Unusual Photoemission Spectral Function of Quasi-One-Dimensional Metals

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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.

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
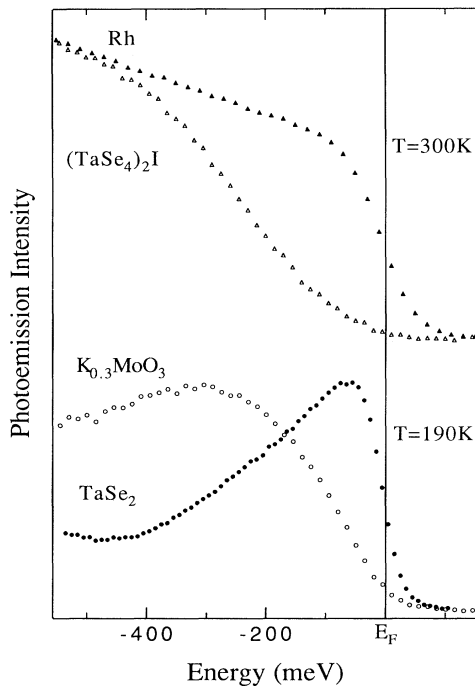
FIG. 1. UPS photoemission spectra of the $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ measured at a temperature just above the Peierls transition. For comparison, the spectra of 2D ($1T$-$TaSe_2$) and 3D (Rh) metals are reported at the same temperatures. All spectra are normalized at their maximum intensity.
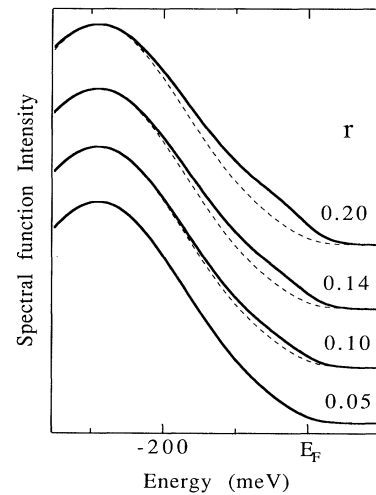

FIG. 2. Calculated spectral functions for several values of the spectral function at the Fermi level (a Gaussian shape was chosen for $\rho(E)$: $\rho(E) = \{\exp[-(E-E_0)/\Delta]^2 + A\}/(1+A)$ for different values of A). The effects of temperature and resolution are investigated as a function of $r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

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

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 $(TaSe_4)_2I$.

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 ($T_P \ll T_P^{MF}$). 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 $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ 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 ($Z \to 0$) 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].

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