavy-fermion systems [15] have demonstrated that high-resolution photoemission is a powerful tool for investigating the low-energy electronic excitations and should be sensitive to the opening of the Peierls gap which is not accessible to conventional photoemission measurements. Surprisingly, we showed recently [16] that well-resolved spectra of 1-dimensional systems in their metallic phase above the Peierls transition do not reveal the existence of a Fermi edge which, however, is recognized as the essential characteristic of metals. Starting from this quite unusual situation, we investigate in the present study the temperature dependence of the spectral function through the Peierls transition. Our aim is to look for possible manifestations concomitant to the gap opening.

$K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$ single crystals have been grown by electrolytical reduction from the fluxed melt at 550 °C. Clean samples were prepared by cleavage in a vacuum of $1 \cdot 10^{-10}$ Torr. Our spectrometer, equipped with a helium-discharge lamp producing very narrow photon lines at 21.2 eV (He I) and at 40.8 eV (He II), has a total energy resolution better than 20 meV. The angular resolution, on the other hand, is $\pm 3^\circ$. The calibration of the energy was achieved by measuring the low-temperature Fermi edge on an adjacent Cu sample.

As shown in previous studies [17, 18], the UV-photoemission spectra of these samples are dominated by the valence band structure between -2 and -10 eV and a small feature near the Fermi level reflects the conduction band which, in these oxides, results from the formation of hybridized Mo 4*d* and O 2*p* states [19]. This band, empty in the MoO_3 oxide, is partially filled by the alkali *s* electrons. In fig. 1, we have reported the high-resolution He I photoemission spectra of the conduction band in $K_{0.3}MoO_3$ for different temperatures (the spectra for $Rb_{0.3}MoO_3$ are very similar). These spectra, normalized to their area, are all characterized by a pronounced structure centred at about -300 meV and by a vanishing intensity at the Fermi level. Surprisingly, the spectrum of the metallic phase does not exhibit a step at the Fermi energy which is always characteristic of a metal. In contrast to a previous study [17], no angular dependence of the spectral function is observed. This has been confirmed on several surfaces. With decreasing temperature, a deformation of the spectrum is shown, with an additional shift for temperature below the transition temperature ($T_c = 180$ K). This behaviour can be interpreted by a transfer of spectral weight from the vicinity of the Fermi level to higher binding energy. Moreover, the spectral function is modified over a much wider energy range (500 meV) than expected from the opening of a Peierls gap ($50 \div 75$) eV. In the inset, the photoemission intensity at constant binding energy ($E = -70$ meV) is reported as a function of temperature. The spectral intensity slowly

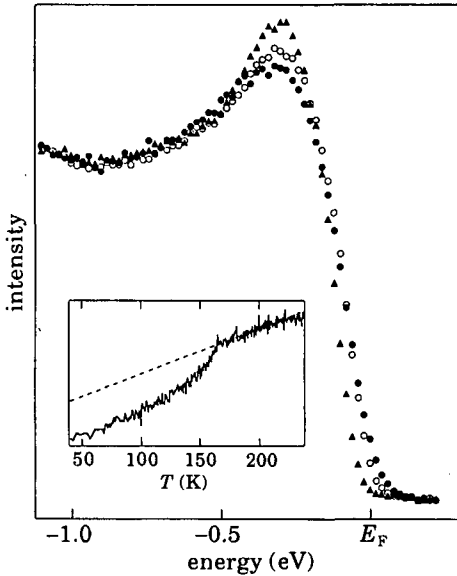


Fig. 1.

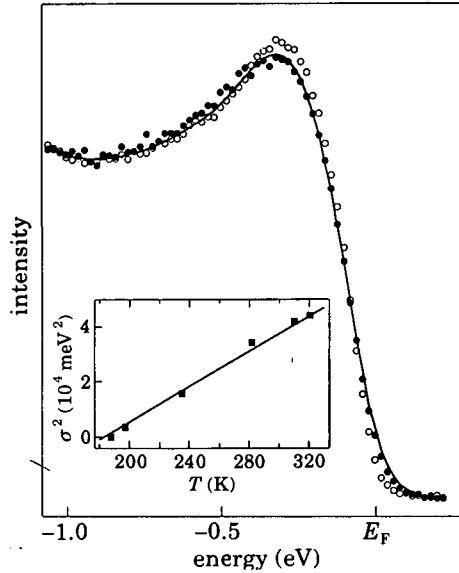


Fig. 2.

Fig. 1. - UPS spectrum at several temperatures (solid triangles $T = 80$ K, open circles $T = 183$ K and solid circles $T = 313$ K). In the inset, we report the temperature dependence of the spectral intensity at binding energy $E = -70$ meV. A monotone decrease is observed at high temperature and a sudden change occurs at 167 K resulting from the electronic transition.

Fig. 2. - Temperature dependence of the spectral function in the metallic phase: the $T = 313$ K spectrum (solid circles) can be reproduced by convoluting the $T = 183$ K spectrum (open circles) with a Gaussian of total width at half maximum $\sigma = 205$ meV (solid lines). In the inset, we plot σ^2 as a function of temperature in the metallic phase.

decreases with decreasing temperature in the high-temperature range, and exhibits a sudden change of slope at $T = 167$ K which is unambiguously correlated with the electronic transition in this compound. The characteristic temperature (167 K) is slightly reduced with respect to the nominal transition temperature ($T_c = 180$ K). Surface effects could be responsible for this behaviour. Disorder or defects at the surface could modify the stability of the charge density wave and then reduce the Peierls transition temperature observed by UV photoemission.

In fig. 2, we examine the spectra above T_c in more details. All spectra for $T > T_c$ intersect at the same energy which is approximately the inflection point of the leading edge ($E = -100$ meV). In this figure, we report the 313 K and 183 K experimental spectra, whereas the solid line represents the convolution of the $T = 183$ K spectrum with a Gaussian of 205 meV width (FWHM). It appears that the convoluted spectrum reproduces the high-temperature spectrum with a satisfactory agreement. In fact, all spectra above T_c are related by such a convolution procedure, and the width at half maximum of the Gaussian, plotted in the inset, shows a square-root dependence of temperature. Thus in the metallic phase, there is no real transfer of spectral weight but only a broadening of the spectrum with increasing temperature. Although such a broadening is currently observed in core level photoemission and interpreted in terms of phonon broadening [20, 21], a temperature dependence of the valence band is puzzling. It has been shown, however, that self-energy effects resulting from electron-phonon coupling can lead to a temperature-dependent

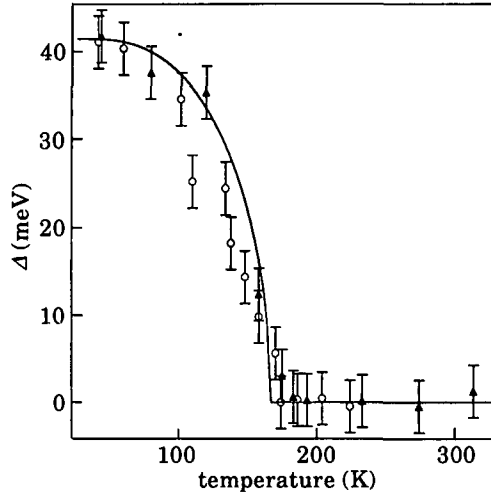


Fig. 3. - Temperature dependence of the phenomenological parameter $\Delta(T)$ for $K_{0.3}MoO_3$ (solid triangles) and $Rb_{0.3}MoO_3$ (open circles). The solid line represents the normalized gap in the BCS model with a transition temperature of $T = 167$ K.

electronic band structure [22, 23]. As electron-phonon coupling is particularly important in charge density wave systems, it could yield a significant broadening of the spectrum.

For temperature lower than T_c , the different spectra are no longer related by a simple convolution. In fact, the spectral function is distorted and shifted to lower energy with decreasing temperature. This behaviour probably results from the modification of the electronic structure and reflects the opening of the Peierls gap. The most direct way to study the evolution of the charge-density-wave-related gap would be to consider the variation of the spectrum in the vicinity of E_F . However, the analysis near E_F is complicated by the broadening that is likely to extend below T_c . In order to avoid this difficulty, we define a phenomenological parameter $\Delta(T)$, which is the shift of the inflection point of the photoemission spectrum with respect to its position at $T = 183$ K. In fig. 3, we report this parameter as a function of temperature. Above 167 K, Δ does not significantly vary with temperature, whereas below 167 K a rapid evolution of Δ is observed. The temperature dependence of Δ shown in fig. 3 demonstrates that this parameter is in some way correlated with the Peierls gap but cannot be identified with it since the evolution of the spectra through the phase transition does not evidence the low-energy feature corresponding to the Peierls gap. However, the solid line in fig. 3 shows that $\Delta(T)$ roughly follows the BCS evolution which controls the temperature dependence of the gap as clearly demonstrated in nuclear magnetic resonance [24] or diffraction experiments [25]. Then, although Δ cannot be interpreted as the order parameter associated with the Peierls transition, its extrapolated zero-temperature value is in good agreement with the order of magnitude of the half-gap estimated from reflectivity measurements ($50 \div 75$ meV).

The photoemission study of these two quasi-unidimensional compounds reveals many surprising behaviours. Although the opening of a Peierls gap is underlying in the temperature dependence of the spectra, neither the metallic state nor the semiconducting state spectra can be understood in a conventional approach. Above T_c , no narrow step revealing the finite density of states at E_F , is observed. We have recently proposed that this behaviour is associated with the 1D character of the materials [16] and would reveal i) the large fluctuations which yield a pseudo-gap in the spectral function well above the transition temperature (as shown on the magnetic susceptibility up to room temperature [26, 27], ii) the

unusual 1D correlations as demonstrated in the exactly solvable Luttinger model [28], iii) the phonon dressing which reduces the weight of the quasi-particle peak in the spectral function [29]. In the semiconducting phase, a modification of the spectrum over 500 meV is observed. As this energy range is still one order of magnitude larger than the energy scale associated with the Peierls transition, the spectroscopic results address fundamental questions concerning the low-energy excitations in 1D materials. To the best of our knowledge, models describing the photoemission spectrum in realistic 1D materials have yet to be developed. In our opinion, such a model should take into account the effect of electron-phonon and electron-electron correlations since both interactions seem to be very singular in one dimension.

