NDnano Undergraduate Research Fellowship (NURF)
2023 Project Summary
NDnano Summer Undergraduate Research
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1. Student name & home university:

Lili Vajtai, Budapest University of Technology and Economics

2. ND faculty name & department:

Prof. Laszlo Forro, Department of Physics and Astronomy

3. Summer project title:

Pursuing superconductivity in novel low-dimensional materials

4. Briefly describe new skills you acquired during your summer research:

I became more familiar with various pieces of laboratory equipment and multiple sample preparation techniques, such as liquid exfoliation, vapor phase and ammonia intercalation, and the proper use of various measurement devices. I have become more independent and confident in my work and immersed in a new cultural and research environment that provides an important experience for my future academic and career choices.

5. Briefly share a practical application/end use of your research:

The end goal of the project is to observe changes in superconducting characteristics for differently prepared samples that might prove useful even in the industry as these properties become easily tunable and optimizable for various applications, e.g., inkjet-printed superconducting circuits.

6. 50- to 75-word abstract of your project:

Transition metal dichalcogenides (TMDCs) are known for having a layered structure that makes it easy to perform exfoliation and intercalation on them. The effect of these procedures has been previously studied separately and it has been found that both methods result in drastic changes in the electronic, optical, and mechanical properties. The goal of the project was to study the effect of intercalation on exfoliated TMDCs with various thickness and their possibly occurring superconducting behavior.

7. References for papers, posters, or presentations of your research:

[1] R. B. Somoano, V. Hadek, and A. Rembaum. “Alkali metal intercalates of molybdenum disulfide”. In: 58.2 (Jan. 1973), pp. 697–701.

[2] Renyan Zhang et al. “Superconductivity in Potassium-Doped Metallic Polymorphs of MoS2”. In: Nano Letters 16.1 (2016). PMID: 26612060, pp. 629–636.

[3] Claudia Backes et al. “Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation”. In: Chemistry of Materials 29.1 (2017), pp. 243–255.

[4] Claudia Backes et al. “Preparation of Liquid-exfoliated Transition Metal Dichalcogenide Nanosheets with Controlled Size and Thickness: A State of the Art Protocol”. In: Journal of Visualized Experiments 2016 (Dec. 2016), e54806.

One-page project summary that describes problem, project goal and your activities / results:

MoS_2 is a well-known, widely studied semiconducting material, that has been actively investigated since the 1970s. It possesses many practical properties, which enabled its application in transistors, batteries, and lubrication in the last few decades. Similar to most other transition metal dichalcogenides (TMDC), MoS_2 exhibits a characteristic layered structure that can be intercalated or exfoliated. The effect of these procedures separately has been studied previously, and it has been found that they both result in drastic changes in the properties of the materials to even induce fascinating phase transitions. In the case of alkali metal intercalated MoS_2 samples, the presence of a superconducting phase was observed [1], which widens the range of possible applications of suitably modified, MoS_2-based materials.

Superconductivity is a phenomenon in certain materials that has been widely studied in the last century, which is defined by its characteristics of zero electrical resistivity and perfect diamagnetism (Meissner effect) in special materials. Such materials are essential for superconducting magnets in NMR and MRI devices, Josephson junctions, and other technological applications. These applications generate a constant demand for new superconducting materials with diverse properties. Superconductivity was observed in bulk MoS_2 intercalated with various alkali metals, with relevant properties depending on the choice of intercalator and stoichiometry [1,2]. The main goal of this project was to combine both intercalation and exfoliation to produce a wide range of materials that can be interesting for both practical applications and general material science. Emerging superconducting behavior and other attributes can be investigated using general characterization methods, with an emphasis on magnetometry measurements. Observing trends in various features can enable further optimization in certain technologies and pave the way for further research.

