UNIVERSITY OF ZAGREB
FACULTY OF SCIENCE
DEPARTMENT OF PHYSICS

Kristijan Velebit

EFFECTS OF SUPERSTRUCTURING ON OPTICAL AND TRANSPORT PROPERTIES OF SELECTED LAYERED MATERIALS

DOCTORAL THESIS

Zagreb, 2015

UNIVERSITY OF ZAGREB
FACULTY OF SCIENCE
DEPARTMENT OF PHYSICS

Kristijan Velebit

EFFECTS OF SUPERSTRUCTURING ON OPTICAL AND TRANSPORT PROPERTIES OF SELECTED LAYERED MATERIALS

DOCTORAL THESIS

Supervisor: Dr. Ana Smontara

Zagreb, 2015

SVEUČILIŠTE U ZAGREBU
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
FIZIČKI ODSJEK

Kristijan Velebit

UTJECAJ SUPERSTRUKTURIRANJA NA OPTIČKA I TRANSPORTNA SVOJSTVA ODABRANIH SLOJEVITIH MATERIJALA

DOKTORSKI RAD

Mentor: dr.sc. Ana Smontara

Zagreb, 2015.

This thesis was made under the mentorship of dr. sc. Ana Smontara as a part of the doctoral study at the Department of Physics, Faculty of Science, University of Zagreb. Presented experimental work was carried out at the 1. Physikalisches Institut, Universität Stuttgart in Germany and in the *Laboratory for the physics of transport phenomena* at the Institute of Physics in Zagreb, Croatia.

Ovaj doktorski rad je izrađen pod mentorstvom dr. sc. Ane Smontare u sklopu doktorskog studija na Fizičkom odsjeku Prirodoslovno-matematičkog fakulteta Sveučilišta u Zagrebu. Predstavljeni eksperimentalni rad proveden je na 1. Physikalisches Institut, Universität Stuttgart (Njemačka) i u *Laboratoriju za fiziku transportnih svojstava* Instituta za fiziku u Zagrebu (Hrvatska).

Acknowledgments

I am very grateful to my supervisor, Dr. Ana Smontara, for introducing me to the research of transport properties in condensed matter physics, for her guidance, and for her attention to details.

I am especially grateful to Dr. Eduard Tutiš for sharing his knowledge with me and for being an unlimited source of advice and support.

I wish to thank Prof. Dr. László Forró, Prof. Dr. Ivo Batistić, Dr. Jovica Ivkov, Prof. Dr. Neven Barišić, Prof. Dr. Ante Bilušić and Dr. Petar Popčević for shaping and aiding my scientific career in many ways, and for collaborating in my work. I am also grateful to Prof. Dr. Mario Basletić and Prof. Dr. Mihael S. Grbić for the work they have done on reviewing this thesis.

I am grateful to Prof. Dr. Martin Dressel for the hospitality I received at the 1. Physikalisches Institut, Universität Stuttgart, Germany, and for making this work possible. I thank Prof. Dressel and the researchers of the Institute for sharing their knowledge of optical techniques with me. I appreciate all the help with the preparation of the samples by Chem.-Tech. Gabriele Untereiner. I thank all members of the Institute for their help, and above all, for making me feel welcomed.

Most of all, I am grateful to my wife Karolina, my parents, Duško and Zlatica, and my sister Danijela for showing me love and support over the years.

BASIC DOCUMENTATION CARD

University of Zagreb
Faculty of Science
Department of Physics

Doctoral thesis

EFFECTS OF SUPERSTRUCTURING ON OPTICAL AND TRANSPORT PROPERTIES OF SELECTED LAYERED MATERIALS

Kristijan Velebit

Institute of Physics, Zagreb

Very special electronic phases brought upon by the superstructuring in layered materials have held the interest of researchers for decades. This thesis deals with the effects of the lattice superstructuring on optical and transport properties of pure and doped samples of 1T-TaS_2 and 1T-$TiSe_2$. This work brings the first ever analysis of the optical properties of the nearly-commensurate charge density wave (NCCDW) phase of 1T-TaS_2 at temperatures below 200 K. Optical response of the NCCDW phase is for the first time analyzed with the nano-composite-like nature of the phase in mind. Modeling of the optical response using the Bruggeman effective medium theory is suggested and demonstrated. As a result, localized surface plasmon feature is identified in the optical spectrum, as well as the asymmetry of the optical phonon modes brought upon by the coupling of spatially distinct nano-sized domains which comprise the material. A novel analysis of the superstructure-related phonon peaks which allows the determination of the charge redistribution over the star-like superstructure is presented. Lastly, this work also presents the study of the 1T-$TiSe_2$ compound, where the analysis is focused on the properties of the high temperature phase of the material. The contributions of electron and hole pockets are resolved for the first time, as well as the spectral weights and the scattering rates for each channel. Calculated energy ranges of the quasi-2D hole band settle the ongoing debate and determine that 1T-$TiSe_2$ in the high-temperature phase is a semimetal, with scattering which gets stronger over a wide interval as the temperature approaches the phase transition.