To summarize, we have studied, for the first time, the metal-insulator transition associated with a Peierls distortion by high-resolution photoemission spectroscopy. Although the spectral function cannot be interpreted in a simple way, its overall shift (40 meV) at low temperature is in agreement with the determination of the Peierls gap obtained with indirect techniques. The absence of a Fermi step in the metal and the very large energy range affected by the spectral weight below the transition seem to be incompatible with usual models describing the metallic state and metal-insulator transitions. We think that the 1D character of these materials leads to these singular behaviours and additional works are in progress to confirm this point.

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The authors acknowledge J. MARCUS for the crystal growth of the blue bronzes. Two of us (DM and MG) would like to thank G. A. SAWATZKY and F. DEL DONGO for stimulating discussions. This work was supported by the Fonds National Suisse de la Recherche Scientifique.

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Spectroscopic signatures of phase transitions in a charge-density-wave system: $1T\text{-TaS}_2$

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(Received 7 April 1992)

Photoelectron spectroscopy with high-energy resolution has been utilized to investigate the charge-density wave (CDW) in $1T\text{-TaS}_2$ between 20 and 360 K. Constant binding-energy curves reveal discontinuities in the temperature dependence of the photoelectron spectral function $\rho(E)$, and demonstrate that sudden modifications of the electronic structure, namely, in the vicinity of the Fermi level E_F , mark the first-order CDW transitions. In the commensurate phase, below 180 K, $\rho(E_F)$ reflects the formation of a correlation pseudogap. On disordered surfaces, however, the long-range coherence typical of the commensurate phase is lost, and a normal metallic behavior is recovered.

I. INTRODUCTION

$1T\text{-TaS}_2$ has attracted much interest because of peculiar physical properties, unique among the transition-metal dichalcogenides.¹⁻³ Its layered structure consists of strongly bound S-Ta-S planar building layers coupled by weaker forces. As a result, several macroscopic properties, like the electrical resistivity,⁴ are anisotropic and $1T\text{-TaS}_2$ is generally considered as a quasi-two-dimensional (2D) material. The marked 2D character is exemplified by the calculated electronic structure⁵⁻⁷ and it has been confirmed by angle-resolved photoemission experiments.⁸⁻¹² Suitable nesting conditions of the quasi-2D Fermi surface favor the appearance (at ~ 550 K) of a periodic lattice distortion with a complex charge-density wave (CDW).^{1,13-18} The CDW is incommensurate (I) above ~ 350 K, and commensurate (C) with periodicity $\sqrt{13} \times \sqrt{13}$ below 180 K, while between 350 and 180 K (between ~ 230 and 350 K upon heating), it is *on the average* incommensurate, or quasicommensurate (QC), with commensurate domains arranged in a hexagonal lattice and separated by discommensurations.

Unlike other layered materials, the properties of $1T\text{-TaS}_2$ present an unusual and strong temperature dependence. The electrical resistivity, for instance, exhibits sharp steps at the I-QC and QC-C transitions, and an unbounded rise below ~ 60 K,^{4,19} suggesting large changes in the electronic density of states (DOS). This observation contrasts with the usual assumption that CDW-related effects should be small in a 2D system, since a Peierls gap can only appear over limited portions of the Fermi surface. Additional mechanisms, acting with or besides the CDW, have therefore been invoked. Low-temperature resistivity data, suggestive of variable range hopping conduction,^{20,21} have prompted a model predicting the occurrence of electron (Anderson) localization in the random field created by impurities or defects. Fazekas and Tosatti,²² on the other hand, have stressed the importance of the electronic correlations. Their model maintains that the QC-C transition is accompanied by a

Mott transition, which causes a sudden reduction of the electron density of states at the Fermi level and accounts for the observed resistivity jump.

Photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) measurements have shown that the whole valence band of $1T\text{-TaS}_2$ is affected by the CDW and that clear differences in the electronic density of states characterize the various CDW phases.^{10-12,23,24} These results generally support the model of Fazekas and Tosatti. However, surprisingly, estimates of the energy gap (150–200 meV) based on spectroscopic data are two orders of magnitudes larger than values deduced from transport measurements.¹⁹ Recently, we have shown²⁵ that this inconsistency actually reflects the different sensitivity of the various techniques to the two distinct energy scales of this material. PES and IPES data, in fact, directly display the characteristic energy of the Mott transition, the Coulomb correlation energy $U \sim 200$ meV, but a much smaller energy scale, of the order of a few meV controls the low-temperature properties of the material. This small energy scale, which conventional spectroscopic measurements cannot reveal, emerges from measurements performed with state-of-the-art energy resolution. In this paper we present the results of a photoemission investigation of $1T\text{-TaS}_2$ combining high-energy resolution and an accurate temperature control over a wide range (20–370 K), and show that with these joint capabilities it is possible to identify clear fingerprints of the structural phase transitions.

II. EXPERIMENT

Single crystalline samples of $1T\text{-TaS}_2$ in the form of platelets of approximately $5 \times 5 \times 0.5$ mm³ have been prepared from the elements by reversible chemical reaction with iodine as a transport agent, as described elsewhere.²⁵ The electrical resistance, measured between RT and 20 K with a standard fourpoint technique, presented sharp steps at 180 K on cooling and at 230 K on warming.

The samples, mounted on a He closed-cycle refrigerator, could be indirectly heated, and their temperature, monitored by a Rh-Fe resistance, could be controlled between 20 and 370 K, with an accuracy of $\pm 1^\circ$. Clean mirrorlike surfaces were prepared *in situ* by cleaving the crystals with a sharp blade, at a pressure better than 1×10^{-10} Torr. Under these conditions the surface remained spectroscopically clean over a period of days. Only after prolonged exposure to the residual vacuum at the lowest temperature (~ 20 K) could spurious peaks from adsorbates be observed, but these features readily disappeared after flash heating the sample to 100 K. Photoelectron spectra were collected at photon energies of 21.2 and 1486 eV, with energy resolutions of, respectively, 15 and 300 meV. The estimated angular resolution in the valence-band spectra was $\pm 3^\circ$.

III. RESULTS AND DISCUSSION

Near-normal emission photoelectron spectra of the top 1.5 eV of the valence band of 1T-TaS₂, measured at increasing temperatures between 20 and 356 K, are shown in Fig. 1. The bottom spectrum (356 K) is representative of the incommensurate phase: It exhibits a featureless band cut by a metallic edge whose width is compatible with the width of the Fermi function at that temperature. New structures appear in the QC phase ($230 \text{ K} < T < 350 \text{ K}$) initially at binding energies of 100, 300, and 800 meV. These structures sharpen and shift towards higher binding energy with decreasing temperature, and at 230 K the metallic Fermi edge is clearly separated from the first peak. Below 230 K, in the commensurate CDW phase, a substantial growth of the shallowest peak is accompanied

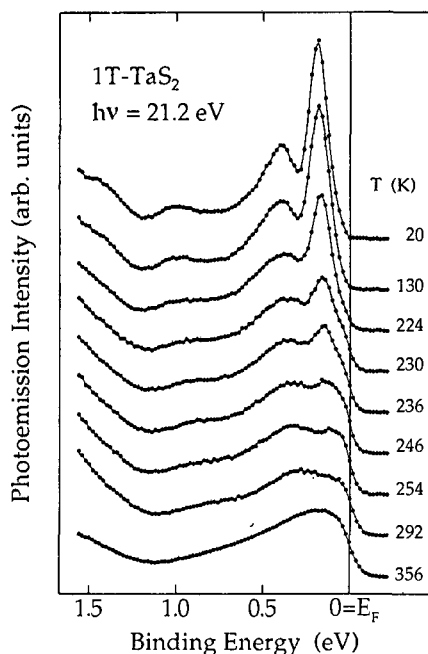


FIG. 1. Near-normal emission valence-band photoelectron (PES) spectra of 1T-TaS₂ collected at increasing temperatures between 20 (commensurate CDW) and 356 K (incommensurate CDW). The solid lines are guides to the eye.

by a rapid decrease of intensity at E_F . At 20 K the valence-band emission is dominated by a sharp peak at 180 meV, and the emission at the Fermi level is vanishingly small. The whole low-temperature spectrum exhibits a strong angular dependence (not shown), but the intensity at E_F remains very small at all angles. These results are consistent with published data, available for $T \geq 120 \text{ K}$.^{10–12,23} The evolution of the spectral function reflects the splitting of the Ta $d_{2,2}$ band into three manifolds (with occupancies of six, six, and one electron per $\sqrt{13} \times \sqrt{13}$ unit cell), under the effect of the CDW,^{11,24} and the occurrence of a Mott localization in the C phase. The prominent peak centered at 180 meV is interpreted as the lower Hubbard subband. No major qualitative changes are observed when the temperature is lowered from 120 to 20 K, but all spectral features become sharper. We shall discuss this point in a subsequent section.