The preparation of exfoliated samples was carried out following an already existing and well-established protocol [3,4]. This includes a sonication procedure that leaves us with a mixture of MoS_2 particles of various sheet length and layer number in a surfactant solution. This step is followed by a separation procedure by size, which can be performed with liquid cascade centrifugation (LCC). Centrifuging the mixture in multiple steps, with increasing centrifugation speed, results in the presence of smaller and smaller particles after each step. Removing and storing the sediment leaves us with particles in different size ranges in a surfactant solution. Figure 1 displays the steps of the exfoliation procedure. It is ambiguous if the presence of the surfactant is beneficial for the properties of the samples, so samples that the surfactant was removed from were also studied.

Some aspects of the protocol described above were investigated and improved. An upscaling in sample quantity had to be performed to produce enough particles, especially of smaller sizes. The effect of changing exfoliation time on size distribution in the resulting samples was also investigated that could enable an optimization for a certain desired sheet thickness.

Various alkali metals were used for intercalating the obtained exfoliated MoS_2. They act as charge donors and therefore were reported to induce metallicity and, ultimately, a superconducting phase transition at low temperatures. The focus of this project was mostly on potassium and sodium, as they are relatively easy to work with and known to be excellent charge donors.

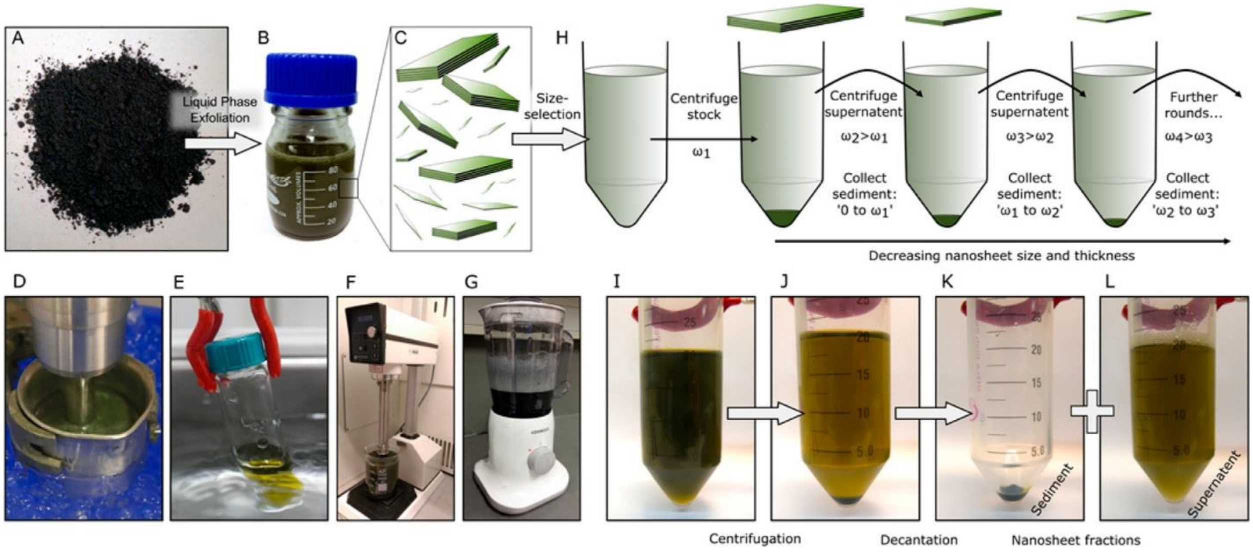

Figure 1: Steps of the sample preparation procedure; A: bulk MoS_2 powder, B: bulk powder mixed with surfactant, C: drawing of MoS_2 sheets of different lateral sizes and thickness; D-G: different methods for performing exfoliation, in the project a sonotrode (D) was applied; H: schematic diagram of LCC; I- L: demonstration of the effect of one centrifugation step and the separation of the sediment and the supernatant [1]

Figure 2: Intercalation in liquid ammonia.

Two different intercalation methods were employed. The first, vapor phase doping, consists of enclosing the intercalator and the host material in a quartz tube and placing them into a furnace that provides thermal energy for activating the intercalation procedure as well as a temperature gradient that induces the diffusion of the intercalator vapor into the material. The other intercalation process occurs in liquid ammonia. In this procedure, the host material and the intercalator are placed into an extra-cold ammonia environment. Alkali metals dissolve in liquid ammonia to form an ionic solution that induces the intercalation procedure (a picture of the resulting mixture is displayed in Figure 2).

