Broken Symmetries and Photoexcitation of 1T-TaS$_2$

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Abstract. Broken symmetries may originate from electron-electron or electron-phonon interaction. Here we present several spectroscopic methods to identify the nature of a correlated groundstate.

1. Introduction

Strong many-body interactions can qualitatively modify the structure of solids, leading to broken-symmetry phases with charge, spin, or orbital order. A notable example of broken symmetry is the softening of a phonon branch due to the strong coupling of a lattice mode with the conducting electrons. The resulting distortion of the nuclear structure comes along with a modulation of the charge density referred to as the charge density wave (CDW). Based on the topology of the electronic structure, the CDW state may lead to an insulating groundstate or preserve portions of the original Fermi Surface. Moreover, unexpected groundstates may emerge from the interplay of the CDW with electronic correlations. Recently, the essential role of the Coulomb repulsion has been demonstrated in the case of VO$_2$ and in the transition metal dichalcogenides. This chapter will describe the Metal-Insulator (MI) transition observed at the surface of the two parent compounds 1T-TaS$_2$ [1] and 1T-TaSe$_2$ [2]. Several spectroscopic techniques are employed in order to identify the nature of the insulating state as well as the stabilization mechanism. Interestingly, the investigation of non-equilibrium states by ultrafast spectroscopy offers a novel and powerful tool to disentangle the electron-electron from electron-phonon interaction.

1T-TaS$_2$ and 1T-TaSe$_2$ consist of strongly bound X-Ta-X (X=S,Se) layers that are weakly coupled by interplane interaction. Such a layered structure determines a marked anisotropy of the electrical resistivity and of the mechanical properties of the material. X-ray scattering [3] and scanning tunneling microscopy (STM) [4] show that 1T-TaS$_2$ displays a pronounced lattice modulation already at room temperature. The strong coupling between valence electrons and phonons periodically distorts the lattice, modifying the spatial distribution of the charge density. In real space, the local distortion leads to metallic clusters containing 13 Ta atoms each. Extended Hückel calculations [5] suggest that the CDW splits the Ta $d$ conduction band into subbands which contain a total of 13 electrons per unit cell. Two subbands, carrying 6 electrons each, are filled and lie below the Fermi level. The Fermi surface is formed by a half-filled subband carrying the 13th electron. The opening of a correlation gap in this subband is responsible for the Metal insulator transition observed in bulk of 1T-TaS$_2$ ($T_c$=180 K) [1] and at the surface of 1T-TaSe$_2$ ($T_c$=260 K) [2].
2. Interplay of Charge Density Wave and electronic correlations

Many physical properties indirectly reflect the dramatic rearrangement of the electronic structure at the transition. Photoelectron spectroscopy, which probes the single-particle spectral function, can provide a direct view of such changes. Figure 1(a) and (b) display the Angle resolved Photoelectron Spectroscopy (ARPES) intensity map of 1T-TaS$_2$ in the metallic and insulating phase, respectively. A broad Ta $d$ band disperses upwards from the zone boundary and crosses the Fermi level roughly at $k_F = 0.25 \Gamma M$. Due to the CDW distortion, the whole band structure should be folded back into the reduced Brillouin zone of the $\sqrt{13} \times \sqrt{13}$ reconstructed structure. However, the spectral weight distribution in reciprocal space is controlled not only by symmetry, but also by the strength of the scattering potential [6]. Therefore, the main band still carries most of the weight in the CDW phase, and only little intensity is transferred to the superlattice or “shadow” bands. As shown by Figure 1(b), the CDW potential splits the occupied part of the Ta $d$ band into subbands at 1 eV, 0.5 eV, and around $E_F$. The latter is susceptible to electronic localization due to the strong Coulomb interaction between electrons. Below the transition temperature, the electronic correlations open and an electronic gap, and a lower Hubbard band emerge at 0.2 eV [7].

Even though the M-I transition is consistent with the Mott scenario, the first order change of CDW symmetry lattice hinder the description of the transition in terms of simple model parameters. Interestingly, such complications do not take place in the parent compound 1T-TaSe$_2$.