A. The incommensurate-quasicommensurate transition

Although Fig. 1 may suggest a smooth temperature dependence of the PES spectral function, a more accurate analysis reveals measurable discontinuities at both the I-QC and the QC-C transitions. In Fig. 2, we compare valence-band spectra measured on both sides of the I-QC transition, at 356 and 347 K. A shift of ~ 100 meV in the peak position and a 15% reduction of the intensity of E_F can be observed at the lower temperature. Given the small difference of less than 10 K, these differences cannot be attributed to normal temperature effects and must therefore be correlated with the CDW transition. We have noticed that this correlation can be established in a very direct way by recording, at a fixed binding energy,

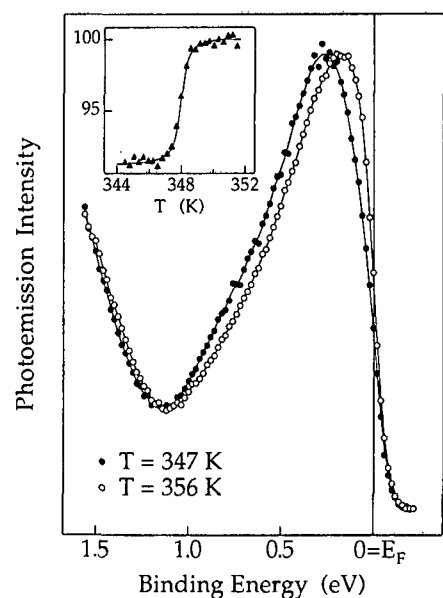


FIG. 2. PES spectra recorded above (open symbols) and below (solid symbols) the I-QC CDW transition temperature. The inset shows temperature dependence of the photoemission intensity (in arbitrary units) at a binding energy of 180 meV, corresponding to the peak in the 356-K spectrum.

the temperature dependence of the photoelectron signal. The inset of Fig. 2 reproduces such a temperature-dependent-constant-energy (TCE) curve collected, around the transition temperature, at the peak's binding energy (180 meV) of the 356-K spectrum. The clear step indicates that, in line with the first-order character of the I-QC transition, the photoelectron intensity presents a discontinuity at the critical temperature. A similar decrease of the photoemission intensity at E_F suggests a reduction of the electronic DOS which can be correlated with the stepwise increase of the electrical resistivity. From Fig. 2 we can then conclude that the I-QC CDW transition brings about a sudden rearrangement of the electronic states of $1T\text{-TaS}_2$ over about 1 eV.

B. The quasicommensurate-commensurate transition

The large anomaly observed in the electrical resistivity at the QC-C transition suggests important modifications of the electronic DOS, which should manifest themselves in the photoemission spectra. This is confirmed by the large changes we have observed in temperature-dependent scans. In Fig. 3(a) we present, in the temperature range 150–300 K, a TCE curve collected at a binding energy of 180 meV (corresponding to the main peak in the low-temperature spectra) during a complete cooling and warming cycle 300→20→300 K. We observe a 100% rise of intensity at 187 K upon cooling and a corresponding intensity drop at 230 K upon warming. The transition at 230 K is not as sharp as the one at 187 K, and the main step is followed by a second one around 245

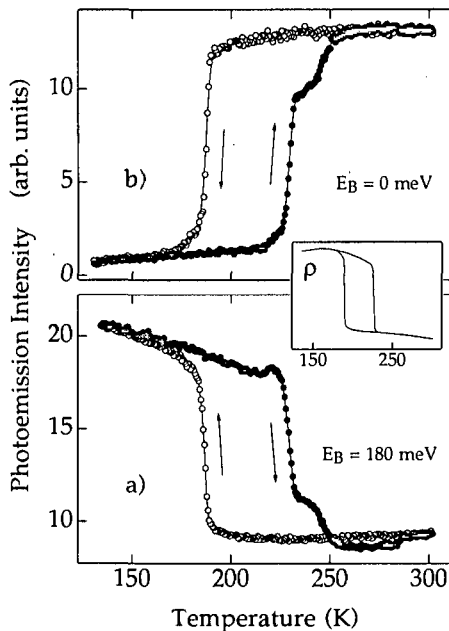


FIG. 3. Temperature-dependent constant-energy (TCE) photoemission intensity curves, collected during a complete cooling (open symbols) and warming (solid symbols) cycle, between room temperature and 20 K: (a) at a binding energy of 180 meV and (b) at the Fermi level. The inset shows the electrical resistivity of $1T\text{-TaS}_2$ (arbitrary units) in the same temperature range.

K. Following this second step, the “warm-up” curve falls below the “cool-down” curve, until a new step at 285 K equals again the two curves.

The curve of Fig. 3(a) reproduces, with the exception of the double step in the “warm-up” curves, the characteristic temperature dependence of bulk parameters. Previous authors²³ had suggested, on the basis of spectroscopic results, that the backtransformation from the correlated low-temperature phase to the normal metallic state should be identified with a structural transition occurring at 285 K from the T (triclinic) phase²⁶ to the QC phase. This conjecture was rather disturbing because it implied that metallic conductivity was recovered ~ 50 K below the Mott transition, when electrons are still localized. The results of Fig. 3 demonstrate unambiguously that the critical temperature coincides with that determined from the electric resistivity. The structural transition at 285 K, which mainly concerns the c axis (perpendicular to the Ta planes), is revealed in Fig. 3 by a small jump in the warm-up curve. The fact that the TCE bears a signature of this transition actually demonstrates that the sensitivity of PES is well adapted to study the close relationship between structural phase transitions and subtle changes in the electronic structure in $1T\text{-TaS}_2$.

On the other hand, the presence of two steps in the warm-up curves of Fig. 3, but not in the resistivity, calls for an explanation. The large, sample-dependent hysteresis, indicative of the influence of defects on the QC-C transition, and the high surface sensitivity (10–20 Å) of PES, suggest that our observations might reflect different pinning mechanisms acting in the bulk and at the surface. In order to verify whether the two steps could be assigned to distinct surface and bulk transitions, we have repeated the measurement with a different photon energy (40.8 eV) and therefore a slightly different probing depth, but the new curves exactly reproduced the results of Fig. 3. We must therefore conclude that both transitions occur at the surface. In the absence of a more systematic study, we can only speculate that cleavage defects could act as pinning centers for the CDW. A cleaved surface will inevitably present both regions with a low density of defects, insufficient to oppose the bulk-driven transition, and regions where the density of defects might be large enough to locally retard the transition to the C phase. The curves of Fig. 3 should therefore be regarded as accounting for a distribution of such surface domains, and the observation of two sharp steps, rather than a broad, continuous transition, would then suggest that these surface defects are only effective above a well-defined threshold density. A combined use of PES and of a surface-sensitive structural technique like scanning tunneling microscopy (STM) should be extremely valuable to elucidate this point.

The temperature dependence of the photoemission signal at the Fermi level, shown in Fig. 3(b), is very similar to that of the main peak [Fig. 3(a)], with sharp edges at 187 K on cooling and steps at 230 and at 245 K on warming. However, the relative intensity variations are about ten times as large, and of opposite sign; moreover, the transition at 285 K is not visible. Opposite temperature dependences of the spectral function at E_F and at 180

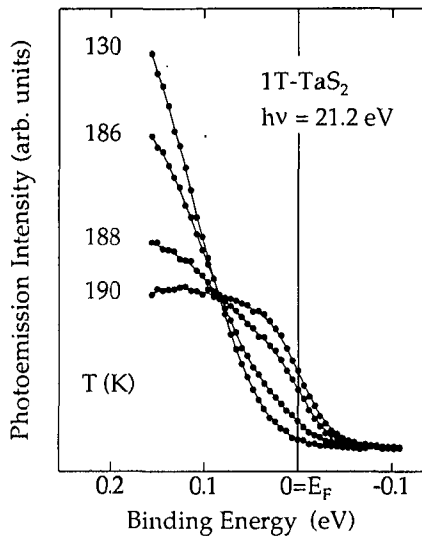


FIG. 4. PES spectra of a small energy region around the Fermi level at the QC-C CDW transition upon cooling. The transition is characterized by a sudden loss of intensity at E_F and by the growth of a peak at a binding energy of 180 meV.

meV were already suggested by the analysis of Fig. 1, which indicates a transfer of spectral weight from the Fermi level to the main peak. It is quite interesting to observe here that this transfer abruptly takes place at the QC-C transition temperature. The sharp 90% intensity drop at 187 K, and similar observations made at different emission angles, mark a collapse of the Fermi surface explaining the related tenfold increase in resistivity. These rapid modifications can be well appreciated from the raw spectra of Fig. 4. Again it must be stressed that since the instrumental broadening is smaller than the intrinsic thermal broadening, these spectra provide a faithful image of the (temperature-dependent) spectral function.

C. The low-temperature correlated state

The sudden collapse of the Fermi surface implied by the TCE's of Fig. 3(b) is consistent with the prediction, by Fazekas and Tosatti,²² of a Mott transition taking place at the QC-C critical temperature. This transition corresponds to the localization of electrons from a narrow band straddling the Fermi level into molecularlike orbitals of the star-shaped 13-atom clusters that constitute the fundamental units of the distorted structure.²² The separation between the center of mass of the occupied lower and the unoccupied upper Hubbard subbands, which yields a good estimate of the strength of the on-site Coulomb correlation U , can be determined from PES (e.g., Fig. 1) and IPES (Ref. 24) spectra to be approximately 200 meV. This circumstance has led a number of spectroscopists to conclude that 1T-TaS₂, in the commensurate phase, is a semiconductor with a gap of the order of 200 meV, in contradiction with the resistivity measurements. The results of Figs. 3 and 4, obtained with high-energy resolution, show, on the contrary, that the density of states at the Fermi level is small but finite well beyond the QC-C transition temperature. This point has

been discussed in a recent paper.²⁵ The photoemission intensity at E_F , $\rho(E_F)$, decreases linearly with decreasing temperature, but a real gap never opens, even at temperatures much lower than the resistivity minimum (~ 60 K). This observation is crucial to understanding the physical properties of 1T-TaS₂, because it indicates that the Fermi surface does not completely disappear at the transition temperature and that the QC-C transition must be regarded as a gapless Mott transition, a possibility already envisaged by Fazekas and Tosatti.²² 1T-TaS₂ would then exhibit a weak metallic character even at low temperature if a disorder-driven localization, which is bound to occur in the deep pseudogap formed by the overlapping tails of the Hubbard subbands,^{27,28} did not prevent metallic conduction. The low-temperature electrical conductivity is therefore controlled by the energy separation between the mobility edge and the Fermi level. A rough estimate, based on the temperature of the resistivity minimum, yields ~ 5 meV for this characteristic energy.²⁵

The modifications of the PES spectrum in the C phase are not limited to the crucial region around the Fermi level. Changes in the valence-band emission over more than 1.5 eV can be observed in Fig. 5, where we compare spectra taken at 165 and 20 K. All the spectral structures appear sharper and more intense in the 20-K spectrum (solid symbols), while the integrated intensity remains, within the experimental accuracy, constant. In particular, the progressive contraction of the main peak around its center accounts for the low-temperature behavior of the TCE's of Fig. 3. It is tempting to interpret the measured contraction as the spectroscopic consequence of an increasing CDW amplitude. The growth of the CDW below the QC-C transition, suggested by the temperature dependence of the Hall coefficient²⁹ and by x-ray-photoelectron-spectroscopy data on the Ta 4*f* core levels,^{30,31} should in fact lead to a further localization of the conduction electron wave functions within the 13-

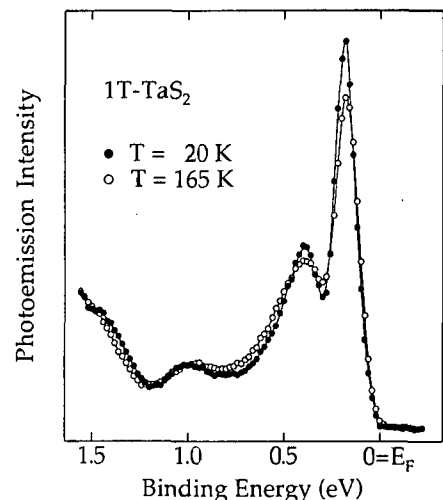


FIG. 5. Valence-band PES spectra of 1T-TaS₂ in the C CDW phase. The spectral features are sharper and more intense in the lower temperature (20-K) spectrum.

atom clusters. The progressive development of a molecular like situation would necessarily result in sharper spectral features. However, additional temperature-dependent sources of broadening that cannot be easily quantified, like the influence of electron-phonon scattering on the (k -dependent) spectral function,^{32,33} and more general temperature effects in the electronic structure,³⁴ cannot be excluded.

