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Optical Studies of Layered Chalcogenides

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Introduction

The 1T-TaS₂ is a member of the multi-layered transition metal dichalcogenide (TMC) compounds family. It has been under research for several years. 1T-TaS₂ has a very complex layered crystal structure. It is interesting that this compound demonstrates several metal-to insulator phase transitions (MIT). Phase transitions are fairly common

in nature. One obvious example is water freezing at zero degrees Celsius (°C) and vaporizing at one hundred °C. In case of 1T-TaS₂ we have phase transitions which manifest themselves by an abrupt change of resistivity.

The 1T-TaS₂ has unique electrical properties. At higher temperatures resistivity of this material is small; thus, one can say the material behaves as a metal. At lower temperatures resistivity increases; thus, one can say the material behaves as an insulator. There are two temperatures where the 1T-TaS₂ compounds show abrupt changes in resistivity. These are two MIT transitions, occurring at 180 and 350K^{1,2} (Fig. 1), which we are interested in.

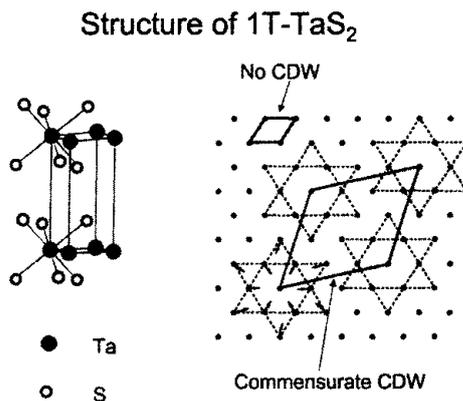


Figure 1. The layered structure, atomic positions, displacements, and “star-of-David” in the $\sqrt{13} \times \sqrt{13}$ phase of the 1T-TaS₂.

It is important to study the MIT transitions of 1T-TaS₂, because they occur at relatively high temperatures. This can be an advantage for IR detectors (bolometers), in terms of time and cost, whereas compared to Si- based detectors (bolometers), which work at liquid He temperatures (-269 °C) and take a valuable time to refill, and purchase He, where He costs \$5-6/lit. As a result of continuous experiments and analyses, TMC’s could be put to further use, as the infrared detectors. Thermal vision is one of the possible applications.

It is very important to understand every detail of the 1T-TaS₂ transitions; thus any experimental data, which could shed light on the mechanism of transitions, in the outcome will most likely be appreciated. In this project we focus our studies on the optical properties of 1T-TaS₂ at its phase transitions, 180 and 350K. In particular we are interested how optical properties of 1T-TaS₂ are affected by phase transitions.

Properties of 1T-TaS₂

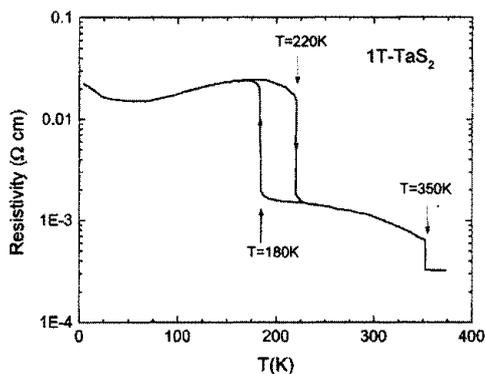


Figure 2. Resistivity of the 1T-TaS₂ as a function of temperature.

In this project we use optical spectroscopy to study optical properties of the 1T-TaS₂. Phase transitions, as mentioned above, affect the 1T-TaS₂. The 1T-TaS₂, responds to these phase transitions in two ways. It changes its structure and resistivity. Sometimes it is more convenient to talk about the 1T-TaS₂ compound's conductivity, which is the inverse of resistivity.

The 1T-TaS₂ crystallizes in CdI₂-type structure (Fig.2). The main building block of this structure is a S-Ta-S sandwich. In particular 1T-TaS₂ is constructed from hexagonally arranged Ta layers, which are fitted between hexagonally arranged S layers. The plane parallel to these sheets unveils a cleaving, because of weak Van der Waals coupling. This layered structure results in two-dimensional properties of TaS₂ (Fig.2). This lower dimensionality results in mechanical and electronic properties.

Another good example of a layered structure is graphite. Graphite layers are easily peeled from each other. We take advantage of this fact by using graphite in pencils. When vertical pressure gets applied to a pencil, the graphite does not break; however, when the pencil gets vertical pressure applied and horizontal movement, the graphite layers peel off leading to the marks on the paper, consequently we are able to write.

