NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2024 Project Summary

1. Student name & home university:
   Kitti Soos, Budapest University of Technology and Economics

2. ND faculty name & department:
   Prof. Laszlo Forro, Dr. Bence Markus, Dr. David Beke, Department of Physics & Astronomy, Stavropoulos Center for Complex Quantum Matter

3. Summer project title:
   Tailoring the electronic/magnetic properties of MXenes

4. Briefly describe new skills you acquired during your summer research:
   During my summer research, I gained experience in material characterization, for example VSM (Vibrating Sample Magnetometry) and ESR (Electron Spin Resonance), handling air-sensitive materials, operating a glove box and a vacuum system, and expanded my overall laboratory experience. I also gained knowledge of 2D materials and the vapor phase doping method.

5. Briefly share a practical application/end use of your research:
   A practical application of my research is in developing advanced materials that can be used in spintronics and energy storage devices, potentially leading to more efficient and powerful technologies in these fields.

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

MXenes, a recently discovered family of two-dimensional materials, present an opportunity to tune magnetic properties through intercalation. In this study, MXenes were doped with chloride salts such as $CrCl_3$ and $MnCl_3$ using a vapor phase doping method. The chloride salts successfully intercalated into the MXene layers, leading to altered electronic interactions and a notable impact on their magnetic properties. This research provides new insights into the potential of MXenes in magnetic applications.

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

[1] Hantanasirisakul K, Gogotsi Y. Electronic and Optical Properties of 2D Transition Metal Carbides and Nitrides (MXenes). Adv Mater. 2018 Dec.

[2] Double transition-metal MXenes: Atomistic design of two-dimensional carbides and nitrides - Scientific Figure on ResearchGate.

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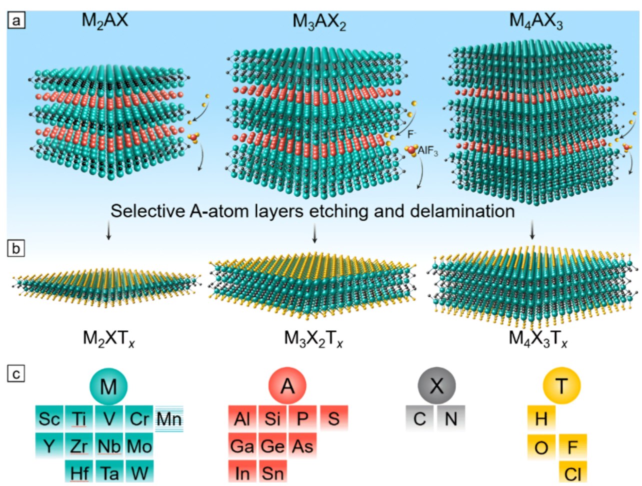
One-page project summary that describes problem, project goal and your activities / results:

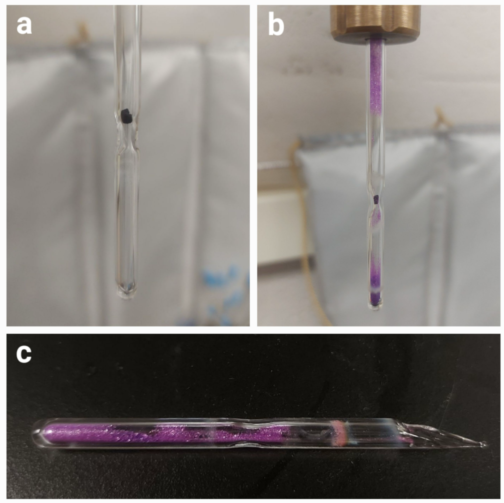
The 2011 discovery of 2D titanium carbide ($Ti_3C_2T_x$) marked the beginning of extensive research into MXenes, a family of two-dimensional materials. These exhibit a variety of properties, including high electrical conductivity, large surface area, and good mechanical strength, making them promising candidates for numerous applications. The ability to tune the properties of MXenes, such as layer spacing, and electronic structure, offers significant opportunities for tailoring them to specific applications. In my project, I focused on exploring the potential of magnetic property tuning in Ti_3C_2 by doping it with chlorine salts.