D. The effect of surface disorder

As a last point, we consider the influence of surface disorder on the evolution of the charge-density wave. Disorder, as a driving force for localization, has been regarded in the past as the primary cause of the diverging low-temperature electrical resistivity in $1T$ -TaS₂. Subsequent measurements on irradiated samples,³⁵ where the density of defects, and therefore the amount of disorder, could be accurately controlled, have, however, demonstrated that added disorder reduces the low-temperature resistivity by suppressing the transition to the commensurate phase. The suppression of the QC-C transition can be understood as the consequence of local pinning of the CDW phase by defects, which prevents the development of a coherent low-temperature ground state. From the previous discussion, we can expect the disorder-driven suppression of the commensurate phase, and the appearance of metallic conduction, to be accompanied by visible changes in the electronic DOS, and therefore in the PES spectral function.

In an attempt to test this hypothesis, we have examined surfaces prepared by cleavage in UHV immediately followed by scraping with a thin-wired tungsten brush. The amount and the nature of disorder thus induced in the sample is admittedly ill defined, but our procedure can find some justification in its simplicity and, *a posteriori*, in the striking results reported in Fig. 6. There we compare the PES spectrum of an as-cleaved surface with the spectrum of the same sample after scraping; similar curves have been obtained on all surfaces prepared with the same procedure. The disappearance of the main peak at 180 meV coincides with a redistribution of spectral weight over the whole band and with the recovery of a clear metallic edge. Structures at 400 and 900 meV are indicative of a persisting CDW distortion, and, overall, the spectrum of the “disordered” surface closely resembles spectra collected in the QC phase, although, because of the lower temperature (20 K), the Fermi edge is considerably sharper. Since the low-temperature spectra of cleaved surfaces exhibit a vanishingly small intensity at E_F at all emission angles, macroscopic effects (e.g., misoriented crystallites) can be ruled out, and we can conclude that the perturbation acts at a microscopic level in such a way that a metallic phase has been stabilized at low temperature.

The nature of this low-temperature phase is clarified by the analysis of the Ta $4f$ core lines, whose shape is highly sensitive to the CDW. The inset of Fig. 6 shows the Ta $4f_{7/2}$ line for the as-cleaved and the disordered surface. The splitting of the $4f$ line into two well-resolved com-

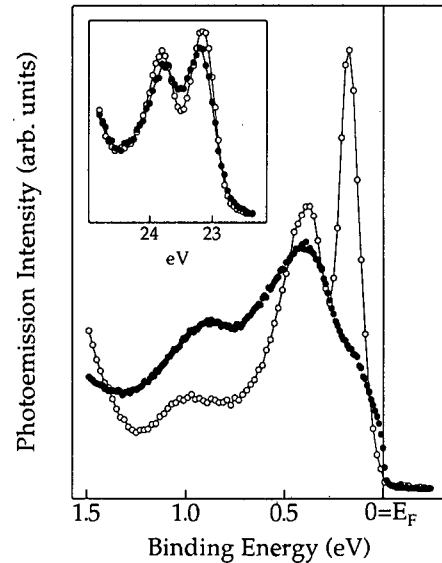


FIG. 6. Valence-band PES spectra of a cleaved $1T$ -TaS₂ surface at 20 K (open symbols) and of the same sample, mechanically disordered by brushing (solid symbols). The inset shows x-ray-photoelectron spectra of the Ta $4f_{7/2}$ core level for the cleaved (open symbols) and the disordered (solid symbols) surface.

ponents in the spectrum of the as-cleaved sample reflects nonequivalent Ta sites, and it is consistent with previous measurements of the C phase. In the spectrum of the disordered surface, instead, the two components are broader, and their apparent separation is noticeably reduced. This is exactly the evolution expected for a transition from the long-range order of the C phase to the domain structure of the QC phase.^{30,31} Our results therefore confirm that disorder inhibits the formation of the coherent state represented by the C phase, and yield a direct image of the disorder-stabilized metallic phase.

IV. CONCLUSIONS

The physical properties of $1T$ -TaS₂ are determined by the intrinsic instability of its quasi-2D Fermi surface. We have investigated the rearrangement of the electronic density of states that accompanies the transitions between different CDW phases, and we have identified precise spectroscopic signatures of each phase. We have shown that photoelectron spectroscopy, in the temperature-dependent constant-energy mode, reveals an impressive correspondence between structural and electronic properties of this material, which was not fully recognized in previous investigations. The high-energy resolution of our measurements allows us to demonstrate the formation of a correlation pseudogap in the commensurate CDW phase. This observation is not accessible to more conventional experiments where the energy resolution is typically larger than the intrinsic breadth of the metallic Fermi edge at the transition temperature. The stabiliza-

tion of a low-temperature metallic ground state by defects has also been briefly discussed. These results demonstrate that the bringing into play of high resolution and of an accurate temperature control establishes photoemission as a powerful and promising tool for the investigation of the subtle relationship between the low-energy properties of solids and the relevant electronic states.

ACKNOWLEDGMENTS

This work has been supported by the Fonds National Suisse de la Recherche Scientifique. We gratefully acknowledge discussions with Y. Pétroff. Many thanks are due to C. Paladión and G. Montenegro for a critical reading of the manuscript.

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Spectroscopic observation of charge-density-wave-induced changes in the electronic structure of 2H-TaSe₂

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Received 26 April 1993

Abstract. We have performed a high-energy-resolution photoelectron spectroscopy investigation of the quasi-two-dimensional material 2H-TaSe₂. Temperature-dependent constant-binding energy curves reveal that characteristic changes in the electronic density of states occur continuously through the second-order charge-density-wave (CDW) transition at 122 K. The photoelectron spectra indicate that different parts of the Fermi surface are unequally affected by the CDW and suggest the formation of an energy gap in the ΓK direction of the Brillouin zone.

1. Introduction

The physical properties of low-dimensional metallic materials are dominated by intrinsic electronic instabilities (Peierls 1955, Overhauser 1962) that reflect a strong enhancement of the generalized static electronic susceptibility $\chi(q)$ at selected wavevectors spanning the Fermi surface. Charge-density-wave (CDW) transitions represent a typical example. In strictly one-dimensional (1D) materials, where the Fermi surface consists of parallel planes and the bare susceptibility χ_0 diverges for $q \mapsto 2k_F$ and $T \mapsto 0$, a charge modulation with wavevector $2k_F$ can develop below a characteristic temperature T_P^0 for a sufficiently strong electron–phonon interaction (Chan and Heine 1973). A mean field treatment of the Fröhlich electron–phonon Hamiltonian shows that the formation of the CDW is accompanied by a metal–insulator transition, and that the temperature dependence of the energy gap $\Delta(T)$, which is an order parameter of the transition, has a BCS form (in particular, $2\Delta(0) \sim 3.5 k_B T_P^0$).

Many experimental investigations of quasi-1D systems have confirmed the occurrence of Peierls transitions, but direct observations of the modifications produced by the CDW on the electronic states near the Fermi surface are scarce. Photoelectron spectroscopy (PES) can potentially yield this information, which is fundamental in order to understand the thermodynamic and transport properties of these materials. Recently a high-resolution PES investigation of the molybdenum blue–bronze K_{0.3}MoO₃, a typical quasi-1D material, has revealed clear signatures of the metal–insulator transition (Dardel *et al* 1992a). An increasing number of results suggests, however, that in 1D systems the observation of the Peierls scenario may be obscured by unique correlation effects that dominate the spectral function (Dardel *et al* 1991, Hwu *et al* 1992).

Quasi-2D materials do not present these peculiar 1D spectral properties, and therefore are good candidates for a spectroscopic investigation of Peierls instabilities. The description of CDW formation in 2D systems differs in several respects from the simple 1D model.

The electronic susceptibility strongly depends on the shape of the Fermi surface, and the characteristic 1D divergence is suppressed (Fehlner and Loly 1974). Fermi-surface-driven instabilities are therefore generally weaker in 2D. Nevertheless, under particular nesting conditions, or as a result of saddle-point singularities (Rice and Scott 1975), χ_0 can be sufficiently enhanced for a CDW to develop. At variance with the 1D case, 2D materials remain metallic in the presence of the CDW, since energy gaps can open only at discrete points of the Fermi surface, corresponding to the new periodicity. Moreover, the weak-coupling description must be replaced by a strong-coupling model incorporating the effects of anharmonicity, to explain the experimental observation that the ratio $2\Delta(0)/k_B T_P$ is always considerably larger than the BCS value (McMillan 1977, Varma and Simons 1983).

