Switching between macroscopic charge ordered quantum states by charge injection in 1T-TaS$_2$

Jan Gospodarič
Supervised by: prof. dr. Dragan Mihailovič
March 10, 2015

Abstract

The purpose of this paper is to demonstrate ultrafast switching between macroscopic charge-ordered quantum states at high temperatures induced by charge injection, an experiment done at Jozef Stefan Institute. First we point out instabilities of metals to formation of charge density waves. We use this knowledge to analyse phase diagram of 1T-TaS$_2$, which is the sample used in the experiment. This helps us understand the experiment theoretically. We see that this mechanism could be easily integrated in future faster non-volatile memory devices.
## CONTENTS

1 Introduction 3

2 CDW 3
   2.1 Electron gas .......................................................... 3
   2.2 CDW in 3D ............................................................. 5

3 IT-Tantalum (IV) sulfide 5
   3.1 General properties .................................................. 5
   3.2 Phase diagram ........................................................ 6

4 Experiment 8

5 Theoretical view of the experiment 8

6 Conclusion 10
1 Introduction

The search for new computing technologies is driven by the continuing demand for improved memory performance. Current electronics functionality of non-volatile memory devices is either based on manipulating local concentrations of electrons in transistors (flash), or using switching between degenerate ground states in magnetic and ferromagnetic materials (hard disk drive). But research has shown that resistive random-access memory (RRAM) is most likely to succeed in the race to develop a new, more scalable, high capacity, high performance and reliable memory device. One type of RRAM is offered by structural phase transitions switching between metallic and insulating phases by the motions of ions, but their speed is limited to slow formation of states. A better possibility might be quantum electronic systems. Microscopic quantum electronic system involve decoherence because of environmental influence, but on the other hand such macroscopic system do not. [1][2]. In this presentation I will discuss the possibility of using macroscopic quantum systems in memory devices.

Instabilities of some crystals to formation of charge density wave (CDW), due to anisotropy of crystal structures, will be introduced. Using this knowledge, we will try to understand the formation of multiple CDW states in 1T-TaS$_2$ and after that ultrafast non-thermal switching between different metastable electronically ordered states by pulsed electrical charge injection in 1T-TaS$_2$, which was done in Jozef Stefan institute by the supervision of prof. dr. Dragan Mihailović. One state involves a CDW commensurate with the underlying lattice and shows insulating behaviour. The other "hidden" nearly-commensurate metal state can be achieved by non-equilibrium conditions. A theoretical explanation of this mechanism, which is not yet fully developed, will be introduced. This fast 30 ps switching mechanism with sharp switching thresholds suggests new opportunities for the use of macroscopic quantum states in electronics, especially for an ultrafast non-volatile quantum charge-order resistive random access memory (QCOR-RAM).[1] This paper contains some similarities with the seminar Hidden states transitions from the author Jan Ravnik, which describes switching between states with laser photo excitation.

2 CDW

2.1 Electron Gas

The Fermi surface of a 1D electron gas is simple, it consist of two points, $+k_f$ and $-k_f$. The dispersion relation for a 1D free electron gas is $\epsilon_k = \hbar^2 k^2/2m$. We will note Fermi energy as $\epsilon_f = \hbar^2 k_f^2/2m_e$, where $m_e$ is the mass of an electron, $k_f$ is the Fermi wavevector, which can be noted as $k_f = N_0 \pi/2L = N_e \pi$, where $N_o$ is the total number of electrons, $L$ is the length of the 1D chain and $N_e$ is the number of electrons per unit length and per spin direction. The response of an electronic gas to a time independent potential $\phi(\vec{r}) = \int_q \phi(\vec{q}) e^{i\vec{q}\cdot\vec{r}} d\vec{q}$ is calculated with the framework of linear response theory. The rearrangement of the charge density, expressed in terms of an induced charge $\rho^{ind}(\vec{q}) = \int_q \rho^{ind}(\vec{q}) e^{i\vec{q}\cdot\vec{r}} d\vec{q}$ is related to $\phi(\vec{r})$ through $\rho^{ind}(\vec{q}) = \chi(\vec{q}) \phi(\vec{q})$, where $\chi(\vec{q})$, the Lindhard response function[3], is given in $d$ dimensions by

$$\chi(\vec{q}) = \int_{k \leq k_f} \frac{d^d k}{(2\pi)^d} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}},$$

where $f_k = f(\epsilon_k)$ is the Fermi function. Evaluated susceptibility (Figure 2.1 a)) demonstrates that as you lower the dimension, the knee in the curve for three dimensions at $q = 2k_f$ becomes a kink in two dimensions and a singularity in one dimension. The most significant contribution to the integral comes from vectors that connect two Fermi surfaces shown in figure 2.1 b).[4] In 1D there is one vector that connects all points of the Fermi surface, which is the reason for the singularity. The peak in one-
dimension is also known as a Kohn anomaly.\cite{5} It shows that an external perturbation lead to a divergent charge redistribution. This means that the 1D electron gas is unstable to the formation of periodically varying electron charge or electron spin density. This waves have a wavevector of $2k_f$.

