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Charge density waves in $1T$-TaS_2: an angle-resolved photoemission study

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Abstract

The transition metal dichalcogenide $1T$-TaS_2 is a layered material exhibiting charge density waves. Based on angle-resolved photoemission experiments mapping spectral weight at the Fermi surface and density functional theory calculations we discuss possible mechanisms involved with the creation of charge density waves. At first the flat parts of the elliptically shaped Fermi surface appear to play an important role via Fermi surface nesting. A closer analysis of the charge density wave induced new Brillouin zones and the possible energy balance between elastic deformation energy and electronic energy points to a more complicated scenario.

Keywords: Charge density waves; $1T$-TaS_2; Angle-resolved photoemission

Low-dimensional systems have particularly attracted interest through the discovery of high-temperature superconductors (HTc's). Many angle-resolved photoemission (ARPES) experiments have been conducted on such materials. With the improvement of the energy and momentum resolution on the experimental side, the interpretation has become very sophisticated and many unusual signatures in the spectral function have been found. Among them is the signature for the opening of a pseudogap, for a sort of collective mode (of unknown origin) and, very recently, for a spontaneous symmetry breaking of time reversal symmetry [1]. Also, stripes, i.e., doped holes that are self-organized, a sort of density waves, appear to play an important role [2]. Nevertheless, the final word about the mechanism behind HTc is not spoken. It is therefore important to relate these findings and apply the

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same sophistication in the analysis to other layered materials.

Layered transition metal dichalcogenides are a class of quasi-two-dimensional (2D) materials. Many exhibit charge density waves (CDWs) and even become superconducting at low temperatures. Indeed, there is renewed and growing activity on these materials [3,4]. $1T$-TaS_2 is such a material exhibiting CDWs and a quite complex phase diagram as a function of temperature [5,6]. The studies on such materials serve a better understanding of the mechanisms at work in low dimensional electron systems in general.

In the present article, we discuss the occurrence of CDWs in $1T$-TaS_2. From ARPES and density functional theory (DFT) calculations we analyze the shape of the Fermi surface (FS) with respect to possible nesting and the arrangement of the new CDW-induced Brillouin zones (BZs). We consider different possible ingredients in the energy balance governing the occurrence of the CDWs.

ARPES measurements have been done at room temperature (RT) in a modified VG ESCALAB Mk II spectrometer using monochromatized He Iα ($h\nu = 21.2\,\mathrm{eV}$) photons [7]. The sequential motorized sample rotation has been outlined elsewhere [8]. The energy and angular resolution was 20 meV and $\pm 0.5^\circ$, respectively. Pure $1T$-TaS_2 samples were prepared by vapor transport [9,10] and cleaved in situ at pressures in the lower 10^{-10} mbar region. The accurate position of the Fermi level (E_F) has been determined on a polycrystalline copper sample. Cleanness and quality have been checked by X-ray photoelectron spectroscopy and by low energy electron diffraction (LEED), respectively. Well-defined LEED superspots confirmed the presence of the CDW-induced reconstruction. X-ray photoelectron diffraction was used to determine the sample orientation in situ with an accuracy of better than 0.5°.

Band structure calculations have been performed using the WIEN package implementing the FLAPW method within the framework of DFT [11]. For the exchange-correlation potential the generalized gradient approximation was used [12]. We considered the photoemission process in assuming a free electron final state without the introduction of any matrix elements effects [13].