The metallic layered dichalcogenides of group V transition metals have a pronounced quasi-2D character. They are characterized by strongly anisotropic physical properties and by approximately cylindrical Fermi surfaces, determined by the metal d_{z^2} bands (Graebner 1977). These materials have been the object of extensive theoretical and experimental investigation since it was realized that anomalies in their transport properties could be explained by the occurrence of CDWs (Wilson *et al* 1974, Moncton *et al* 1975; for exhaustive reviews see Wilson *et al* 1975, Withers and Wilson 1986). Previous photoemission studies of 1T-TaS₂, which is an unusual member of this family because of the complex interplay of CDW, strong electronic correlations and disorder, have revealed clear spectroscopic fingerprints of CDW transitions (Manzke *et al* 1988, Dardel *et al* 1992a,b).

In this paper we consider the trigonal prismatic polytype (2H) of TaSe₂, which is a characteristic 2D CDW material. Structural investigations have shown that 2H-TaSe₂ presents a second-order transition to an incommensurate triple CDW at 122 K, followed by a first-order lock-in transition to a 3×3 commensurate phase at 90 K (Wilson *et al* 1974, Moncton *et al* 1977, Brouwer and Jellinek 1980). Clear signatures of the CDW transition have been observed in thermodynamic transport (Harper *et al* 1977, Nuñez-Regueiro *et al* 1985), optical (Barker *et al* 1975, Campagnoli *et al* 1977) and Mössbauer (Pfeiffer *et al* 1984) measurements. A 20% decrease of the magnetic susceptibility below 120 K indicates that the electronic structure is appreciably affected by the CDW, and the observation of a charge modulation by surface-sensitive techniques like He backscattering (Boato *et al* 1979, Brusdeylinks *et al* 1989) and scanning tunnelling microscopy (STM) (Coleman *et al* 1985) ensures that the CDW persists to the surface region. As in other 2H materials, however, the amplitude of the distortion and the energy gained through the transition are small, and previous angle-resolved PES measurements did not reveal characteristic spectral features indicative of a Peierls gap (Smith *et al* 1985). Similarly, a study of the Ta core lines could not resolve the inequivalent Ta sites expected for the distorted structure (Hughes and Pollak 1976). In an effort to reassess the extent of the CDW-induced modifications of the electronic structure we have carried out a new PES study of 2H-TaSe₂. We have performed measurements at a few selected emission angles, with a considerably improved energy resolution and accurate temperature control. The results of this exploratory investigation reveal for the first time a clear reduction of spectral weight at the Fermi level correlated with the transition to the CDW state.

2. Experimental details

Samples of 2H-TaSe₂ in the form of platelets of approximately $5 \times 5 \times 0.1$ mm³ were prepared from the elements by a reversible chemical reaction with iodine as a transport agent. The samples were mounted in good thermal contact with a closed-cycle refrigerator, and the

temperature could be continuously varied between 20 K and room temperature by indirect ohmic heating. Clean mirror-like surfaces were prepared by cleavage in a vacuum of 1×10^{-10} torr. The build-up of contamination was estimated from the evolution of the PES spectra with time. Noticeable changes in the spectra could be observed only after many hours of exposure to the residual gases at the lowest temperature (20 K). The temperature-dependence spectra presented below were all collected within a few hours, and no sign of contamination could be observed on that time scale. Photoelectrons excited with monochromatic photons from a He resonance lamp ($h\nu = 21.2$ eV) were analysed with a spherical electrostatic analyser, and the total energy resolution was better than 20 meV. The PES spectra have been collected with a moderate angular resolution of approximately $\pm 3^\circ$, which proved nevertheless sufficient to reveal k -dependent modifications of the band structure induced by the CDW.

3. Results and discussion

Figure 1 shows a set of valence band spectra of 2H-TaSe₂, collected at various polar angles along the Γ K direction at a sample temperature of 60 K, in the commensurate CDW phase. The investigation of this particular direction in the Brillouin zone is particularly interesting because nesting of the Fermi surface occurs preferentially along this line (Wexler and Woolley 1976, Wilson 1977), and also because of the presence, close to 0.5Γ K, of a saddle point that could favour the formation of the CDW (Rice and Scott 1975). The spectra of figure 1 are in good agreement with the results of a previous angle-resolved investigation (Smith *et al* 1985), even if the two sets of data have been collected at slightly different photon energies (16.8 eV versus 21.2 eV). The topmost spectrum corresponds to near-normal emission, and the total angular excursion covered by these spectra is 22° . The structures appearing within 0.5 eV of the Fermi level reflect emission from the half-filled Ta 5d₂ subband, which determines the shape of the Fermi surface and controls the development of the CDW. The presence of two distinct features, both well visible in the 17° spectrum, is at least qualitatively consistent with the existing bandstructure calculations, if superlattice Umklapp bands are taken into account.

An investigation of the temperature dependence of the PES spectral function throughout the Brillouin zone was clearly beyond the scope of the present paper. We have instead carried out detailed temperature-dependent measurements at two representative angles: 10° , where the spectral changes were found to be small; and 22° , where variations appeared to be largest. The following discussion will be based on results relative to these two polar angles. The signal at E_F in the 10° and 22° spectra would correspond, in the unreconstructed Brillouin zone, to k -values close to one third and, respectively, one half of Γ K. In the presence of the 3×3 superlattice, however, the situation is considerably more complex due to the additional Umklapp processes. From an inspection of figure 10 of Smith *et al* (1985), and taking into account the finite angular resolution, we can estimate that both spectra probe different portions of the reconstructed Fermi surface. An overview of the temperature evolution of the 22° valence band spectrum is provided by figure 2, where we compare two spectra collected at 160 K (unreconstructed phase) and at 20 K (commensurate CDW phase), normalized to the same integrated intensity. The two spectra present noticeable differences: the main structure at ~ 0.25 eV is sharper and more intense at the lower temperature, and the whole region within 200 meV of E_F undergoes a complex modification. These spectral changes would be partly or totally suppressed in experiments carried out with conventional energy resolution ($\Delta E \sim 0.1\text{--}0.2$ eV).

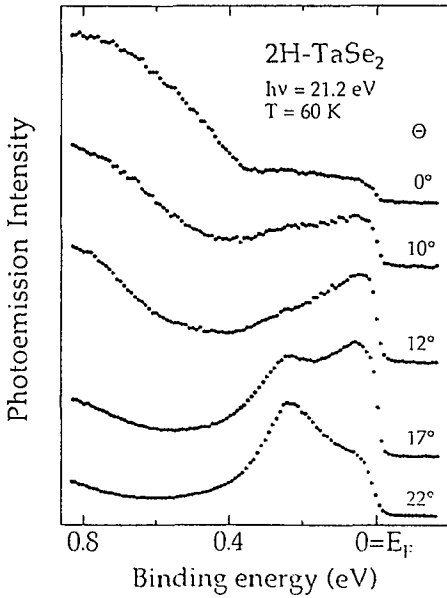


Figure 1. Photoelectron spectra of 2H-TaSe₂ collected at 60 K, in the commensurate CDW phase, along the ΓK direction. Θ is the polar emission angle, and the topmost spectrum corresponds to near-normal emission.

The temperature evolution of the spectral function can be better appreciated from the difference spectra of figure 3, obtained by subtracting the 160 K spectrum (taken as a normal metal reference) from spectra collected at 120 K, 80 K, and 20 K, and normalized to the same integrated intensity. The difference spectra exhibit two prominent structures, reflecting distinct temperature-dependent spectral changes. The first is a positive peak at 0.25 eV with a negative sideband, whose amplitude increases at lower temperature. It reflects the sharpening and growth of the main feature of figure 2, as pictorially illustrated for the simple case of a gaussian peak by the inset of figure 3. The second signature is a negative peak centred at E_F . In this region the normal temperature evolution of the metallic edge, reflecting the sharpening of the Fermi function, yields a ‘sine-like’ structure, actually observed in the 120 K curve, just at the onset of the CDW. At lower temperature, the growth of the negative peak indicates a transfer of spectral weight away from the Fermi level. The spectral weight missing at E_F builds up between 0.1 and 0.2 eV, where it overcompensates a negative sideband of the first structure. The 20 K difference spectrum actually exhibits a peak at ~ 0.1 eV.

The results of figures 2 and 3 are evidence for two distinct relevant temperature effects in the PES spectra: the sharpening and growth of a band feature at 0.25 eV; and the shift of spectral weight away from the Fermi level. The first effect can be rationalized within the framework of band theory according to the standard interpretation of photoemission (Shevchik 1977, White *et al* 1987). It reflects the Debye–Waller factor associated with the contribution to the peak from direct transitions, and temperature-dependent k -space averaging from phonon-assisted indirect transitions. At low temperature the amplitude of direct transitions is larger, and k -space averaging, responsible for the energy broadening of

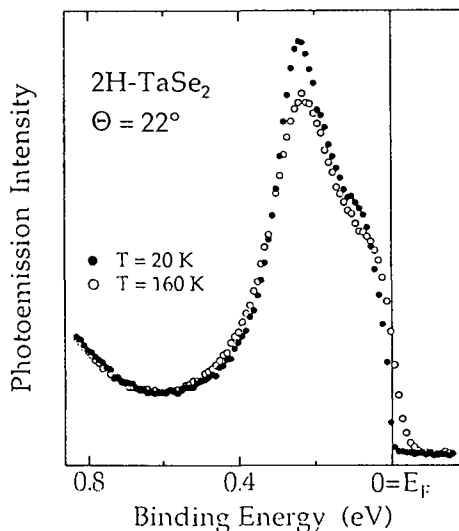


Figure 2. Photoelectron spectra collected in the absence ($T = 160$ K, open symbols) and in the presence ($T = 20$ K, full symbols) of the CDW. The polar angle $\Theta = 22^\circ$ corresponds to a point in k -space close to 0.5Γ K. The spectra have been normalized to the same integrated intensity.

