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Spectroscopic observation of charge-density-wave-induced changes in the electronic structure of 2H-$TaSe_2$

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Abstract. We have performed a high-energy-resolution photoelectron spectroscopy investigation of the quasi-two-dimensional material 2H-$TaSe_2$. 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 $K_{0.3}MoO_3$, 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.

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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 $2\Delta(0)/k_BT_P$ 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-TaS_2, 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 $TaSe_2$, which is a characteristic 2D CDW material. Structural investigations have shown that 2H-$TaSe_2$ 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-$TaSe_2$. 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-$TaSe_2$ in the form of platelets of approximately $5\times5\times0.1$ mm^3 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 $\pm3°$, 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-$TaSe_2$, collected at various polar angles along the ΓK 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 0.5 ΓK, 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 $5d_{z^2}$ 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 ΓK. 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 ($\Delta E \sim 0.1$–0.2 eV).

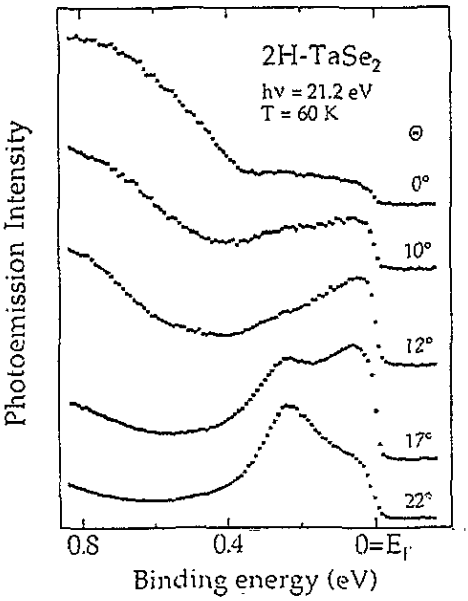

Figure 1. Photoelectron spectra of 2H-$TaSe_2$ collected at 60 K, in the commensurate CDW phase, along the ΓK direction. Θ is the polar emission angle, and the topmost spectrum corresponds to near-normal emission.

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

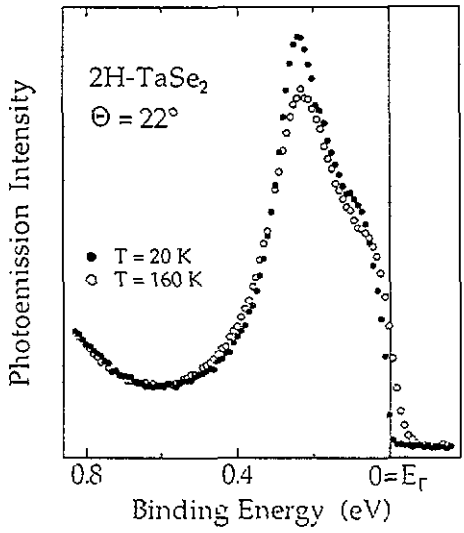

Figure 2. Photoelectron spectra collected in the absence (T = 160 K, open symbols) and in the presence (T = 20 K, full symbols) of the CDW. The polar angle $\Theta = 22°$ corresponds to a point in k-space close to 0.5 ΓK. The spectra have been normalized to the same integrated intensity.

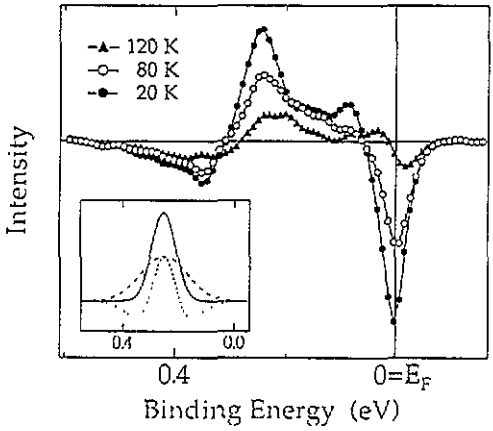

Figure 3. Difference spectra obtained by subtracting, at emission angle $\Theta = 22°$, the T = 160 K spectrum taken as a normal metal reference, from spectra collected at progressively lower temperatures, in the presence of a CDW. All spectra had been previously normalized to the same integrated intensity, 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.