Figure 2.1: a) Susceptibility in three dimensions. Wavevectors $k$ and $q$ appear in the equation 2.1 and the Fermi energy as energies $\epsilon_k$ and $\epsilon_{k+q}$, therefore the equations depend only on the length of the wavevectors. Data for the figure adopted from ref.\cite{4}. b) Fermi surface topology for 1D and 2D free electron gas. The arrows indicate pairs of states, differing by the wavevector $q = 2k_f$. We see that in 1D all of the arrows connect surfaces, on the other hand we have a very different situation in 2D. Data for the figure adopted from ref.\cite{4}.

The consequence is that because of a periodic modulation of potential with a wave vector $q$ the system lowers its total energy by forming a gap in the energy dispersion at wave vectors $\pm q/2$. If the gap is in the Fermi surface ($q/2 = k_f$), this can lead due to the electron-phonon interaction to a lattice modulation. This is connected with the Peierls instability (Figure 2.2) in which the dimerization of a 1D chain of atoms can occur spontaneously because the electronic energy saved by opening up a gap in the spectrum near the Fermi surface can outweigh the elastic energy cost of the dimerization and the system undergoes a transition from a metal to an insulator\cite{6}.

Figure 2.2: The Peierls instability for a 1D metal, with one electron at each site of an atomic chain of period $a$. The energy band is half-filled with the Fermi wavevector at half of the Brillouin zone $\pi/a$. The electron density is constant in space. Doubling the period will lead to a modulation of the electronic density (CDW), and thus a new structure. The doubling of the unit cell will reduce the Brillouin zone to half, which leads to a gap right at the Fermi energy. The system undergoes a metal-to-insulator transition. Data for the figure adopted from ref.\cite{6}.

If the wave vector $q$ turns out to be a simple rational fraction of $\pi/a$, where $a$ is the length of the vector defining a primitive unit cell, the CDW is said to be commensurate with the underlying lattice. However is is more usual for the wave vector $q$ not to be a simple multiple of $\pi/a$ so the CDW is incom-
mensurate (Figure 3.3 a)). There is an analogous instability for the formation of spin-density waves, which are seen in ferromagnet and antiferromagnets.\cite{5} \cite{4} \cite{7}

## 2.2 CDW IN 3D

System with both atoms and electrons has a far more complicated Fermi surface. In three dimensions a density wave can not produce an energy gap at all points on the Fermi surface. In real metals is very often happens that two pieces of Fermi surface (cylindrical or nearly flat) are approximately translated from one to another in $k$-space by a fixed wave vector $\vec{q}$. This can give rise to a peak in the susceptibility and a resulting instability. The formation of the charge-density wave is said to nest the Fermi surface. \cite{5}. A charge density wave, with wave vector $\vec{q}$, can produce energy gaps along the region of the Fermi surface for which this nesting is possible.

![Illustration of CDW nesting](image)

*Figure 2.3: Demonstrated examples of the Fermi surface nesting by a wavevector, which is noted with the red arrow. Examples represent materials with very little band dispersion in axis perpendicular to the basal plane. Outer square in the first example and hexagons in the other two examples represent the first Brillouin zone. Data for the figure adopted from ref.\cite{8}.*

Several experimental techniques can be used to characterize the CDW. Electron and neutron diffraction experiments help determining crystal lattice structure. Scanning tunnelling microscope (STM) image of charge density modulation in the CDW phase can be used to characterize real space orientation and phase of the CDW relative to underlying lattice. Also, measurements of specific heat and resistivity show changes between the normal state and different CDW states. \cite{9}

## 3 1T-TANTALUM (IV) SULFIDE

### 3.1 GENERAL PROPERTIES

TaS$_2$ belongs to a group of materials called transition-metal dichalcogenides (TMDs). These are materials that can be denoted as MX$_2$, where M is a transition metal within group 4-10, and X represents a chalcogen element within group 16 \cite{9}. One of its forms 1T-TaS$_2$ has a simple crystal structure, composed of planes of Tantalum (Ta), surrounded with a trigonal (T) symmetry with approximately octahedral arrangement by Sulphur (S) atoms. Other form 2H-TaS$_2$, which will not be discussed in this paper, has a similar structure with trigonal prismatic arrangement by Sulphur (S) atoms.