The TaS₂ can go either way with a 1T phase or a 2H phase. The difference between the 1T phase and 2H phase is the crystal geometry's of the new structures. The 2H phase has a hexagonal coordination of S atoms around Ta atoms. The 1T phase has the trigonal coordination of S atoms around Ta atoms.

At each of the two-phase transitions, the 1T-TaS₂ gets affected in its resistivity (and conductivity) (Fig.2). At 350K, the 1T-TaS₂ gradually increases its resistance until 180K, where a sudden increase in resistance marks second transition. This transition is accompanied by the change in 1T-TaS₂ crystal structure. One can describe this change through the formation of a charge density wave (CDW). In other words, there is certain periodicity in charge distribution on the atoms of this compound. Charges interact with each other through Coulomb's law. This interaction will be accompanied with the interaction between atoms of the structure. As a result, at some point CDW may win and lead to structural changes. In 1T-TaS₂ this happens at 180K. At this temperature the 1T-TaS₂ clusters into a $\sqrt{13} \times \sqrt{13}$ superlattice, which is built of 13 Ta atoms forming a so-called "Star of David" cluster^{2,7} (Fig.2). This arrangement can be described by the displacement of Ta atoms towards "star center" Ta atom (Fig.2).

Instrumentation

Half of this project was completed in UNF, and the other half was completed in UF. For the measurements at UF we used a Bruker spectrometer for far-infrared spectra range, and a Perkin-Elmer grating spectrometer (PE) for near infrared to visible range.

The Bruker spectrometer is based on the idea of Michelson Interferometer. It is formed of three essential sections. The first section consists of a light source and scanner. The light from the source passes through a filter, which can vary, and eventually focuses onto the sample, in the cryostat, by the help of the scanner. We use an aluminum mirror as a reference for our measurements, because aluminum is 99% reflective in the far infrared spectral range. This aluminum mirror on the sample holder gets placed into the cryostat.

From the cryostat, the light continues to the detector (Si-bolometer). A bolometer comprises of doped silicon, which reacts to reflectance from a sample. A computer analyzes the data by performing the Fourier's transfer from the interferogram. As a result we obtain a power spectrum from the mirror. After using the aluminum mirror as a reference, we position our sample so that it takes the place of the mirror. Therefore the experimental conditions are the same. By dividing signal measured from the sample by the signal measured from the mirror we are able to get the reflectance of our sample.

It is critical to realign the cryostat, when positioning the sample on the sample holder. At visible range, this aligning process gets completed with ease. At infrared ranges, however, since the human eye cannot see the infrared light, we use an infrared sensitive card to align the sample with the light. This card, although it works, indicates the infrared light vaguely. With some experience we were able to achieve a good alignment and to proceed with the measurements.

The Perkin-Elmer grating spectrometer (PE) also consists of three essential sections: the light source, cryostat, and grating. In the PE's case we had two different gratings, in which we needed to switch throughout the measurements. The ideology of the measurements is similar to the Bruker.

The difference is in the fact that for PE we directly measure the reflectance from the sample using different. Note that in case of Bruker we measured the interferogram which was later converted into power spectrum.

For the measurements at UNF we had a custom-made cryostat holder (thanks to the help from UF workshop). This was necessary in-order to firmly attach the cryostat to the Newport table (8x10 ft.²), and eventually to reduce the amount of disturbances from the cryostat hose. In addition to the custom-made cryostat holder, other necessary Newport products were ordered from the Newport catalog to be compatible with the Newport table.

The Newport table has a special characteristic, which is the ability to dump vibrations. One can say it "floats" on air suspended legs. The table consists of four legs, which are isolators, and three of the legs contain special gadgets attached to the joint between the bottom of the table and the isolator. These three gadgets and four isolators are attached to each other, and to a pump, by tubing. Once the table is leveled, and the pump fully pumps the isolators, the arms on the three gadgets will pressurize and lift the table. If pressure gets applied to the top of the table, the arm on one or more of the gadgets will recognize the pressure and release air from the isolator to re-level the table.

The table is the base for our Raman setup which is currently under construction.