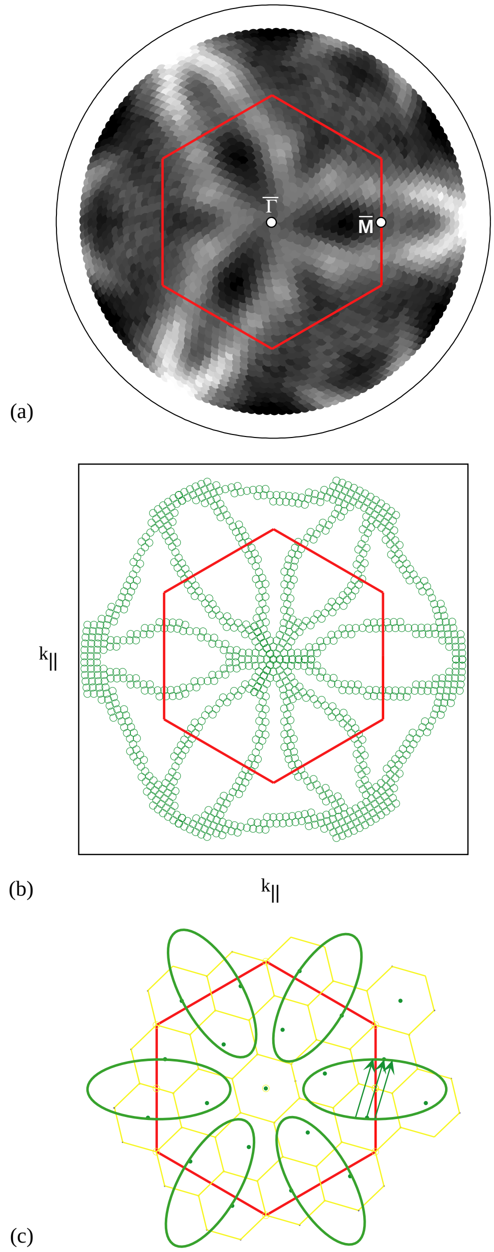

Fig. 1. (a) Experimental Fermi energy intensity map taken with HeI radiation at room temperature, plotted linearly in $k_{||}$; high intensity is in white; center and outer circle correspond to normal and 90° emission, respectively; the hexagon represents the normal state BZ. (b) Corresponding density functional theory calculated map for the normal state. (c) Superposition of normal- and CDW-state BZs, together with a sketch of the FS contours; possible nesting vectors are plotted (see text).

Fig. 1(a) displays the result of an E_F mapping experiment at RT. At RT the CDW is well established as seen in LEED (not shown) and consists of commensurate CDW domains of approximately 70 Å in diameter [14,15] with incommensurate regions in between. The RT phase is called the quasi-commensurate phase in contrast to the commensurate ("C") phase below 180 K where no incommensurate regions exist anymore. The first-order transition to the "C"-phase is accompanied by a jump in the resistivity of more than an order of magnitude (see e.g. Ref. [16]). $1T$-TaS_2 in its unreconstructed or normal state consists of hexagonal Ta planes sandwiched between sulfur atoms. In the ionic picture Ta[Xe]$4f^{14}5d^{3}6s^{2}$ gives four of its five electrons to the two sulfur (S[Ne]$3s^{2}3p^{4}$) atoms creating a system with one d-electron per unit cell. Indeed, band structure calculations for the normal state [16] display a single Ta d-band dispersing close to E_F. The calculation for the E_F scan (Fig. 1(b)) represents a cut through the FS and is in good agreement with the experiment (Fig. 1(a)). The BZ of the non-reconstructed structure is also drawn in Fig. 1(a). It is important to note that despite the presence of the CDW at RT, the experiment exhibits the symmetry of the normal state BZ, as is also evident from the good agreement of experiment (Fig. 1(a)) and normal state calculation (Fig. 1(b)). This observation has been discussed previously [16] and is a consequence of the spectral weight distribution, as measured by ARPES, remaining strongest along the bandstructure of the non-reconstructed phase [17]. The experiment only shows strong intensity for three of the six ellipses, a fact which has been attributed to the final state scattering of the outgoing photoelectron [18].

Another important point to notice is that the FS appears pseudogapped [19], i.e., the E_F map (Fig. 1(a)) does not actually represent the locations of quasi-particle peaks crossing E_F. As a matter of fact no clear crossing has been observed in ARPES data. A careful study of experimental data combined with bandstructure calculations including the lattice distortion concluded that the pseudogap can be explained by the splitting and backfolding of bands introduced by the new BZs [20].