All TMDs have a fairly strong intralayer covalent bonding between the metal and the chalcogens, and weak interlayer van der Waals bonding. The quasi two dimensional structure gives rise to anisotropy in physical properties. The weak interlayer bonding permits intercalation of ions, metal atoms and also organic molecules. This can cause dramatical changes in physical properties of the host. It also allows to easily cleave bulk crystals along the surface to make few-layer or even single layer samples. \cite{9}

If we look at a simple ionic model. Based on the atomic energy levels, valence $p$ orbitals from S are lower than $d$ orbitals in the metal Ta. There are 6 $p$ bands (two S atoms) per unit cell which are
occupied by 8 electrons from S and another 4 from Ta. That leaves one electron from Ta that occupies d-bands per formula unit. The d bands are split by the crystal field as shown in figure 3.1 c). Therefore we would expect 1T-TaS$_2$ to be metallic. Due to hybridization and band splitting, the orbital picture in real compound is far more complicated.\cite{8}

![Figure 3.1: a) Sketch of few planes of 1T-TaS$_2$. Yellow spheres represent Tantalum atoms, violet spheres represent Sulphur atoms.\cite{10} b) Trigonal (T) symmetry in 1T-TaS$_2$ with approximately octahedral coordination around metal sites. 2H-TaS$_2$ with similar structure with trigonal prismatic arrangement of Sulphur atoms is also shown. Data for the figure adopted from ref.\cite{9}. c) Schematic illustration of electronic bands in 1T-TaS$_2$. Abscissa represents density of states. Lower d band is partially filled, making 1T-TaS$_2$ a metal. Data for the figure adopted from ref.\cite{9}.

### 3.2 Phase diagram

What makes this group of materials so challenging for a study is the existence of many phase transitions. 1T-TaS$_2$ is no exception, it is a particularly important system in which competition between Coulomb interaction, lattice strain and a Fermi surface instability lead to a number of macroscopic quantum states with different electronic charge orders.\cite{11} At high temperatures the system with one electron in d electron band is in a metallic phase, where at $T = 550$K a transition to incommensurate CDW (ICCDW) phase occurs. At $T = 350$K the system undergoes a transition to nearly commensurate CDW (NCCDW) and at $T = 180$K to commensurate CDW (CCDW), accompanied with abrupt change of the resistance $R$ and insulating behaviour.\cite{11}

The CDW state is mostly driven by the Fermi surface instability, resembling the ones found in Peierls (quasi) 1D system, which we described before. The Peierls-like behaviour in 1T-TaS$_2$ is substantially more complex. Weak interlayer interactions, implying little band dispersion along the axis perpendicular to the basal plane, result in large flat areas of the Fermi surface, closely satisfying the criteria for good nesting.\cite{8} This nesting is very similar to the examples demonstrated in Figure 2.3.

Structural phase transformations are caused by the triple coplanar charge density waves. In the ICCDW phase there are three CDWs, each one is parallel to one of the primitive vectors. CDW wavevectors rotate by $110^\circ6'$ at the transition to the NCCDW. They rotate gradually, as the temperature is lowered, to $13^\circ54'$ at the transition to the CCDW, which is described below.\cite{8} \cite{12}

The CCDW phase is geometrically the simplest among the CDW phases in the material. The displacement of the atoms leads to the formation of David-cluster star shaped polarons, where twelve Ta Atoms within the layer move inwards towards a thirteenth central Ta atom ($\sqrt{3} \times \sqrt{3}$ superlattice), very much alike the Periels instability. The d band is split into sub-bands by the CDW. Twelve out of the thirteen electrons of the new unit cell occupying the electronic states below the energy gap created by the deformation (up to 0.4eV below $E_f$). The ‘thirteenth’ electron on the central Ta atom presides above the deformation-induced gap, filling a half-filled narrow metallic band straddling the Fermi energy. This
band is split into two Hubbard bands, demonstrated in Figure 5.1. Upper unoccupied Hubbard band merges with the upper unoccupied band. Lower occupied band is \( \approx 0.2eV \) below \( E_f \) and still above the valence band. The high cost of adding an additional electron to 13th electron band causes this stable C state to form an Mott insulator. [13]

The neighbouring NCCDW phase equally contains the David-star clusters, although they are arranged in a less uniform manner. X-ray studies in the 1T-TaS\(_2\) reveal that in the NCCDW phase several tens of stars organize into roughly hexagonal domains, locally reproducing the CCDW phase. The domains are separated by triangular regions where the amplitude of the deformation is reduced. [11] [13] Stability of each phase can be explained with the approximate free energy dependence to the CDW wavevector in the equilibrium in figure 3.3 b).

