On the Phase Transitions in $1T$-TaS$_2$.

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Abstract. – The temperature-dependent electronic structure of $1T$-TaS$_2$ near the Fermi level, determined by means of angle-resolved photoemission with high-energy resolution of 35 meV, exhibits a distinct energy gap associated with a metal-semiconductor transition at 180 K on cooling, whereas on warming up the retransformation occurs in the electronic structure at 280 K. The complex phase transformation behaviour including the resistivity can be consistently explained between 400 K and 120 K. For the metal-semiconductor transition Mott-Hubbard localization of the d conduction electrons driven by critical interlayer coupling seems most likely.

The layered transition metal dichalcogenide $1T$-TaS$_2$ has been intensively investigated in the past few years because of the formation of strong charge density waves (CDWs) [1, 2] and electronic localization at low temperatures [3]. $1T$-TaS$_2$ is known to exhibit three main CDW phases well known from electron and X-ray diffraction: the low-temperature commensurate CDW phase (CCDW) below about 180 K the high-temperature incommensurate phase (ICDW) above 350 K, and in between the nearly commensurate phase (NCCDW) present at room temperature. The appearance of the NCCDW phase and the peculiar temperature behaviour of the conductivity above and below the NCCDW-CCDW phase transition account for the extraordinary physical properties of $1T$-TaS$_2$ in comparison with other transition metal dichalcogenides. These result from the possibility of a domainlike CDW structure with discommensurations in the NCCDW phase [4, 5], eliminating all of the Fermi surface with decreasing temperature, and/or from the localization being of collective nature (Mott-Hubbard localization) or caused by disorder (Anderson localization) [3, 6-8]. Recently, the situation became even more complex by the observation of an additional phase transition at about 280 K during the warming-up cycle, accompanied by a new, so-called T phase between 220 K and 280 K [9-11].

Angle-resolved photoemission with high resolution in energy and angle is known to be a powerful tool for studying the electronic structure just below the Fermi level, E_{F} [12-14].

Recent photoemission measurements of $1T$-TaS$_2$ have shown that the commensurate CDW phase is semiconducting due to a rearrangement of the electronic structure in the vicinity of E_{F} [14-16]. This was concluded from a comparison of spectra taken at room

temperature and below 180 K. In this letter we report on high-resolution angle-resolved photoemission data ($\Delta E = 35$ meV), showing the full temperature dependence of the electronic structure of $1T$-TaS_2 in the entire range between 400 K and 120 K, and its relation to the resistivity.

The changes of the density of states at E_F explain directly the temperature dependence of the resistivity in the NC phase which is determined by a continuous reduction of the Fermi surface. At the NC-C phase transition, this continuous CDW effect is convoluted by an additional effect localizing simultaneously the d conduction electrons and opening an energy gap. In the C phase the entire crystal is in a semiconducting gap state. During warming-up the crystals exhibit the well-known resistivity drop at 220 K, whereas from the photo-emission spectra the localization gap is still present and unchanged up to 280 K. These, at first view, contradictory properties correlate with a peculiar conductivity behaviour in the T phase of $1T$-TaS_2.

Single crystals of $1T$-TaS_2 were prepared from the elements by iodine vapour transport in closed quartz tubes with an excess of chalcogen (3 mg/cm^3) within a temperature gradient of 860 °C to 760 °C. After 40 days, the tubes were rapidly quenched in cold water to ensure retaining of the $1T$ phase. The structure and quality of the samples were controlled by standard X-ray techniques and by low-energy electron diffraction (LEED), and by measuring the temperature-dependent electrical conductivity, applying the methods of van der Pauw and Schnabel [17].

The crystals were cleaved in ultra-high vacuum of about 10^{-10} mbar and cooled by use of a helium evaporation refrigerator. During the measurement of a spectrum the temperature was held constant within ± 5 degrees. The photoemission spectra were taken with He I resonance radiation ($\hbar\omega = 21.23$ eV) and synchrotron radiation from the DORIS II storage ring at the Hamburger Synchrotronstrahlungs-Laboratorium, HASYLAB. The electrons were detected, using a 180° spherical analyser mounted on a goniometer (improved LEYBOLD-HERAEUS 3 DARES). An overall energy resolution of 35 meV was chosen for the He I and 70 meV for the synchrotron radiation spectra together with an angle resolution of $\pm 0.5°$.