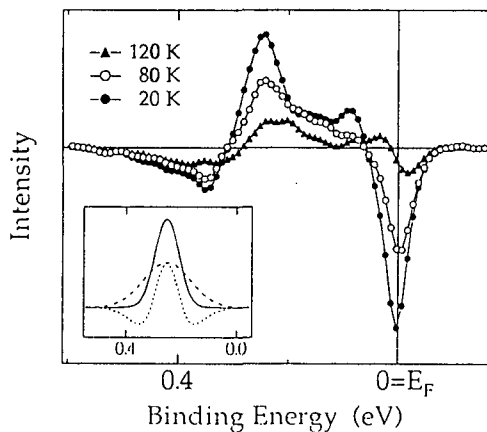


Figure 3. Difference spectra obtained by subtracting, at emission angle $\Theta = 22^\circ$, the $T = 160$ K spectrum taken as a normal metal reference, from spectra collected at progressively lower temperatures, in the presence of a CDW. All spectra had been previously normalized to the same integrated intensity, as in figure 2. Inset: the effect that a temperature-dependent peak width has on a difference curve is schematically illustrated by subtracting a gaussian peak (FWHM = 0.2 eV, broken curve) from a sharper gaussian peak (FWHM = 0.1 eV, full curve) of equal integrated area; the difference curve (dotted) has a positive peak and negative sidebands.

dispersive features, is strongly suppressed, in agreement with our observations. Further contributions from modifications of the band structure, via temperature-dependent self-energies, cannot however be excluded (Allen and Heine 1976). On the other hand, no conventional arguments can be invoked to explain the loss of spectral weight at E_F , and it is tempting to associate this observation with the opening of a gap concomitant with the transition to the CDW state. In order to check the validity of this hypothesis it is necessary to investigate with high-energy resolution the temperature evolution of the PES spectra in the crucial region close to the Fermi level.

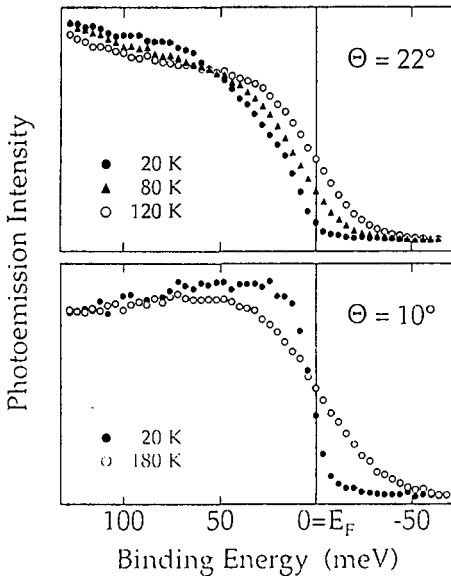


Figure 4. High-resolution spectra of 2H-TaSe₂. The spectra have been normalized to the same integrated intensity over an energy window of 1 eV, as in figure 2, but only the critical near- E_F region is shown. Top: $\Theta = 22^\circ$; spectral intensity is progressively lost at E_F with decreasing temperature, and partially recovered around 50–100 meV. Bottom: $\Theta = 10^\circ$; a small reduction of spectral intensity at E_F is masked by the change of spectral shape due to the temperature-dependent Fermi function.

Figure 4 shows the Fermi level region of high-resolution valence band spectra collected at various temperatures at the emission angles $\theta = 10^\circ$ and $\theta = 22^\circ$, and normalized as in figure 2. The two sets of spectra display a rather different temperature dependence. At 22° the photoemission signal at E_F drastically decreases with decreasing temperature, and it approaches zero at 20 K. At the same time the PES intensity increases around 50–100 meV, and a distinct feature can be observed at ~ 80 meV in the 20 K spectrum. At 10° most of the spectral changes are due to the sharpening of the Fermi edge, although a reduction of the intensity at E_F can be observed between 180 K and 20 K.

The most direct way to establish a correlation between the onset of the spectral changes observed around E_F in figures 3 and 4 and the transition to an ordered CDW state is to record the PES intensity at E_F as a function of temperature. We have shown elsewhere (Dardel *et*

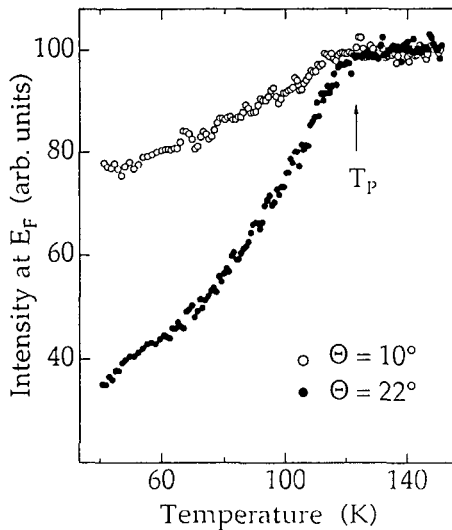


Figure 5. Temperature-dependent constant-energy curves (TCEs) representing the temperature dependence of the spectral intensity at the Fermi level $I(E_F)$ for two emission angles: $\Theta = 10^\circ$ (open symbols) and $\Theta = 22^\circ$ (full symbols). For both angles a change of slope is observed around the CDW transition temperature $T_P = 122$ K. The intensity loss is larger at $\Theta = 22^\circ$, in agreement with the results of figure 4.

al 1992a–c) that this procedure provides a sensitive probe of Fermi-surface-driven phase transitions. Two such temperature-dependent constant-energy curves (TCE), recorded at 10° and 22° emission, while cooling the sample, are shown in figure 5. The PES signal exhibits at both emission angles a sharp change of slope at the critical temperature T_P , and a subsequent reduction at lower temperatures. This reduction unambiguously reflects, at least for the k -values sampled by our measurements, the CDW-induced rearrangement of the band structure of 2H-TaSe₂. The intensity reduction is considerably more pronounced at 22° . At 40 K the intensity of the 22° TCE is reduced to $\sim 30\%$ of the room-temperature (RT) value, while the 10° TCE appears to saturate at $\sim 80\%$ of the RT value. It is interesting to notice that the change of slope of the TCEs occurs right at T_P . Local phase fluctuations of the CDW, that are believed to play an important role in determining the form of the electrical conductivity (Naito and Tanaka 1981), do not seem therefore to affect in an appreciable way the electronic density of states. Also, the TCEs of figure 5 do not show any characteristic features that could be associated with the lock-in transition at 90 K, in sharp contrast with the case of 1T-TaS₂, where the transition to a commensurate state coincides with a dramatic disruption of the Fermi surface. This remarkably different spectroscopic behaviour is consistent with the fact that, unlike 1T-TaS₂ or 1T-TaSe₂, the transport properties of 2H-TaSe₂ vary smoothly through the lock-in transition, and with the very small associated specific heat anomaly ($\sim 10^{-3}$ times that of 1T-TaSe₂).

The above results allow us to address the issue of the opening of a CDW gap in 2H-TaSe₂. As expected from general arguments, the physical properties of the material indicate that gapping occurs only over a fraction of the Fermi surface. The 20% reduction of the magnetic susceptibility in the CDW phase suggests a comparable Fermi surface loss, but contrasting estimates have been presented. The appearance below T_P of a structure at 0.3 eV in the

reflectivity spectra (Barker *et al* 1975) was interpreted as a manifestation of the Peierls gap, and a removal of just about 1% of the Fermi surface was inferred. Campagnoli *et al* (1988) have, on the other hand, interpreted a similar feature in their thermoreflectance spectra as representing only one of the many new optical transitions possible within the d_{z^2} manifold split by the 3×3 CDW distortion. Subsequent bandstructure calculations for the distorted structure have confirmed that the notion of a single gap appears inappropriate for 2H-TaSe₂, and that several optical gaps appear at various energies within the d bands as degeneracies are lifted in the CDW phase throughout the Brillouin zone (Doran and Woolley 1981). More recently, a gap value ~ 80 meV (and $2\Delta(0)/k_B T_F \sim 15$, indicative of strong coupling) has been proposed, based on the occurrence of breaks at ± 80 meV in the STM current-voltage characteristic (Wang *et al* 1990). The exact meaning of such observations in a material like 2H-TaSe₂ remains however somewhat unclear.

The spectroscopic data presented in figures 4 and 5 demonstrate the removal of electronic states from the Fermi level region. In particular, for 22° emission essentially all the spectral weight at E_F is suppressed at 20 K, suggesting the opening of a gap or a deep pseudogap close to $0.5 \Gamma K$. The missing spectral weight is recovered further from E_F , and the weak structure at ~ 80 meV could actually be related to the STM observation. We notice however that the low-temperature spectra are also enhanced at higher binding energies (100–150 meV), suggesting that, due to the finite angular resolution, our spectra reflect an average of a range of k -dependent gaps. A detailed PES investigation of this region of the Brillouin zone with a much improved angular resolution, impossible with our present apparatus, could contribute to elucidate this point.

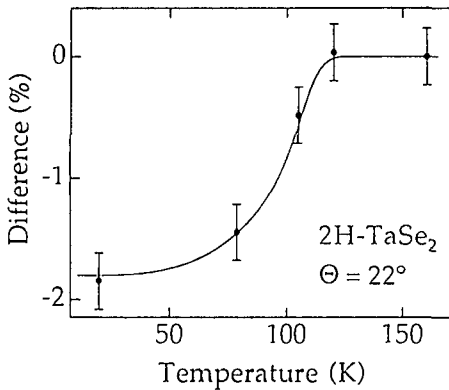


Figure 6. The data points represent the temperature dependence of the mean energy $\mu(T)$ of the photoelectron energy distribution curves of 2H-TaSe₂ at an emission angle $\Theta = 22^\circ$ normalized with respect to the value $\mu(160 \text{ K})$. An energy window of 1 eV has been used. The variation of $\mu(T)$ below 120 K reflects a net energy lowering at this emission angle. The curve is a guide to the eye.