The high cost of adding an additional electron to 13th electron band causes this stable C state to form an Mott insulator. [13]

Figure 3.2: a) Sketch of the Fermi surface of 1T-TaS\(_2\), showing large flat areas satisfying the nesting criteria. Data for the figure adopted from ref. [8]. b) The T-dependence of the resistance \( r(T) \) on temperature cycling. The inserts show schematically the lattice distortions associated with an individual polaron and their ordering in NC and C state respectively. \( \sqrt{3} \times \sqrt{3} \) superlattice cell is presented with yellow colouring. We see that the phase transition from NCCDW to CCDW is first order transition. [11]

The neighbouring NCCDW phase equally contains the David-star clusters, although they are arranged in a less uniform manner. X-ray studies in the 1T-TaS\(_2\) reveal that in the NCCDW phase several tens of stars organize into roughly hexagonal domains, locally reproducing the CCDW phase. The domains are separated by triangular regions where the amplitude of the deformation is reduced. [11] [13] Stability of each phase can be explained with the approximate free energy dependence to the CDW wavevector in the equilibrium in figure 3.3 b).

Figure 3.3: a) Schematic free energy landscape of the 1T-TaS\(_2\) as a function of the wavevector \( q \). \( q_I, q_{NC}, q_C \) are the wavevectors corresponding to the incommensurate (I), nearly commensurate (NC) and commensurate (C) states, shown schematically in real space. The individual polaron is also shown. [1] b) A 1D schematic representation of all three CDW phases. It should be noted that NCCDW also includes higher order harmonics [14]. The blue CDW corresponds to \( q_{NC} \).
4 EXPERIMENT

Experiment shows that under non-ergodic conditions created by pulsed charge injection, a metastable state can be reached, which is not part of the known thermodynamic phase diagram. These states are referred to as hidden states (H). The remarkable stability of the new state, whose extrapolated lifetime exceeds the age of the universe below \( \approx 20 \) K, is highly unusual. Crystal samples used for this experiment were thick between 20 and 120 nm. They were exfoliated from bulk samples and put on a sapphire substrate. Multiple gold contacts were made using laser direct photolithography. The resistance was measured either in two or four contact configuration with low currents \(< 1 \mu A\) to minimize Joule heating.

Distance between contacts was typically between 1 and 8 \( \mu \)m.

At low temperatures \((T = 4K)\), when 1T-TaS\(_2\) is in commensurate state, a single pulse from a constant current source \((\approx 10 \mu s)\) applied to the crystal leads to an immediate drop in R by nearly three orders of magnitude. The system is stable in this new low resistance metallic state until heated. Measuring R upon heating, it gradually merges with the cooling curve at around \(T \approx 80\) K.

The value of the switching current pulse has to be high enough for the system to reach the H state or else no change in resistance is detected. This threshold value is extremely sharp and it also varies with temperature. Its typical values change linearly with the distance between the contacts and were \(\approx 1\) V/\(\mu\)m. Switching occurs with current pulse lengths \(\tau_W < 1\)s, because of concurrent erasure caused by Joule heating. The shortest current pulse was limited by the measuring devices to 30 ps.

The H state can go back to the C state by resistively heating the device (Joule heating). This was done by applying longer (10 s) electrical pulses, which raised the temperature of the device and switching the samples back to high resistivity state. This allows us to perform repeatable write and erase cycles. \[1\]

![Figure 4.1: a) Resistance of 1T-TaS\(_2\) when cooled from room temperature to 4 K (blue dots). After a W pulse (2 mA, 10 V, 1 \(\mu\)s) applied to the sample, the resistance dropped to \(\approx 80\) Ohms. The sample is then heated to 100 K (red dots).[1]

b) The final state reached after the W pulses appears to always have the same resistance when switched under the same conditions, to within < 2% (here \(V = 20\) V, \(\tau_W = 5\) \(\mu\)s, \(T = 26\) K), while the resistance after the E pulse (\(V = 7\) V, \(\tau_E = 10\)s) varies somewhat (note the logarithmic scale).[7]