Fig. 1(c) displays a sketch of the situation with both, the $(\sqrt{13}\times\sqrt{13})-R\,13.9^\circ$ reconstructed (small hexagons) and the un-reconstructed BZs plotted. We have an elliptically shaped normal state FS with evidence for nested parts along the flat parts of the ellipses (see arrows in Fig. 1(c)) [21]. The important question is what drives the CDW. Is it the classical Peierls transition as in 1D? If this is the case, what do we expect from a strongly nested quasi-1D FS? Fig. 2(a) displays the case of a strongly nested FS as indicated by arrows connecting nested (parallel) parts of the FS contour. One electron per atom (and unit cell) of chains of atoms with distance a is assumed. Therefore the Fermi vector $k_F = \pi/(2a)$ since the quasi-1D band is half filled. The BZ boundary is located at $2k_F = \pi/a$ (Fig. 2(a)). If the lattice is distorted in order to double the periodicity, i.e., to introduce a CDW with wave length $2a$, elastic energy has to be paid. At the same time a doubling of the periodicity in real space results in reducing the dimension of the BZ by a factor of two. The consequence is that the BZ boundary is now located at $k_F = \pi/(2a)$ and the band is full (two electrons per unit cell, due to the doubling of the periodicity) with the opening of a gap at the new BZ boundary at $\pi/(2a)$ and a corresponding gain of electronic energy. Therefore, what we expect from a strongly nested FS is that its nested parts disappear (due to the gap opening) with the occurrence of the CDW (Fig. 2(b)).

However, looking carefully at Fig. 1, this is not what we observe. The boundaries of the new BZs are not along the expected nested parts of the normal state FS (indicated by arrows in Fig. 1(c)) indicating that we do not have a quasi-1D system.

It is necessary to explore the ingredients of the energy balance of the transition [22]. The energy balance of elastic energy paid and electronic energy gained is expressed in terms of the susceptibility $\chi(\vec{q})$ (polarization function or Lindhard function), the elastic spring constant of the lattice, c, and the magnitude of the electron–lattice interactions g, to be $-\Delta^2_{CDW}(N\chi(\vec{q})-(c/2g^2))$, where $-\Delta_{CDW}$ is half of the gap size and $\vec{q}$ the wave vector of the lattice distortion [22]. The

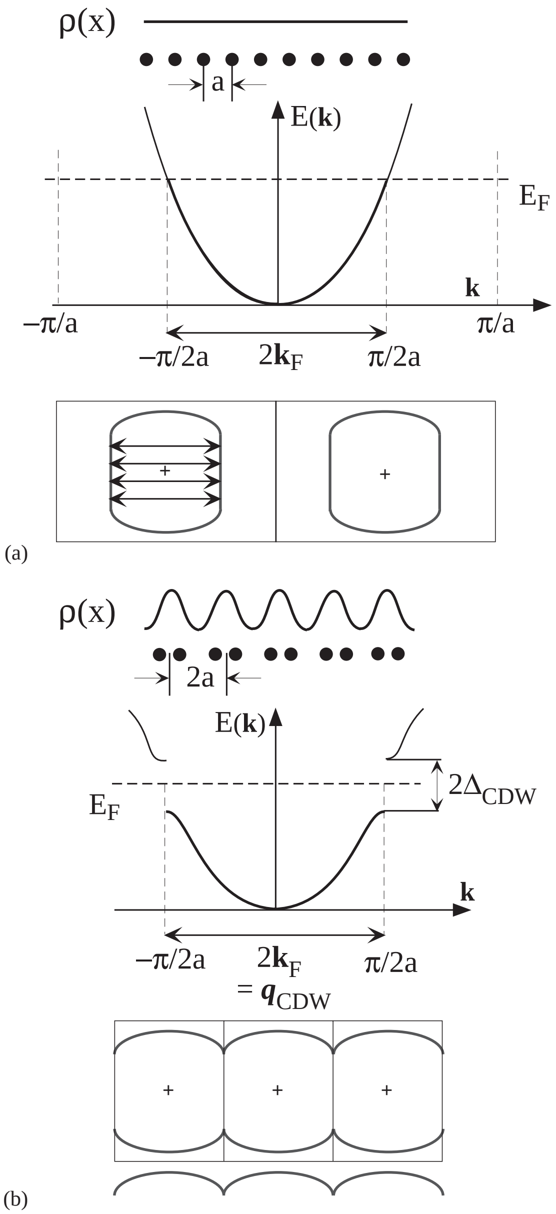

Fig. 2. Sketch of the behavior of the bandstructure and Fermi surface contours of a quasi-1D system with one electron per unit cell (see text).