(148 pages, 49 figures, 4 tables, 155 references)

Keywords: layered materials, transition metal dichalcogenides, superstructuring, charge density wave, effective medium theory, localized surface plasmon, asymmetric phonon modes, charge redistribution, optical conductivity, infrared spectroscopy

Language of the original: English

Supervisor: Dr. Ana Smontara

Thesis defense committee:

1. Assoc. Prof. Dr. Mario Basletić,
   Faculty of Science, Department of Physics, Croatia

2. Dr. Ana Smontara, senior scientist,
   Institute of Physics, Croatia

3. Prof. Dr. László Forró,
   Ecole Polytechnique Fédérale de Lausanne, Switzerland

4. Assist. Prof. Dr. Neven Barišić,
   Technische Universität Wien, Austria

5. Dr. Eduard Tutiš, senior scientist,
   Institute of Physics, Croatia

Thesis accepted: October 13, 2015

Thesis is deposited in The Central Library for Physics, Faculty of Science - Department of Physics, Bijenička c. 32, Zagreb.

TEMELJNA DOKUMENTACIJSKA KARTICA

Sveučilište u Zagrebu
Prirodoslovno-matematički fakultet
Fizički odsjek

Doktorska disertacija

UTJECAJ SUPERSTRUKTURIRANJA NA OPTIČKA I TRANSPORTNA SVOJSTVA ODABRANIH SLOJEVITIH MATERIJALA

Kristijan Velebit

Institut za fiziku, Zagreb

Vrlo posebne elektronske faze koje nastaju superstrukturiranjem slojastih materijala već desetljećima zaokupljaju pažnju istraživača. Ovaj doktorski rad proučava efekte superstrukturiranja kristalne rešetke na optička i transportna svojstva čistih i dopiranih uzoraka 1T-TaS_2 i 1T-$TiSe_2$. Rad donosi prvu analizu optičkih svojstava faze približno sumjerljivog vala gustoće naboja (*engl*. NCCDW) 1T-TaS_2 na temperaturama ispod 200 K. Po prvi put je optički odziv NCCDW faze analiziran uzimajući u obzir njenu nano-kompozitnu prirodu, te je predloženo i provedeno modeliranje optičkog odziva pomoću Bruggemanove teorije efektivnog medija. Kao rezultat, u optičkom spektru je identificiran učinak lokalnog površinskog plazmona, kao i asimetrija fononskih modova do koje dolazi zbog vezanja optičkog odziva prostorno razdvojenih nano-domena. Nadalje, predložena je nova analiza intenziteta super-strukturnih fononskih vrhova koja omogućava određivanje redistribucije naboja u zvjezdastoj superstrukturi. Napose, ovaj rad predstavlja i istraživanje 1T-$TiSe_2$, gdje je analiza usredotočena na svojstva visokotemperaturne faze materijala. Po prvi put su razlučeni doprinosi elektronskih i šupljinskih pobuđenja, te njihova spektralna težina i jačina raspršenja. Proračuni energijskog raspona kvazi-dvodimenzionalne šupljinske vrpce omogućuju zaključenje dugotrajne debate u korist zaključka da je 1T-TiSe2 u visokotemperaturnoj fazi "polumetal" (*engl*. semimetal), s raspršenjem koje jača preko vrlo širokog intervala u kojem se temperatura približava točki prijelaza.

(148 stranica, 49 slika, 4 tablice, 155 referenci)

Ključne riječi: slojeviti materijali, dihalkogenidi prijelaznih metala, superstrukturiranje, val gustoće naboja, teorija efektivnog medija, lokalizirani površinski plazmon, asimetrični fononski modovi, preraspodjela naboja, optička vodljivost, infracrvena spektroskopija

Jezik izvornika: engleski

Mentor: dr. sc. Ana Smontara

Povjerenstvo za obranu doktorata:

1. Izv. prof. dr. sc. Mario Basletić,
   Fizički odsjek, PMF, Hrvatska

2. Dr. sc. Ana Smontara, znanstvena savjetnica,
   Institut za fiziku, Hrvatska

3. Prof. dr. sc. László Forró,
   Ecole Polytechnique Fédérale de Lausanne, Švicarska

4. Dr. sc. Neven Barišić, znanstveni savjetnik,
   Technische Universität Wien, Austrija

5. Dr. sc. Eduard Tutiš, znanstveni savjetnik,
   Institut za fiziku, Hrvatska

Rad prihvaćen: 13. listopada 2015.