MXenes are composed of transition metals bonded with carbon and/or nitrogen atoms. They are created from the so-called MAX phases, which are layered structures containing a transition metal (M = Ti, Nb, etc.), an A-group element (A = Al, Si, etc.), and carbon and/or nitrogen (X). During the production, the A element from the MAX phase is selectively etched away, leaving behind thin, 2D layers. The general formula for MXenes is $M_{n+1}X_nT_x$, where T_x represents surface terminations left from the etching processes [1]. These termination groups can influence the pristine material's properties. The MXene flakes are held together by van der Waals force, allowing for the intercalation of other molecules.



1. Figure The structure of the possible MAX phases (a) and MXenes (b). The constituent elements of these (c). [2]

I used vapor phase doping also known as vapor transport method to intercalate the chloride salts into the MXene. Using a gas-welder torch, I fabricated two-zone quartz tubes to separate the dopant and the host material. Firstly, I annealed the pristine MXene under vacuum at 400 °C to remove most of the surface terminations. In a glove box, under an argon atmosphere, I placed the chloride salt at the bottom of the tube. Then, I sealed the tube in a vacuum of the order of 10^{-7} mbar This sample was then placed in a tube furnace, where the temperature difference between the intercalant and the pristine material was maintained at 5-10 °C. This temperature and chemical potential gradient enabled the intercalation process. I used various salts, such as $CrCl_3$, $MnCl_2$, $EuCl_3$, $GdCl_3$, and $NiCl_2$. The annealing temperature depends on the utilized chloride. It was chosen based on graphite intercalation compound and doped polyacetylene studies, where people used the same method.



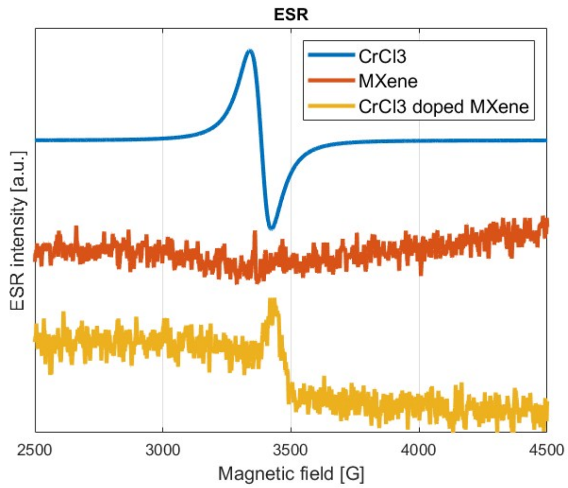
2. Figure An MXene in the two-zone quartz tube (a), the MXene and the $CrCl_3$ on the vacuum system (b), the sealed sample before annealing (c).

After the doping process, I conducted material characterization to analyze the structural and magnetic changes in the MXenes. X-ray Diffraction (XRD) was used to investigate the structural changes and confirm whether the chloride salt had successfully intercalated into the MXenes layers. XRD is essential for determining crystal structure, and layer spacing by analyzing the diffraction patterns of X-rays passing through the material. This helps identify shifts in lattice parameters due to intercalation.

I also utilized Electron Spin Resonance (ESR) to investigate the changes in electronic interactions within the material. These electronic changes can also indicate that intercalation has occurred. ESR is a sensitive method for detecting unpaired electrons, providing insights into the local electronic environment and magnetic properties at the atomic level. This technique allowed me to observe alterations in the electronic structure caused by chloride salt doping, providing a deeper understanding of how the intercalation affected the MXene's magnetic behavior.