A series of energy distribution curves (EDCs) near E_F is shown in fig. 1a), taken at normal emission ($\vartheta = 0°$) for various temperatures during cooling. At least, four features (assigned A-D) are visible in the spectra. Peak D at about 1.3 eV binding energy is associated with the uppermost S-$3p$ valence band which is found to differ from band structure calculations by about 1 eV [16]. The p-valence band maximum as well as the entire p-valence band is only weakly affected by the CDW formation [16]. Below 1 eV binding energy, at room temperature a broad and less structured band is visible up to the Fermi level, which groups into distinct emission maxima (A-C) at low temperatures. This is associated with the Ta-$5d$ conduction band cut at E_F. According to band structure calculations for the normal phase of $1T$-TaS_2 [18, 19] (above about 540 K), the d band should be located at Γ well above E_F. At 300 K it becomes visible due to the fact that the crystal is already in the NCCDW phase. It is argued that this phase consists of a domainlike structure of locked-in regions separated by line defects (discommensurations), across which the CDW phase changes rapidly [4, 5]. In the C phase the manifold of the CDW-induced features below E_F can be understood by a folding-down procedure of the d band, according to the new smaller Brillouin zone including the atomic displacements of the periodic lattice distortion [14].

With decreasing temperature, the CDW-induced structures become more distinct and show only weak energy shifts down to about 200 K. Between 180 K and 160 K, however, the energies shift abruptly (see A and C) and simultaneously a prominent peak A is showing up. At E_F, the emission decreases to zero (in fig. 1 for the Γ point), showing the opening of an
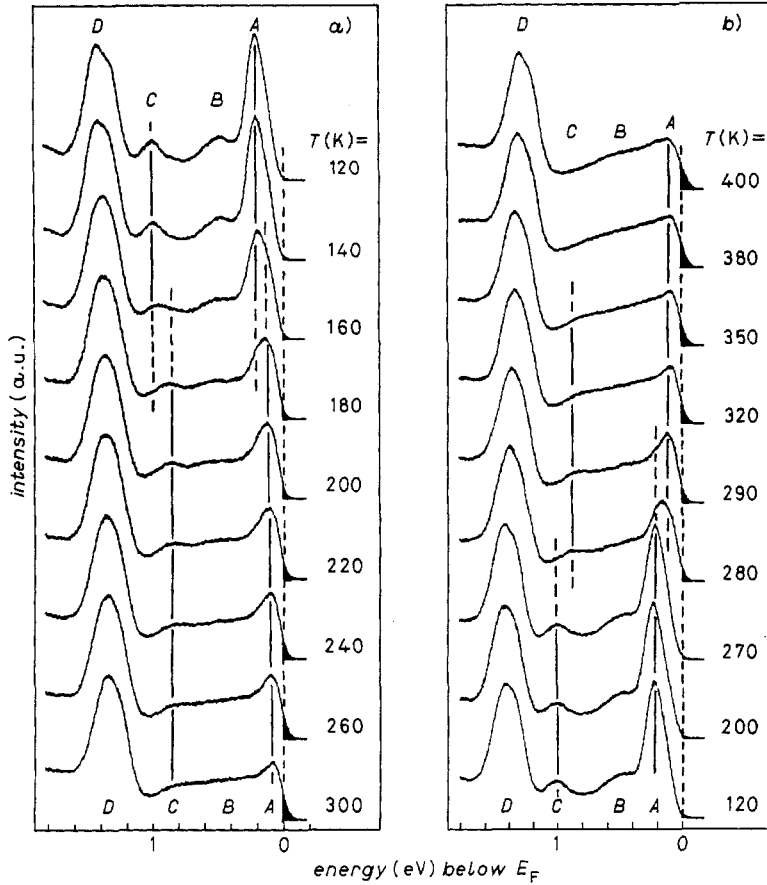
Fig. 1. – Temperature-dependent energy distribution curves taken at normal emission ($\vartheta = 0°$) with He I radiation during a cooling cycle (left) and a warming-up cycle (right). The spectra are normalized with respect to the emission of the p-valence band maximum (peak D), which is only weakly affected by the CDW formation [16]. Energy resolution 35 meV; the temperatures were stable within ± 5 degrees for each spectrum. The assignments are given in the text.

energy gap. Thus, during cooling a transition from a metallic to a semiconducting state is found in the electronic structure at about 180 K. Below about 160 K, the intensities as well as the energies of peaks A-C remain essentially unchanged.