The characterization of the samples was performed with various techniques. First, UV-Visible spectroscopy was used on the exfoliated TMDC solutions to record the absorbance of the sample as a function of the irradiation wavelength. According to a previous study, the exciton peaks appearing in the spectra shift with varying the number of layers, and a correspondence between the two quantities was observed (Figure 3 Left, the shift was indeed observed in the energy of the marked exciton peaks) [3,4]. A phenomenological formula for computing the number of layers from the energy of one of the excitons was published, and the investigation of its validity and limitations is in progress for samples without surfactant. The protocol was also checked for validity among different batches (Figure 3 Right, the number of layers in samples from different batches are consistent).

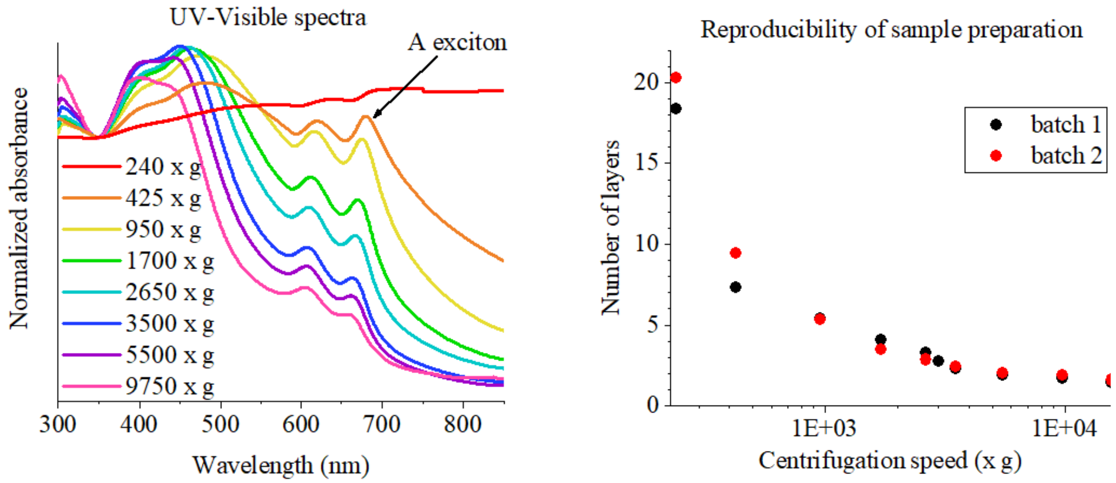

Figure 3: Left: UV-Visible spectra (absorbance as a function of wavelength) for numerous samples separated at different centrifugation speeds; Right: Number of layers for samples of different batches as a function of centrifugation speed.

Direct measurement of particle sizes can be performed by atomic force microscopy (AFM). This technique enables the recording of images of objects in the size range of nanometers, which makes it suitable for imaging exfoliated sheets. It can also measure the statistical distribution of a sample to determine the mean sheet size and number of layers. AFM is limited in differentiating between MoS_2 particles and possible dust particles. Analyzing a particular area of the sample can be challenging, but this method provides a more direct and precise estimate for the average number of layers compared to UV-Visible spectroscopy. Therefore, it is a useful validation for the above-described calculation based on UV-Visible spectra, which is much easier to extract data from and therefore is more useful in determining layer numbers on a routine basis. A sample image can be seen in Figure 4. The visible plateaus clearly indicate the layered nature of the material. The layer step height for MoS_2 is around 1.9 nm, indicating that the particle shown has ~10-30 layers.