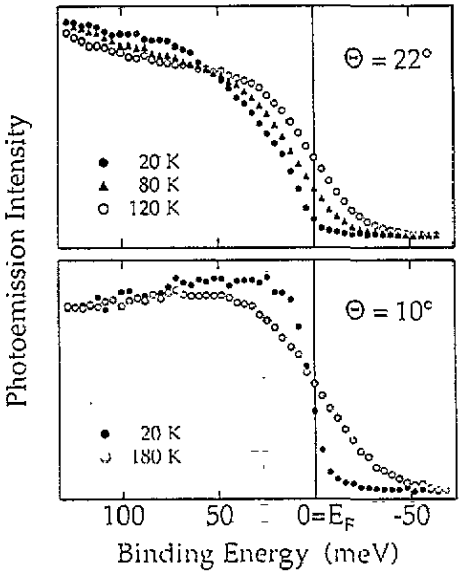

Figure 4. High-resolution spectra of 2H-$TaSe_2$. The spectra have been normalized to the same integrated intensity over an energy window of 1 eV, as in figure 2, but only the critical near-E_F region is shown. Top: $\Theta = 22°$; spectral intensity is progressively lost at E_F with decreasing temperature, and partially recovered around 50–100 meV. Bottom: $\Theta = 10°$; 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 $\theta = 10°$ and $\theta = 22°$, 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*

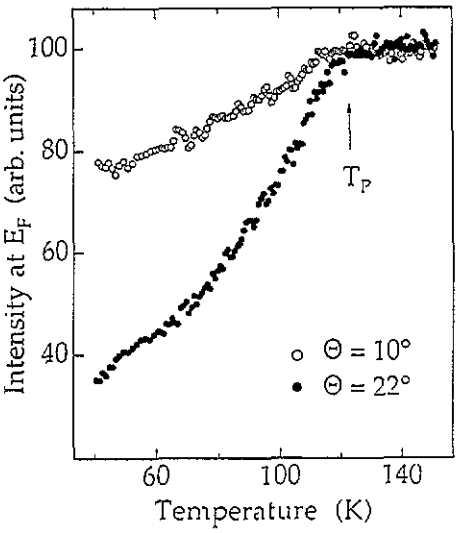

Figure 5. Temperature-dependent constant-energy curves (TCEs) representing the temperature dependence of the spectral intensity at the Fermi level I(E_F) for two emission angles: Θ = 10° (open symbols) and Θ = 22° (full symbols). For both angles a change of slope is observed around the CDW transition temperature T_P = 122 K. The intensity loss is larger at Θ = 22°, 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-$TaSe_2$. The intensity reduction is considerably more pronounced at 22°. At 40 K the intensity of the 22° TCE is reduced to ~30% of the room-temperature (RT) value, while the 10° TCE appears to saturate at ~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-TaS_2, 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-TaS_2 or 1T-$TaSe_2$, the transport properties of 2H-$TaSe_2$ vary smoothly through the lock-in transition, and with the very small associated specific heat anomaly (~10^{-3} times that of 1T-$TaSe_2$).

The above results allow us to address the issue of the opening of a CDW gap in 2H-$TaSe_2$. 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} manyfold 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-$TaSe_2$, 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 $2\Delta(0)/k_BT_P \sim 15$, 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-$TaSe_2$ 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 ΓK. 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.

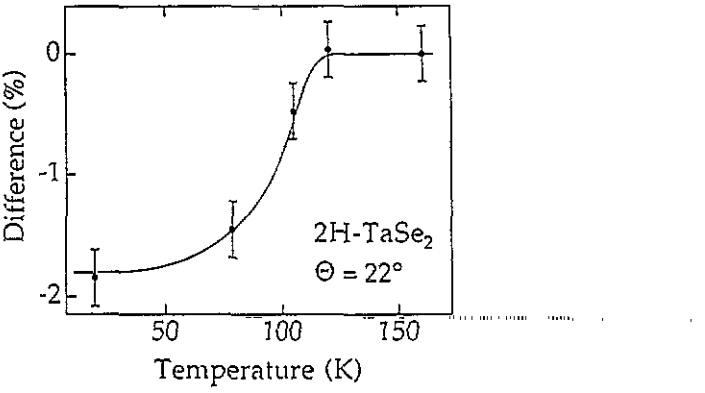

Figure 6. The data points represent the temperature dependence of the mean energy $\mu(T)$ of the photoelectron energy distribution curves of 2H-$TaSe_2$ at an emission angle $\Theta = 22°$ normalized with respect to the value μ(160 K). An energy window of 1 eV has been used. The variation of $\mu(T)$ 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 $\Theta = 22°$, 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 $\Theta = 10°$ 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-$TaSe_2$ 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-TaS_2) 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-$TaSe_2$, 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.

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