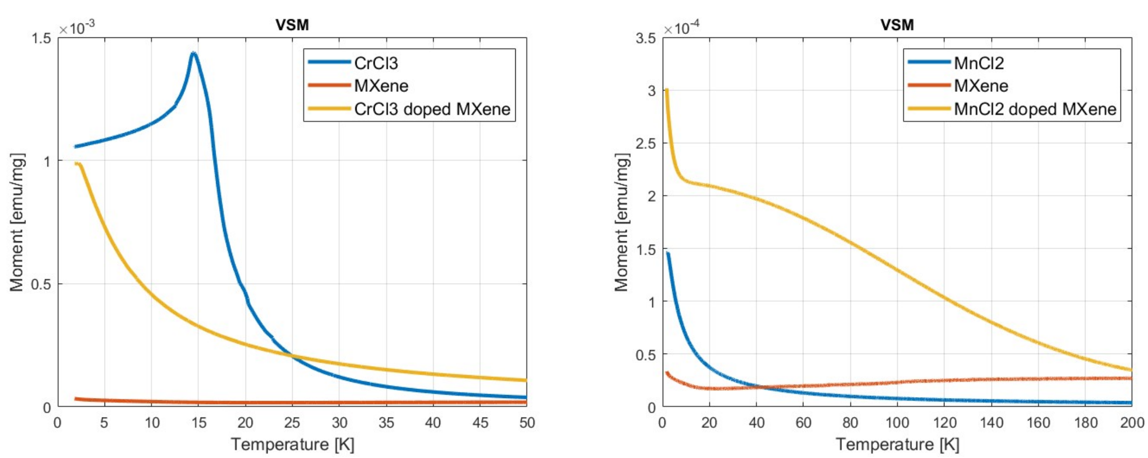
Furthermore, I analyzed the magnetic properties using Vibrating Samples Magnetometry (VSM), a technique that measures the magnetic response of a material when exposed to an external magnetic field. VSM is crucial for determining key magnetic parameters such as magnetization, phase transitions, and magnetic susceptibility. This method provided a detailed assessment of how the chloride intercalation influenced the magnetic properties of the MXenes, contributing valuable information on their potential use in applications.

On the doped materials, I observed a noticeable increase in volume with most of the chloride salts used. Additionally, these samples showed approximately a 10% increase in mass. I conducted reference measurements on the pristine material and the dopants, in addition to the measurements on the doped MXenes. I performed most of my experiments and measurements on the $CrCl_3$-doped samples, where I observed significant changes. I opened one sample in air and another in an argon atmosphere and measured them using ESR. The results clearly indicated that the doped material is air-sensitive, with its structure altering due to exposure to humidity or oxygen. I also investigated the impact of the MXene's annealing temperature on the surface terminations. Under the vacuum conditions used, there was no significant difference between the sample annealed at 400 °C and the one annealed at 600 °C. To ensure accuracy, I confirmed that during the annealing of the sealed sample, only intercalation occurred, without affecting the MXene structure. The difference in spectra between the doped materials and the pristine MXene and intercalant (3. Figure) suggests that the material has undergone a change, with its electronic interactions being altered.



3. Figure The ESR spectra of the $CrCl_3$, the pristine MXene, and the $CrCl_3$ doped MXene

Based on the magnetization measurements performed with the VSM, I can conclude that the project was successful, as I was able to modify the MXene's magnetic properties. While the Ti_3C_2 is a paramagnetic metal, some of the dopant chloride salts (which are insulators) exhibit antiferromagnetic properties, and others are paramagnetic. Specially, $CrCl_3$ has an antiferromagnetic phase transition at 15 K. The $CrCl_3$-doped MXene became paramagnetic, showing a 30-fold increase in magnetic moment at low temperatures. I fitted the magnetization curves using the Curie-Weiss law, and the results suggest that the doped material is an uncorrelated paramagnet. A different sample, doped with $MnCl_2$, which is paramagnetic, exhibited signs of a ferromagnetic phase with a Curie temperature of approximately 200 K, in addition to its paramagnetic properties. Other samples also displayed changes in their magnetic properties, demonstrating that I was able to fine-tune the MXenes' magnetism. However, these results require further investigation to gain a deeper understanding.



4. Figure The magnetic moment temperature dependence of the $CrCl_3$, pristine MXene, and $CrCl_3$-doped MXene (left) and the $MnCl_2$, pristine MXene, and $MnCl_2$-doped MXene (right).