It is interesting to notice that our results are consistent with the expected local lowering of the electronic energy, required for the formation of the CDW to be energetically favourable. We have calculated, for various temperatures, the first moment (mean energy) $\mu(T)$ of the

photoelectron energy distribution curves at $\Theta = 22^\circ$, over an energy window of 1 eV. The quantity $[\mu(160) - \mu(T)]/\mu(160)$ thus obtained is reported for various temperatures in figure 6. Although an interpretation of the angle-resolved PES spectra exclusively in terms of initial electronic states would be abusive, the sudden variation around T_P observed in figure 6 suggests a lowering of the electronic energy in the CDW phase, at least in the region of k -space probed by our spectra. The smaller-intensity variation observed at $\Theta = 10^\circ$ in figures 4 and 5 shows that, even if a distinct signature of the transition is visible, the corresponding electronic states are less affected by the CDW. This small spectral change may just reflect a minor rearrangement of bands, in line with general predictions of bandstructure calculations. A different interpretation is however possible. Previous angle-resolved PES results (Smith and Traum 1975) have pointed out that, close to normal emission, indirect transitions give an unusually strong contribution to the measured spectrum. If we assume this contribution to be important also near 10° , the spectral weight at E_F might represent an average over a significant part of the small 3×3 Brillouin zone. In this case the TCE of figure 5 could reflect the temperature dependence of the total DOS, more than a local property in k -space.

4. Conclusion

The results of a temperature-dependent PES investigation of 2H-TaSe₂ demonstrate that the CDW induces characteristic k -dependent modifications of the electronic structure. To the authors' knowledge this is the first direct spectroscopic observation of the effects of a Peierls instability on the electronic structure at the Fermi surface. In previous investigations this observation was obscured by competing phenomena (like the Mott localization in 1T-TaS₂) or by the peculiar spectral properties of 1D materials (e.g. in the blue-bronze). A fine temperature control and a high-energy resolution allow us to reveal the onset of the CDW transition at ~ 120 K. The temperature dependence of the photoemission signal is consistent with the second-order character of the transition expected from a simple treatment of the Peierls instability and from more elaborate models, and experimentally established by recent He scattering experiments. On the other hand, the photoemission spectra do not reveal any changes that could be related to the much studied transition from the incommensurate to the low-temperature commensurate state. We expect that further valuable information could be gained by a similar and more detailed study with higher angular resolution along high-symmetry lines in the Brillouin zone. The present results already point out, however, that accurate spectroscopic measurements can provide new stimulating information on materials like 2H-TaSe₂, that have been investigated for about 20 years for their importance as almost ideal testgrounds for models of electron-phonon interactions and Fermi-surface-driven instabilities.

Acknowledgments

This work has been supported by the Fonds National Suisse de la Recherche Scientifique. The authors gratefully acknowledge many stimulating discussions with Dr F Bardamu and Professor X Bestombes.

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Europhys. Lett., **24** (8), pp. 687-692 (1993)

Possible Observation of a Luttinger-Liquid Behaviour from Photoemission Spectroscopy of One-Dimensional Organic Conductors.

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(received 22 June 1993; accepted in final form 22 October 1993)

PACS. 79.60C – Clean metals.

PACS. 72.15N – Collective modes; low-dimensional conductors (inc. synthetic metals).

PACS. 71.20H – Organic compounds, polymers, and complex systems.

Abstract. – High-resolution photoemission experiments have been carried out on one-dimensional organic conductors in their normal state. In contrast to usual metals, the spectral function vanishes at the Fermi level and no Fermi edge is detectable. These results are consistent with a Luttinger description and an exponent α of the spectral function at the Fermi level larger than 1 is found. This result corroborates recent nuclear-magnetic-resonance experiments. Such a large correlation exponent shows that the 1D Hubbard model is not appropriate and strong long-range interactions must be assumed to play an important role in these materials. The compatibility with other correlation functions is discussed.

In a recent letter, we have presented an intriguing spectroscopic behaviour in a particular class of metals: the photoemission spectrum of charge density wave quasi-one-dimensional systems does not exhibit the characteristic Fermi edge in their metallic phase [1]. We have discussed this striking result in terms of the singular behaviours prevailing in one-dimensional systems and we have identified three possible causes of the observed reduction of the spectral weight at E_F : one-dimensional (1D) fluctuations, correlations and phonon effects [1,2]. First, the thermodynamical 1D fluctuations are very large and suppress any transition at finite temperature. Thus, the finite transition temperature observed in real quasi-1D materials results from a residual transverse coupling between chains but the one-dimensionality is reflected by the presence of large critical fluctuations extending well above the actual transition temperature. These fluctuations induce a pseudogap in the metallic phase that significantly reduces the spectral weight just below the Fermi level [3,4]. Secondly, singular correlation effects are known to occur in one dimension [5,6]. Although 3D strongly correlated systems are well described in the framework of Fermi liquids (FL),

correlations destroy this picture in 1D. The adiabatic continuity is no longer valid and low-energy excitations cannot be represented by quasi-particles (all the degrees of freedom are collective and the excitations are bosonlike). Moreover, the momentum distribution function does not exhibit the emblematic discontinuity of Fermi liquids at the Fermi momentum (k_F) and the electronic spectral function vanishes at the Fermi level [7]. Finally, the polaronic effects have been considered. Photoemission of an electron could be accompanied by the excitation of molecular vibration modes. Thus, the system left behind could be in several excited phononic states leading to a transfer of spectral weight from the vicinity of E_F to higher binding energies [8,9].

In inorganic systems, the relative importance of these different mechanisms cannot be discriminated and it is possible that their physical properties result from a complex interplay of them. It is therefore important to examine materials where one of these mechanisms dominates. In this paper, we present a photoemission study of a series of quasi-one-dimensional organic compounds (the Bechgaard salts: tetramethyltetraselenafulvalene $(\text{TMTSF})_2\text{X}$ with $\text{X} = \text{ClO}_4, \text{PF}_6$ etc.). These materials generally behave as good metallic conductors and exhibit at low temperature (below $T < 12$ K) various phase transitions resulting from competing ground states (superconducting, charge or spin density waves, spin Peierls, etc.). A large amount of experimental data shows that the electronic correlations are at the origin of richness of the phase diagram in these materials [10,11]. Thus, in contrast to the previously studied inorganic materials where electron-phonon interactions are important, electronic correlations play the dominant role in the Bechgaard salts. Moreover, critical fluctuations associated with the low-temperature transition are expected to be small in the metallic temperature range. In this letter, we show that photoemission spectra exhibit strong deviations from the Fermi-liquid picture and are more consistent with a Luttinger-liquid character of these 1D metals.

The Bechgaard salts consist of a zig-zag stacking of TMTSF planar molecules along regular chains. A detailed description of their structure can be found in ref. [12]. These materials exhibit highly anisotropic transport and optical properties revealing a quasi-1D character. In particular, no plasma edge in the polarized-light reflectance spectrum is observed at room temperature and down to 100 K for light polarized along the transverse b direction [13]. Only around 25 K, very close to the SDW transition, a rather well-defined edge near 1000 cm^{-1} is observed (as compared to the edge at 10^4 cm^{-1} for a longitudinal polarization). In addition, the conductivity anisotropy is temperature independent down to about 40 K, as expected for an incoherent transverse conduction [10]. Samples, mounted on a He closed-cycle refrigerator, were cleaned by cleavage in a vacuum of $1 \cdot 10^{-10}$ Torr. Our spectrometer, equipped with a helium discharge lamp producing very narrow photon lines (HeI $h\nu = 21.2$ eV and HeII $h\nu = 40.8$ eV), has a total energy resolution better than 20 meV and an angular resolution of about $\pm 3^\circ$. The position of the Fermi energy (E_F) is determined by measuring the Fermi edge at low temperature on an adjacent Cu reference in electrical contact with the sample. The uncertainty of this determination is estimated to be less than 3 meV.

In fig. 1, we present the HeII photoemission spectrum of $(\text{TMTSF})_2\text{PF}_6$ in the metallic state ($T = 50$ K). We have chosen to measure at a temperature sufficiently low to limit the Fermi-function broadening and still large enough so that the interchain coupling can be neglected. The spectrum is dominated by broad structures with the shallowest one near $E = -1.2$ eV. No angle dependence has been detected and a very weak spectral weight just below the Fermi level is found for all emission angles. Our poor angular resolution (3°) corresponds to an uncertainty of the photoelectron momentum in the chain direction of about $\Delta k = 0.17 \text{ \AA}^{-1}$ (for $h\nu = 40.8$ eV at normal emission) which is a significant amount (about one quarter) of the first Brillouin zone (0.431 \AA^{-1}). Thus, the spectrum of fig. 1 represents a

of the Bechgaard salts, polaronic effects cannot lead to a strong reduction of the quasi-particle feature near E_F .

Since in the Bechgaard salts fluctuations associated with the SDW transition and polaronic effects cannot explain the absence of a Fermi edge in the photoemission spectrum, we now have to investigate if the electronic correlations can be responsible for this peculiar observation in 1D electron systems. Tomonaga [5] and Luttinger [6] have proposed a simple model of interacting 1D electrons with a linearized dispersion and two coupling constants (g_2 and g_4) parametrizing the small- q two-body scattering amplitudes. The salient features of this model are i) the absence of quasi-particles—all low-energy excitations are collective bosonic modes; ii) charge-spin separation (the charge and spin modes propagate with different velocities); iii) all correlation functions can be computed exactly and decay with non-universal power laws. Haldane [19] has suggested that this low-energy structure is universal to a wide class of 1D systems and proposed that Fermi liquids should be replaced by Luttinger liquids in 1D. There is also indirect supporting evidence from NMR for the possible relevance of this picture [15].

The spectral properties of the Luttinger liquid are strongly influenced by electronic correlations and exhibit dramatic differences from the familiar Fermi liquids. Fermi liquids are characterized by a finite jump of the momentum distribution function $n(k)$ at the Fermi momentum (k_F) reflecting quasi-particle excitations, whereas $n(k)$ is continuous at k_F in interacting 1D systems (Luttinger liquids) [20-22]:

$$n(k) = n(k_F) + C|k - k_F|^\alpha \operatorname{sgn}(k - k_F) + D|k - k_F|, \quad (1)$$

where α depends on the model parameters (g -coupling strengths), C and D are two constants. The Fermi-liquid discontinuity is recovered in the non-interacting limit $\alpha = 0$. For $\alpha > 1$, the last term dominates and a linear variation near E_F is expected. The absence of quasi-particle excitations is also reflected on the form of the spectral function. The momentum-integrated spectral function $\rho(\omega)$ consists entirely of an incoherent background, and it vanishes at the Fermi energy, according to the asymptotic power law [7, 22-24]

$$\rho(\omega) \approx \omega^\alpha. \quad (2)$$

As in the X-ray edge problem [25], this singular behaviour results from the fact that, because of interactions, a single-particle excitation is dressed with an infinite number of particle-hole pairs.