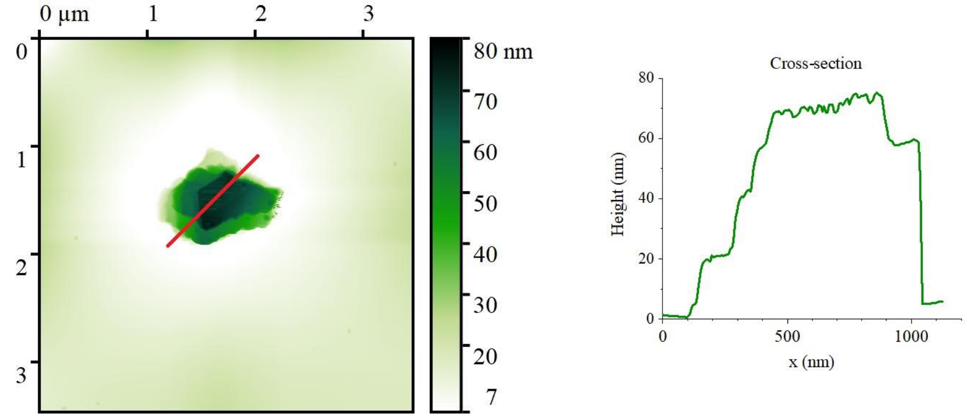

Figure 4: Left: AFM image taken of an exfoliated MoS_2 particle; Right: height profile along the red line on the left.

Furthermore, Raman spectroscopy was also utilized to characterize the samples. These spectra usually contain sharp peaks that originate from exciting vibrations in the lattice structure of the sample, known as optical phonons. The energy, width, and relative amplitudes of these peaks are therefore characteristic of the vibrational modes and symmetries of the lattice, so their shifts and possible disappearance can reflect structural changes to the lattice. Such spectra were reported in the literature for MoS_2 samples with different layer numbers and systematic shifts in characteristic peaks were observed. These shifts were reproduced in the spectra, so they can be used as another cross-checking method for the previously obtained estimate of layer numbers.

Moreover, the photoluminescence of the prepared samples was studied. The phenomenon corresponds to different optical transitions in the samples and is usually present as much wider peaks than the ones corresponding to Raman transitions, so it is easy to differentiate between the two. The investigation of how changing irradiation wavelength and power affects the photoluminescence spectrum is still in progress.

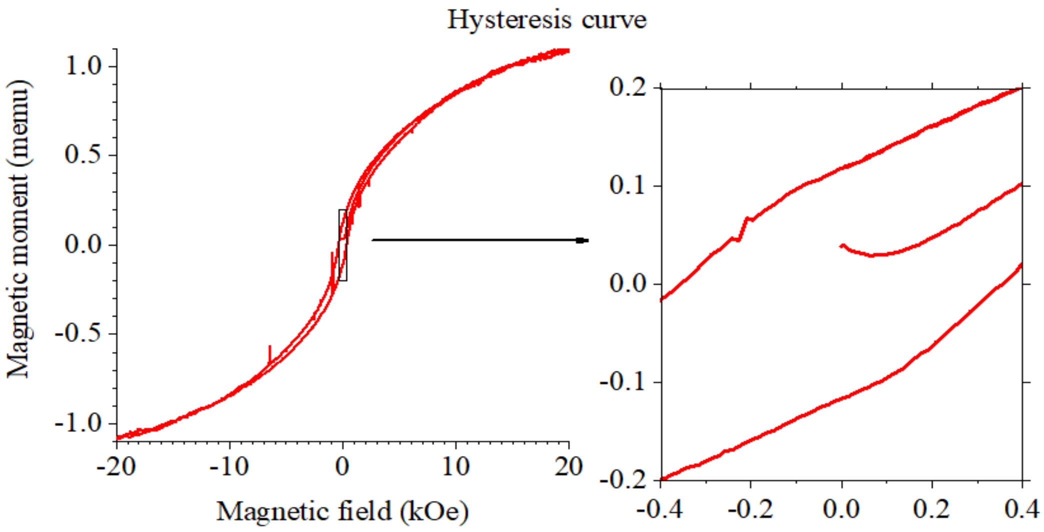

Figure 5: Hysteresis curve of one of the K-doped samples, recorded at 1.8 K.