In principle, the electronic structure near E_F behaves in a reverse way in the warming-up cycle, shown in fig. 1b).

However, the retransformation from the semiconducting gap state to the metallic state with closing of the gap occurs at about 280 K. In the temperature regime, 120 K $<$ $< T < 270$ K, one observes no essential changes in the spectra. This behaviour was observed also at other points of the Brillouin zone and was verified using different samples.

The observations in the electronic structure during the cooling cycle seem to be in qualitative accordance with that, found in transport measurements, whereas during warming-up these quantities behave extremely differently. This is illustrated in fig. 2 by comparing the temperature-dependent resistivity of our samples which agrees with previous results [6] (with the exception of the transition at 285 K), with the energy difference between peak A (above T_c the emission maximum A) and the Fermi level. This difference is taken as only a rough measure for what happens in the entire electronic
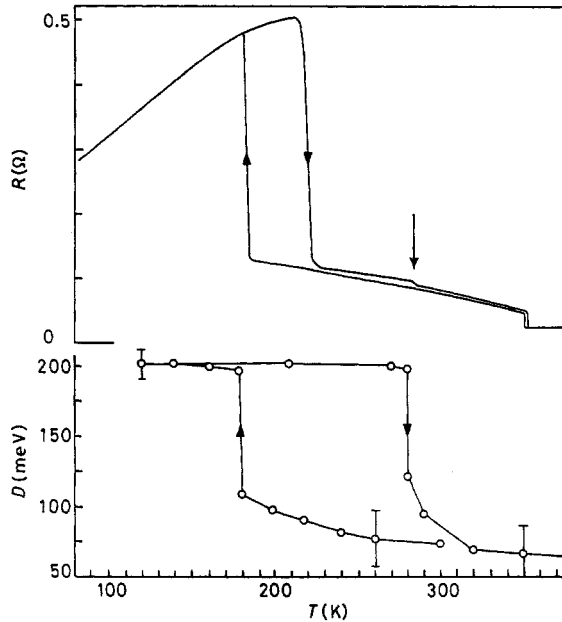
Fig. 2. – Top: temperature-dependent resistivity of our samples with current parallel to the layers. The arrow indicates the new T to NCCDW phase transition at 285 K in accordance with ref. [9]. The feature at 350 K is due to the NC-IC phase transition. Bottom: energy difference, D, between peak A and the Fermi level of fig. 1. A similar temperature dependence has been derived from the intensity or heights of peak A. The slopes directly below and above the phase transitions result from the fact that the energy positions are determined at the centre of gravity of peak A. At 180 K and 280 K the energy position of both resolved structures are shown (see text).

structure during the phase transitions. But obviously it nicely reflects the main differences between transport and electronic structure.

In order to gain new insight into the complex temperature behaviour of 1T-TaS$_2$ the measured changes should be analysed in more detail. Starting with the cooling cycle, for the NCCDW phase, 350 K $\geqslant T \geqslant$ 180 K, the resistivity $R(T)$ increases weakly with decreasing T. This, for a metal, unusual temperature behaviour can be explained by the weak, but distinct reduction of emission at E_F (see fig. 1a)). This continuous decrease of emission at E_F (which is related to approximately the density of states (DOS) [15, 16]) observable down to about 180 K provides clear evidence that, with reduced temperature, in the NC phase an increasing portion of the Fermi surface is lost due to a growing CDW gap. One possible explanation gives the domain model proposed for the microstructure of the NC phase [4, 5, 20]. It is assumed that with decreasing temperature the locked-in domain grow destroying an increasing part of the Fermi surface. Thus, regarding the magnitude of the resistivity, the NC phase is metallic and its unusual temperature dependence can be understood by the spatially averaged changes of the DOS (E_F) [1].

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[1] The energy shifts of maximum A are not due to simple temperature effects which are expected to show a linear temperature dependence down to the Debye temperature, finally decreasing to zero for $T \to 0$. This can be directly deduced from our measurements shown in fig. 1b). Between 400 K and 350 K (temperature difference of 50 K) the DOS (E_F) exhibits no changes, whereas between 350 K and 290 K (temperature difference of 60 K) the changes are remarkable. This demonstrates that simple temperature changes in TaS$_2$ are much smaller and can be neglected.