In fig. 2, we report the calculated momentum-integrated photoemission spectral function for several values of α at zero temperature. In the non-interacting limit ($\alpha = 0$), the spectral density would be a constant. Correlation effects lead to a significant decrease in the spectral-weight near E_F and a broad maximum appears around $(\omega\Lambda/v_F) = 1$ in order to obey the spectral weight sum rule (v_F is the Fermi velocity and Λ is a momentum transfer cut-off in the interactions [23]). For $\alpha < 1$, the spectral function exhibits an infinite slope at E_F and will be hardly distinguishable from a true Fermi edge experimentally. The slope is zero for $\alpha > 1$ which compares favourably with fig. 1. For large α , spectral weight near E is very low and the momentum-resolved spectral functions do not exhibit any significant dispersion [23]. An identification of the maximum with broad feature at $E = -1.2$ eV would be abusive: the approximation of a linear dispersion is certainly questionable on this energy scale (the bandwidth is estimated to be of order of 1 eV [10] in these materials). Moreover, the -1.2 eV feature could also reflect low-lying orbitals of the TMTSF molecules [26]. However, the most important result is the absence of Fermi edge and photoemission weight near E_F , which clearly indicates that the band states on the Fermi surface do not contribute near E_F . This

partial momentum integration. A close-up of the region near the Fermi level clearly shows that no Fermi edge is detectable (inset of fig. 1) as previously observed in the inorganic quasi-1D materials ($K_{0.3}MoO_3$ and $(TaSe_4)_2I$) [1]. In the present case, the fluctuation and polaronic effects are unlikely to be responsible for a vanishing intensity at E_F . Near 12 K the Bechgaard salts undergo a metal-insulator transition toward a spin density wave state and experiments lead to a single-particle gap Δ which is close to the BCS value $2\Delta = 3.5k_B T_{SDW}$ [14], in contrast to CDW systems, like $K_{0.3}MoO_3$, where Δ is usually significantly larger than the BCS value. Thus, as T_{SDW} is very close to the mean-field transition temperature, the SDW transition in $(TMTSF)_2PF_6$ has a strong 3D character and the corresponding fluctuations take place close to the critical temperature as also indicated by the narrow region of 3D antiferromagnetic fluctuations ($\Delta T/T_c \approx 0.1$) detected by NMR [15]. Owing to the small value of the transition temperature, these fluctuations would induce a very narrow pseudogap (a few meV width). Recent optical measurements of $(TMTSF)_2PF_6$ [16] seem to rule out the existence of such a pseudogap in the optical spectrum above the SDW transition and show no evidence of a narrow resonance at zero frequency as implied by other studies [17]. This contrasts with the situation encountered in CDW systems like $K_{0.3}MoO_3$ where a large pseudogap was found above the CDW transition [18]. Polaronic effects, on the other hand, reduce the quasi-particle weight by a factor directly related to the mass of the polaron so that, as no spectral weight is observed near E_F , the effective mass would be huge and should be reflected in transport properties. As no evidence of a large polaronic enhancement of the effective mass is found in resistivity and optical measurements

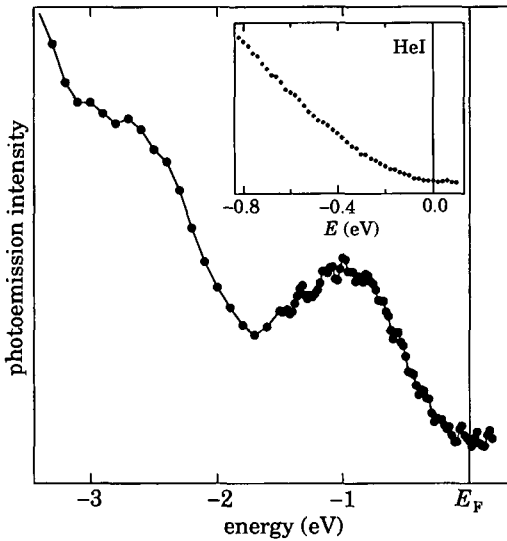


Fig. 1

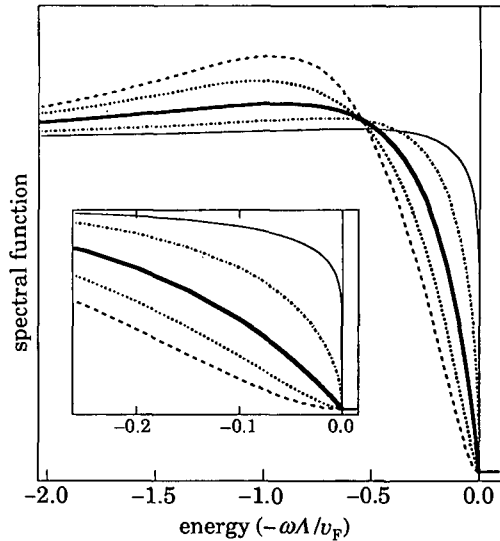


Fig. 2

Fig. 1. - HeII photoemission spectrum of $(TMTSF)_2PF_6$ at $T = 50$ K. In the insert, the HeI spectrum near the Fermi level clearly shows with better statistics that no Fermi edge is detectable and that the correlation exponent is larger than 1. Similar spectra are obtained in other Bechgaard salts like $(TMTSF)_2ClO_4$ and $(TMTSF)_2AsF_6$

Fig. 2. - Calculated spectral function of the Luttinger model for various correlation exponents α (— $\alpha = 0.125$, - · - $\alpha = 0.5$, — $\alpha = 1$, ··· $\alpha = 1.5$, - - - $\alpha = 2$). We have assumed $g_{4||} = 0$ and $g_{2||} = g_{4\perp} = g_{2\perp}$ implying specific relations between α and the renormalized charge and spin velocities v_ρ and v_σ (cf. ref. [23]).

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behaviour suggests that the usual Fermi-liquid picture is no longer valid in these 1D metals.

As shown on the low-energy part of the calculated and experimental spectra (inset of fig. 1 and 2), consistency of the experiments with a Luttinger-liquid picture would require a surprisingly large correlation parameter $\alpha > 1$. It is interesting to notice that such a large α value is incompatible with the standard Hubbard model which yields a maximum value $\alpha = 1/8$ (for infinite U). Then strong interactions of longer range, like inter-site electronic interactions in the extended Hubbard model, are required to increase α . But, is $\alpha > 1$ compatible with the other experimental quantities? The exponents of the various correlation functions of the Luttinger model can all be expressed as a function of the charge correlation exponent K_ρ [27]. For the spectral function (2), this relation is $\alpha = (K_\rho + K_\rho^{-1} - 2)/4$. Two other exponents are particularly interesting: the spin density wave exponent $\gamma = 1 - K_\rho$ and the $4k_F$ CDW exponent ($\delta = 2 - 4K_\rho$). γ determines the temperature dependence of the $q = 2k_F$ contribution to the nuclear spin-lattice relaxation rate $T^{-1}(2k_F) = T(T/E_F)^{-\gamma}$ [28]. Recent NMR measurements yield $\gamma = 0.85$ implying $K_\rho = 0.15$ and $\alpha = 1.25$ [29] in good agreement with our spectroscopic estimate. Therefore, two independent measurements, photoemission and NMR, support a low value of the charge correlation exponent K_ρ (large value of α). For $\alpha > 1$, strong $4k_F$ CDW fluctuations are expected ($\delta > \gamma$). However, no $4k_F$ diffuse signal in X-ray diffraction experiments is observed in $(\text{TMTSF})_2\text{PF}_6$ [30]. This is puzzling, but it is neither observed in $(\text{TMTTF})_2\text{PF}_6$, where charge localization below 250 K is clearly related with large $4k_F$ CDW fluctuations. The absence of a $4k_F$ diffuse signal therefore does not imply a small α . Moreover, while there is no clear signature of charge localization in the d.c.-transport properties, infrared data even at room temperature apparently require a sizeable degree of charge localization [31]. Obviously, due to a more pronounced dimerization, charge localization and $4k_F$ CDW fluctuations are more important in $(\text{TMTTF})_2\text{PF}_6$. This is fully consistent with the estimate of the SDW exponent from NMR relaxation $\gamma = 1$ (and then $K_\rho = 0$) just below the localization temperature [29] and a larger optical gap: in going from $(\text{TMTTF})_2\text{PF}_6$ to $(\text{TMTSF})_2\text{PF}_6$, K_ρ increases leading to a decrease of the $4k_F$ fluctuations and, correlatively, a decrease of the charge localization temperature which could be smaller than the SDW transition temperature.

To summarize, high-resolution photoemission experiments on the metallic phase of the organic compound $(\text{TMTSF})_2\text{PF}_6$ show that the spectral function does not exhibit the characteristic Fermi edge of Fermi liquids. A similar behaviour was previously found in inorganic CDW quasi-1D compounds [1] but in these latter systems electron-phonon interactions and fluctuations are important and cannot be *a priori* neglected. As the physical properties of the Bechgaard salts are dominated by electronic correlations, we can conclude that the striking spectroscopic behaviour is the consequence of 1D electronic correlations. Our measurements unambiguously show the absence of a quasi-particle signature and we propose that these 1D correlated materials, in their normal metallic state, are Luttinger liquids with a correlation parameter $\alpha > 1$. This large correlation parameter suggests the importance of long-range interactions in these materials since a simple Hubbard model cannot yield an α value larger than $1/8$. This speculative idea is corroborated by very recent NMR measurements whose analysis leads to $\alpha = 1.25$.

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We thank Drs. P. BATAIL, P. AUBAN-SENZIER and C. LENOIR for kindly providing us with the samples and we acknowledge Prof. C. BOURBONNAIS, J. P. POUGET and F. MILA for fruitful discussions and Prof. K. SCHÖNHAMMER for sending us the preprint of a paper reporting similar calculations before publication. This work was supported by the Fonds National Suisse de la Recherche Scientifique.

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Le texte complet est déposé à la Bibliothèque de l'Université de Neuchâtel