Experimental Results

We measured the reflectance of our sample as a function of temperature and frequency (Fig.3). Dispersion analysis

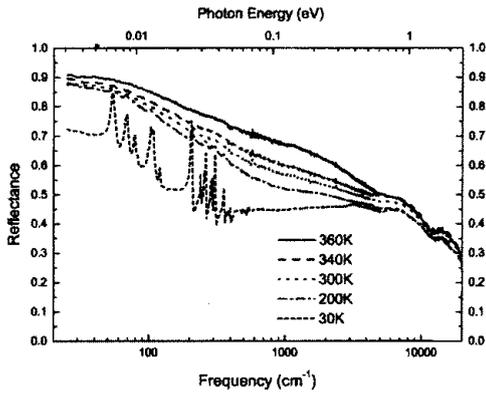


Figure 3. Temperature dependent reflectance of the 1T-TaS₂.

allowed us to get optical conductivity from the reflectance data. By looking at these results, the phase transitions were apparent. From the conductivity versus frequency data (Fig. 4), only the phonons that reacted to the

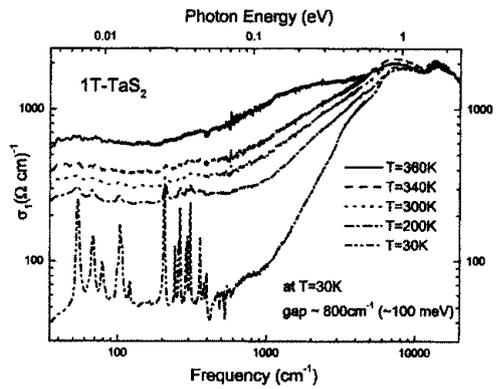


Figure 4. Temperature dependent conductivity of the 1T-TaS₂.

phase transitions were analyzed. Fifteen apparent phonon peaks were taken to account, and the rest were considered as noise (Fig.5). These peaks were analyzed by fitting them to a Lorentzian lineshape; thus,

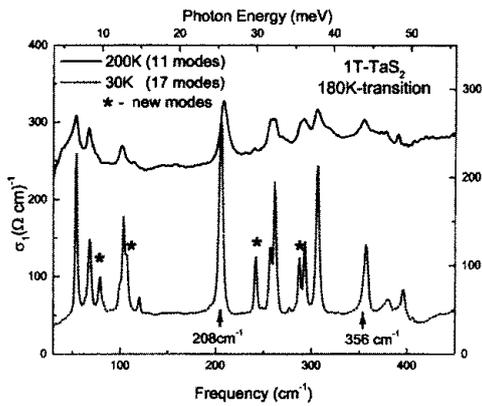


Figure 5. Analyzed apparent phonons modes.

resulting with the frequency and width of each phonon.

We plotted frequency and width of the phonon modes as a function of the temperature, and compared the plots for all the phonon lines we were able to detect.

In general one can describe a phonon as a mass on a spring. When temperature decreases the distance between atoms usually decreases. This means that the

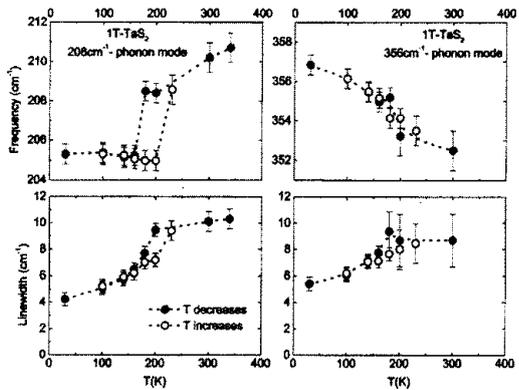


Figure 6. The 208 cm⁻¹ and the 305 cm⁻¹ phonon.

length of the spring gets shorter, or in other words one can say that the spring constant gets bigger. Frequency of the oscillator is proportional to the square root from the spring constant. If the spring constant gets bigger at lower temperatures then corresponding frequency should be higher. Therefore one can expect that frequencies of the phonon modes should increase as temperature of the crystal is lowered. We do

see such a behavior for most of the modes with the exception of one phonon mode at 208 cm^{-1} (Fig.5). One can clearly see that this phonon does not act the same way as the other phonons do (Fig.6). We suggest that this phonon is associated with the vibrations of S atoms. It was suggested⁷ that the S layer bulges at phase transition. It is possible that such anomalous behavior of the 208 cm^{-1} phonon mode is associated with such structural displacement.

Conclusion

From our results for the infrared measurements, we observed the phase transitions at 350K and 180K (Fig.2). Additional phonon modes were found below the 180K-phase transition.

We believe that the 208 cm^{-1} phonon's behavior could be due to the buckling of the S atom layers during the 180K-phase transition. A similar effect has been observed in other compounds, known as high-temperature superconductors⁸.

Our measurements do shed light on the physics of 1T-TaS₂ compounds; however, the phonon at 208 cm^{-1} frequency indicates that extra research is necessary for the full understanding of this compound. In particular a crystal lattice dynamics calculations could help in understanding of this effect. We hope that our results will initiate such calculations and consequently answer the question of anomalous behavior of the 208 cm^{-1} phonon mode in 1T-TaS₂.

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