As the focus of the project was on examining magnetic properties, measurements with a vibrating sample magnetometry (VSM) device were also carried out, which can be used for determining magnetic moments at different temperature and magnetic field values. Since the main interest was the phenomenon of superconductivity, protocols suitable for showing signs of such behavior were implemented. One of these is the comparison of zero-field cooled (ZFC) and field cooled (FC) measurements (Figure 6). Data is recorded in both cases during the heating of the samples at the same non-zero magnetic field. For the FC measurements, the samples were previously cooled at the same magnetic field of 50 Oe, while in the case of ZFC measurements, the cooling was performed without magnetic field. The difference between the two datasets reflects magnetic memory effects, and it is identifying of superconductors that the two curves separate at the transition temperature. This effect was observed in the case of an approximately 20 layer thick, potassium intercalated sample. Hysteresis curves were also recorded at various temperatures, and measurements that show diamagnetic behavior at the start and cusps at zero magnetic field identify type-II superconductors (Figure 5). This can also be observed in the aforementioned hysteresis loop, with a large paramagnetic background, from which it can be concluded that the sample does indeed exhibit superconducting characteristics.

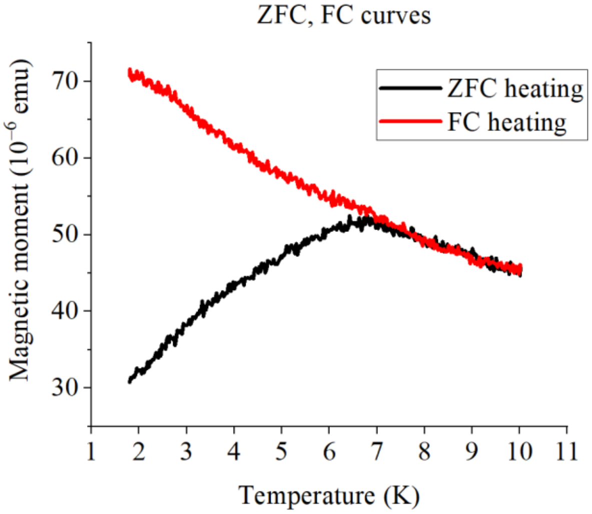

Figure 6: Comparison of ZFC and FC measurements of K-doped exfoliated MoS_2. The magnetic field for the FC measurement was 50 Oe.

Further magnetometry measurements were performed using a superconducting quantum interference device (SQUID), which is known to be a highly sensitive instrument for measuring magnetic moments as a function of temperature and magnetic field, and therefore suitable for ascertaining superconducting characteristics with great accuracy. These characteristics include critical temperature and critical field. These data would be the most valuable in the context of further results, so it is worth continuing the intercalation procedures on different samples as well.

There are many other characterizing methods that also could be used for obtaining valuable data from the samples, including electron paramagnetic resonance, X-ray diffraction, and microwave resistivity measurements, but the above-described methods were prioritized due to their promising and essential nature for the current goals of the project.

Non-intercalated samples, both exfoliated and bulk, were characterized to obtain reference data, to which the effect of intercalation could be compared. Reference data are also valuable on their own, as they might show phenomena not investigated in detail before.

After intercalation, most of the characterizing measurements described above were repeated so that the change induced by solely the intercalator can be tracked. Some of the measurements were not possible to execute, for example, AFM measurements, as the intercalated samples are air and moisture sensitive. Recording Raman spectra on such materials is also a yet unresolved challenge, as the measurement technique includes irradiation with laser light, and the quartz tubes, from which the air-sensitive samples cannot be removed, strongly refract light and repress the signal of the samples.

The project can be continued with further intercalation of the samples using different dopants and characterizing them with an emphasis on possible emerging superconducting behavior. Further characterization methods can be implemented as well and there are numerous effects that can be studied in more detail.

It is easy to see that the project requires future efforts, and during the work, I have encountered many interesting phenomena and challenges that are not strictly part of the original aim of the project. These are all worth studying in more depth in the future, as they might prove useful for future research or possible applications, and they could help us to understand these materials on a deeper level.

During my research, I have gained priceless experience during laboratory work, that will definitely prove useful in my future career. The work environment was great both in the means of laboratory devices and the people around me, who I could learn a lot from. I am very grateful for the opportunity to participate in the research program and be part of the community at Notre Dame.