The transition observed on cooling in transport as well as photoemission at 180 K, is associated with a metal-semiconductor transition accompanied by the opening of an energy gap. Regarding the 180 K and 160 K spectra of fig. 1*a*) in detail, besides the appearance of a prominent low temperature peak *A* one observes also emission at E_F (see the distinct broadening and asymmetric shape, which is also observable at the retransformation temperature around 280 K). Thus, our data reveal strong evidence that besides CDW effects an additional mechanism sets in at about 180 K, being at last responsible for the localization of the conduction electrons, the opening of the energy gap, and the first-order transition observed in $R(T)$. Otherwise, it is less understandable why the continuous CDW formation in the NC phase, which is followed over a wide temperature range between 300 K and 180 K, should show a sudden enhancement within less than 20 degrees. Following the arguments of Fazekas and Tosatti [3], a first-order transition with opening of the gap is likely due to Mott-Hubbard localization.

For $T \lesssim 180$ K the entire crystal is in a gap state. The vanishing DOS (E_F), due to the induced energy gap, is observed along all main high-symmetry directions parallel to the sample surface as well as in $\Gamma A(k_\perp)$ direction [16]. The uppermost *d* band is located by about 200 meV below E_F. Because of the fact that semiconducting transition metal dichalcogenides are usually *n*-doped, due to the tendency of self-intercalation by the transition metal, the full localization gap is expected to be not much larger. The weak resistivity decrease down to 80 K is obviously neither caused by a temperature-dependent density of states nor by impurity carriers (decrease with decreasing T), but must be attributed to a temperature dependence of the electron-phonon scattering. The uppermost *d* band (peak *A*) is found to be strongly localized for $T < T_c$ and shows no measurable dispersion with $k_\perp$ and $k_\parallel$ (see ref. [16]). Interestingly, it reveals a long tail up to E_F. Such a tail of the Hubbard subband is proposed for 1*T*-TaS$_2$ by Fazekas and Tosatti [3]. Anderson localization (proposed by Di Salvo and Graebner [6]) in the overlapping tails could then be a possible explanation for $R(T)$ at very low temperatures.

During warming-up, re-transition in the electronic structure occurs at (280 ± 5) K. This is in remarkable variance with the strong resistivity decrease already at 220 K but, interestingly, it coincides with the weak drop at 285 K due to the transition from the new *T* phase to the NC phase [9-11]. Again, in the 280 K and 290 K spectra peak *A* is distinctly broadened. Between about 280 K and 350 K (NC phase) the emission at E_F shows the same temperature dependence as discussed above. It should be noted here that the difference between the photoemission and transport measurement cannot be simply explained by their different surface sensitivity. Helium beam diffraction experiments and our LEED studies clearly demonstrated that already the first surface layer reveals the typical CDW effects [21]. In addition, both the coincidence between the transport and photoemission results at the electronic localization temperature (180 K) as well as the fact that the delocalization is found exactly at the transition from the so-called *T* phase to the NC phase at 280 K ask for a better standing explanation.

In attempting to explain the apparently different behaviour of resistivity compared with that of the electronic structure during warming, one should realize that, according to structure investigations, the dominating changes occur in the *c*-axis and stacking sequence. The *a*-axis compression of the *C* phase is found to be completely removed in the *T* phase and there is no change at 280 K [9]. In contrast, the expansion of the *c*-axis in the *C*-phase (perpendicular to the layers) is not completely removed in the *T* phase and a strong additional reduction is observed at 280 K [9]. The effects are much stronger in *c* direction than within the layers. From these observations the following conclusions may be drawn: the localization of *d* conduction electrons associated with an apparent gap in the electronic structure in 1*T*-TaS$_2$ depends on the critical amount of expansion of the *c*-axis. Thus, the

changes in the electronic interlayer coupling are expected to drive the Mott localization. In the entire T phase, interlayer coupling apparently remains sufficiently weak and the maintenance of about one-third of the c-axis expansion seems to determine the localization of d electrons (d_z orbitals). Since, on the other hand, the carrier density remains small (from impurities plus a possible amount from overlapping Hubbard subbands), the lowered resistivity in the T phase points to strongly reduced electron-phonon interaction, compensating totally the small DOS at E_F.

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