susceptibility (appearing in the electronic energy part) connects the charge response, $\rho(\vec{q})$, to a perturbation $V(\vec{q})$ (introduced by phonons) via $\rho(\vec{q}) = -\chi(\vec{q})V(\vec{q})$. The susceptibility can be written as

$$\chi(\vec{q}) = \frac{1}{N}\sum_{\vec{k}} \frac{f_{\vec{k}+\vec{q}} - f_{\vec{k}}}{E_{\vec{k}} - E_{\vec{k}+\vec{q}}},$$

where f and E express the Fermi–Dirac function and the energy eigenvalues at the given $\vec{k}$-vector, respectively. It is clear that only occupied and empty states very close to E_F separated by a vector $\vec{q}$ contribute to the sum, which basically describes the FS nesting. This sum is strongly dependent on the dimensionality and it diverges in 1D [22]. It is also a diverging susceptibility, together with the electron–phonon coupling, which leads to a phonon softening, finally observed in the static lattice deformation induced by the CDW.

What is the role of the susceptibility in the case of $1T$-TaS_2? As seen from Fig. 1(c), it is not clear whether nesting is strong. A clear statement is not possible based on the present data since the system has not chosen to align the new BZs along potentially nested parts (flat parts of the ellipses) of the FS contour as expected for a quasi-1D system. However, from the above formula for the energy balance, we see that even for a moderate susceptibility it is possible to obtain a favorable energy balance if only the electron–phonon coupling is strong enough. The $(\sqrt{13} \times \sqrt{13}) - R\ 13.9^\circ$, reconstructed (large) unit cell is 13 times larger and contains 13 Ta and 26 sulfur atoms. Star-like arrangements develop around one central Ta atom with six nearest and six next nearest neighbors [15]. Realistic band-structure calculations [16] including the CDW-induced star-like lattice distortion show that the single Ta d-band of the normal state is split. In the calculation 7 sub-bands develop, six of them full and the seventh crossing E_F. The reconstructed unit cell contains 13 inequivalent Ta atoms with a total of 13 electrons assuming the ionic picture. In order to place these electrons (two per band), 6 full bands are needed and the seventh half full, crossing E_F. Therefore we can identify two avenues for the system to gain electronic energy. First, the introduction of many small new BZs results in the normal state FS contours to be cut into many pieces and many small gaps contribute to a lowering of electronic states. Second, the reconstruction (unit cell with 13 Ta atoms, 39 atoms in total) leads to a bandstructure where six of seven sub-bands are completely lowered below E_F, again indicative for a lower electronic energy in the CDW state. However, it is not possible to say whether these two observations represent the driving force for the CDW formation or are merely the consequence. Likewise, indications would be needed for an arbitrary system to determine whether it will or will not undergo an instability and what will be the symmetry. In this context, it is interesting to note that the CDW induces a star formation (including 13 Ta atoms) with weak overlap of electronic wavefunctions between the stars possibly being responsible for the localization-induced Mott transition [23]. One could think of these stars as small molecules being the consequence of a Jahn–Teller distortion at the origin of the CDW formation.

In summary, we have discussed CDW formation in $1T$-TaS_2 with respect to the energy balance governing the occurrence of the CDWs. The flat parts of the elliptically shaped FS at first appear to be susceptible for nesting as for a 1D peierls transition. A closer analysis based on the $(\sqrt{13} \times \sqrt{13}) - R\ 13.9^\circ$ symmetry of the CDW shows that this is not the case. Two main fingerprints pointing to a gain of electronic energy are identified, one due to many new, small BZs and one due to the creation of many sub-bands lying completely below E_F.

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