5 THEORETICAL VIEW OF THE EXPERIMENT

Holes with energies \(eV = E_e - E_h = 1 - 10\) eV are launched from the electrode into the sample, where \(V\) is the applied voltage. The same applies to electrons, which are launched from the opposite electrode. They rapidly populate the upper and lower bands of the C state with electrons and holes respectively, followed by scattering amongst themselves and with the lattice until electrons reach LHB and holes UHB. The large asymmetry of the band structure can lead to photodoping effect, where the electron and the hole scatter and lose energy with different rates.
The injected electrons can annihilate with holes in the LHB. They could also localise interstitially in between existing polaron, but this case is not very stable of its high cost in Coulomb energy. Injected holes on the other hand have one other option. They could annihilate with the central 13th electrons of each polaron, removing the charge at the centre of polaron. This annihilation would convert polaronic states to band states (figure 5.1) and leave voids in their places. Because voids repel each other, they form a textured formation similar to NCCDW state. Taking in consideration the NCCDW state, this means that \(1/4 \sim 1/3\) of all available polaron sites are voids. All other injected holes no longer localise, they only contribute to the current between the contacts.

*Figure 5.1: Schematic representation of the electronic bands in the C and the H state. Injection of electron/hole into the UHB/LHB of the C state leads to state conversion from localized states to band states. The charge injection and energy relaxation in the C states is shown on the energy band structure. Electronic bands of Au/Pt contacts are also shown.*

Forming this textured state is extremely rapid, approximate timescale is defined by the energy relaxation of the injected electrons/holes (\(\approx 100\) fs) and the time necessary for the ions to readjust. Latter is of the order of 1/4 period of the CDW amplitude mode period (\(\approx 150\) fs). The CDW amplitude mode period is the period of the radial vibration of ions on the edges of the polaron stars (\(\omega_A = 2.4\) THz).

As demonstrated in figure 5.2 b), we see that during this 100 – 150 fs transition free energy graph changes. When the current is still flowing, the CDW can tunnel to the new potential minimum. We can discuss this transition in terms of macroscopic quantum tunnelling (MQT), which requires that the tunnelling is faster than dissipation of the quantum state. Tunnelling attempt frequency rate is defined by AM frequency, whose period is 450 fs. The decay time of AM is > 5 ps \([1]\), so the condition for the tunnelling is satisfied.

Below threshold, the H’ state is metastable, so upon removing the applied voltage, the charges dissipate and the system reverts back to C state. As demonstrated in figure 5.2 b), we expect that below threshold sample does not fully order into textured state and that after the pulse the barrier between H’ state and C state is comparable to the thermal energy \(k_B T\), which is the reason that after the pulse the system immediately returns back to the C state. The wavevector \(q_{H'}\) does not represent some definite value that corresponds to the charge modulation, because we can not describe this anisotropic state of the system with a simple wavevector.

Above threshold, the voids caused by injection order macroscopically throughout the entire sample with globally broken translational symmetry accompanied with its uniform charge modulation wavevector \(q_H\). When the voltage is high enough and the entire sample orders macroscopically the barrier between the states rises. The barrier is sufficiently larger compared to the thermal energy \(k_B T\), so the system is stuck in the H state. The transition back to the C state requires an energetically costly transfor-
formation, a charge rearrangement of the entire macroscopic system, where electrons in band states have to be converted to polaron states.

Figure 5.2: a) Injection of electron/hole into UHB/LHB of the C state leads to annihilation of polarons, creating voids in their places. [1] b) Schematic free energy landscape before (dashed) and after (black, red, blue) electron injection, showing C, H, H' states respectively. The black curve demonstrates free energy while the voltage is above $V_t$ and the CDW tunnels in terms of MQT to the H state (orange arrow). After the current stops flowing, the system has the potential marked as the red curve. Blue curve represents the potential of the system after the applied voltage $V < V_t$, where the barrier is smaller than thermal energy. Data for the figure adopted from ref. [1]

6 Conclusion

It has already been proven, that H state lifetime can be significantly increased by substrate strain and with substituted compounds (e.g. 1T-TaS$_{2-x}$Se$_x$) have $t_c > 300K$ [1]. This implies that this mechanism could also be operational in room temperature. With the possibility of making fast repeatable write and erase cycles, this mechanism is a good candidate for future memory device. Using more advanced instruments, write speed could be shorten to orders of magnitude faster than the current record 300 ps write speed in non-volatile memory devices [1]. Using optical switching method sup-picosecond timescales were already reached [11]. Besides practical research, we also hope that in near future a better and more detailed theoretical picture of this phenomena will be developed.
REFERENCES