In 1T-TaSe$_2$ the CDW is commensurate up to 500 K. Although the lattice symmetry is preserved, the photoelectron spectra of Fig. 2(a) show the occurrence of a M-I transition at $T_c = 260$ K [2]. This M-I transition occurs only at the surface, while the bulk 1T-TaSe$_2$ remains metallic. We ascribe the occurrence of an insulating surface to the combined effect of CDW distortion and Mott localization. The local CDW amplitude can be monitored through the energy slitting of the core levels Ta $4f^{7/2}$. Figure 2(b) shows two spectral components originating from Ta atoms with different valence [8]. Their energy splitting is proportional to the CDW amplitude and vanishes in the undistorted phase. As shown by the spectra, the splitting is 40 meV (5%) larger in the insulating phase (70 K) than in the metallic one (300 K). Such an increase of CDW reduces the electronic bandwidth. Below the critical value of $T_c = 260$ K, the energy that is necessary for the double occupation of one site becomes larger than the bandwidth. Therefore, the metallic state is no longer stable and electrons localize into the Mott insulating phase.
3. Temporal disentanglement of many body interactions

In the following, we investigate the response of 1T-TaS$_2$ to an ultrafast optical perturbation. Thereby, an intense pulse in the infrared spectral range promotes the system into a highly excited state, whereas an ultraviolet probe pulse emits photoelectrons after a variable time delay. Figure 3 shows a photoelectron intensity map acquired in 1T-TaS$_2$ at 30 K. Large oscillations of the electronic spectra start abruptly at zero delay and endure for many picoseconds [9]. The period of these oscillations corresponds closely to the amplitude mode of the CDW [10]. In real space, this excitation results into the coherent motion of the Ta atoms toward the undistorted lattice. As a consequence, the release of elastic energy leads to the electronic shift the Hubbard peak towards the Fermi level. Subsequently the nuclear structure breathes until a damping force brings the system back to equilibrium.

FIG. 3 Photoelectron intensity map measured in the MI phase (T=30 K) as a function of pump-probe delay and binding energy.

If the Mott insulator is in equilibrium at 30 K, the spectral function displays a Lower Hubbard band (LHB) at 0.21 eV and vanishing density of electronic states at the Fermi level. Just after photoexcitation, the energy density deposited in the electronic system is too large for the existence of a Mott insulator. Figure 4(a) shows the photo-induced transfer of spectral weight from the LHB to the Fermi level [9]. The electronic gap is partially filled by transient electronic states and recovers along with the energy relaxation of the hot electrons. Such midgap states must have very weak coupling to...
the CDW mode, otherwise they would lead to efficient damping of the CDW oscillations. The LHB intensity $I_H$ in Fig. 4(b) is an empirical measure for the transfer of spectral weight toward the pseudogap. The instantaneous decrease and subsequent recovery of $I_H$ can be described by an exponential decay with time constant of 680 fs. It follows that the MI gap collapses on a timescale much shorter than the pump-probe cross-correlation and monotonically recovers with subpicosecond timescale. This finding is consistent with the revival of a MI groundstate whereas it is not consistent with the dynamics of a Peierls insulator.

FIG. 4 Photoelectron spectra of the photoexcited insulator acquired at several pump-probe delays. (b) Intensity of the Lower Hubbard Band as a function of pump–probe delay.

In conclusion, we show that CDW and electronic correlation are both essential for the correct understanding of 1T-TaX$_2$. Moreover the response of electronic states to an ultrafast optical perturbation clearly distinguishes the effects of the CDW and correlations on the band structure.

4. Methods

We performed high-resolution ARPES measurements in Lausanne and at the Synchrotron Radiation Center, University of Wisconsin. The energy and momentum resolution were $\Delta E = 10$ meV and $\Delta k = 0.02$ Å$^{-1}$, and the Fermi level location was determined with an accuracy of 1 meV by measuring the metallic edge of a polycrystalline gold reference. Single crystal samples grown by the usual iodine transport technique were characterized by Laue diffraction and resistivity measurements, which confirmed the assignment to the 1T polytype. They were mounted on the tip of a closedcycle refrigerator and cleaved at a base pressure of $10^{-11}$ torr. We did not observe any sign of surface degradation or contamination over a typical 8 h run. Time-resolved ARPES have been performed at the Freie Universität Berlin. A regenerative Ti:sapphire amplifier provides pulses with center photon energy of 1.5 eV, duration of 50 fs and repetition rate of 200 KHz. Part of the amplifier output is frequency doubled in a BaB$_2$O$_4$ (BBO) crystal and compressed by prisms. The resulting 3 eV beam is
focused on a second BBO crystal in order to generate 6 eV pulses. After traveling through a second prism compressor, these ultraviolet pulses have durations of 80 fs. Both the 1.5 and 6 eV beams are focused on the sample almost collinearly, with focal diameter of 200 and 80 μm, respectively. If not explicitly stated, the data refer to an absorbed pump fluence of $= 135 \mu$J cm$^{-2}$. A delay stage varies the optical path of the 6 eV probe pulse with respect to the 1.5 eV pump pulse. Both beams propagate with an incident angle of 45° with respect to the surface normal and are p-polarized with respect to the plane of incidence. Photoelectrons emitted along the surface normal were detected by a time of flight (TOF) spectrometer with energy resolution of 10 meV and acceptance angle of 3.5°.

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