SYNTHESIS OF NEW CHROMIUM POLYHYDRIDES AT HIGH TEMPERATURES AND PRESSURES

The search for room-temperature superconductors

Anna Blaszkiewicz, Alette Eide, Tomas Ferriter, Liam Horan, Elisabeth Nacino, Michael O'Callaghan, Cameron Viar, Christopher Vistian, William Kane, Karen Murphy, and Rostislav Hrubiak

ABSTRACT

Chromium hydrides are compounds consisting of chromium and hydrogen. Chromium hydrides have been predicted to become superconductors at high pressures and can become stable in excess hydrogen environments. Researching chromium hydrides is largely unexplored due to the high temperature and pressure values that are needed to form the compounds as well as the difficulties with handling hydrogen under pressure.

We conducted an experiment to synthesize theoretically predicted chromium hydrides at pressures between 75 and 83 GPa. CrH_2 and Cr_2H_5 were synthesized at 1862 ± 200 K and 2380 ± 200 K, respectively. Upon decompression, Cr_2H_5 transformed to a novel tetragonal CrH_2 phase that was not predicted by previous models.

INTRODUCTION

- Superconductors are a widely explored subject among researchers in recent years, with many practical uses such as in circuitry and transportation. Chromium hydrides have been predicted to be effective superconductors, and previously successful syntheses of various metal hydrides have encouraged exploration of Cr_xH_y alloys at high pressures. Our team explored the possibilities of synthesizing a chromium hydride at the highest temperature and pressure possible, utilizing a diamond-anvil cell (DAC) and laser heating.
- Molecular CrH_2 and CrH_3 have previously been observed, but only a few studies have investigated chromium hydrides in the solid state. Yu *et al.* applied the evolutionary algorithm USPEX to explore the crystal structures of Cr-H compounds. This algorithm predicted that CrH_2 is stable at pressures higher than 30 GPa, and that Cr_2H_5 is stable at pressures higher than 160 GPa.
- Marizy, *et al.* discovered that after moderate laser heating at a pressure of 31 GPa, the sample transforms into CrH_2. CrH_2 was the highest stoichiometry synthesized within the Cr-H system up to 100 GPa.
- In contrast to previous experiments, our team began laser heating only when the chromium hydride was subject to very high pressure, rather than heating starting at the beginning, as well as studying the effect of decompression. The purpose of this was to investigate a different pressure-temperature path than had been previously measured. Our team synthesized multiple chromium hydrides, including Cr_2H_5, as well as a novel one of which was not predicted to exist by previous models (CrH_2 Tetragonal).

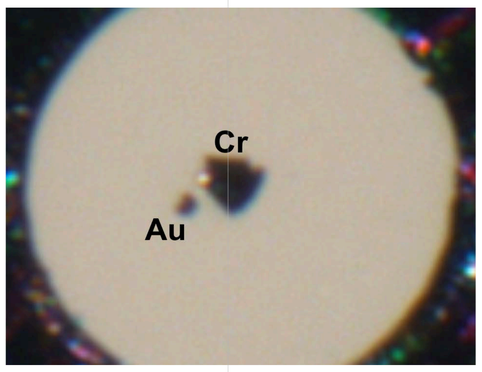

Figure 1: Cr and Au sample in gasket.

Figure 2: The team arrives at Argonne's APS to conduct their research.

PROCEDURE

- A high-purity chromium sample was loaded together with hydrogen in a diamond anvil cell (DAC), using diamonds with culet sizes between 100 and 150 microns in diameter. Two DACs were prepared for the beamline. Tungsten foil was indented between the diamonds and a round hole was created using a laser-machining system in order to create a gasket. Compressed hydrogen gas was loaded into the DAC sample chamber using the gas-loading system.
- The 100 and 150-micron culet diamonds were used to compress the sample to 80 GPa. In intervals of five milliseconds, the double-sided laser heating system was used to heat the samples stepwise up to to temperatures of 2300K, by increasing the laser power incrementally. After each heating, x-ray diffraction data (XRD) was collected. The compressibility was then characterized by XRD from the new phase over an appropriate pressure range by de-compression. XRD patterns were viewed online using Dioptas program. Subsequent refinements of the Cr-H phases were performed on the x-ray data using the GSAS II program.

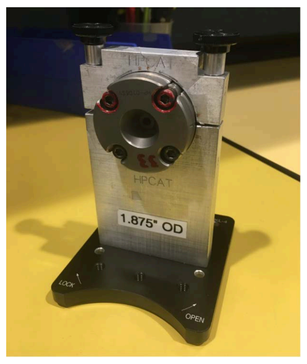

Figure 3: Mounted DAC ready to bring to the hutch.

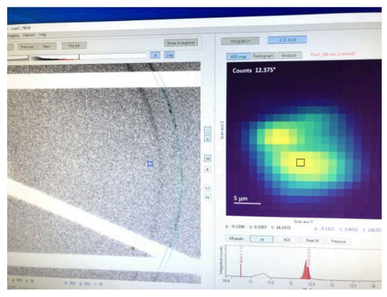

Figure 4: Software image locating Cr sample in the DAC.

RESULTS

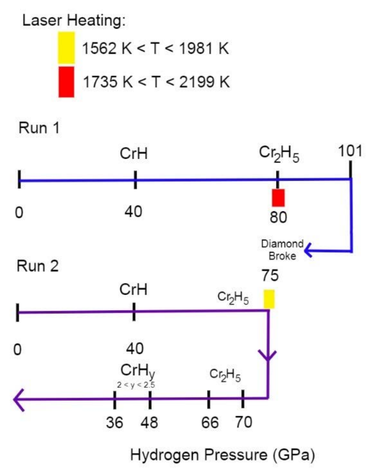

Figure 5: Pressure/Temperature pathway of our samples.

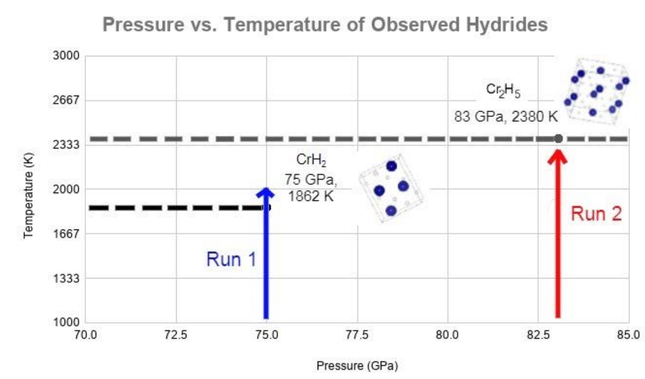

Figure 6: Phases under different Pressure Temperature conditions.

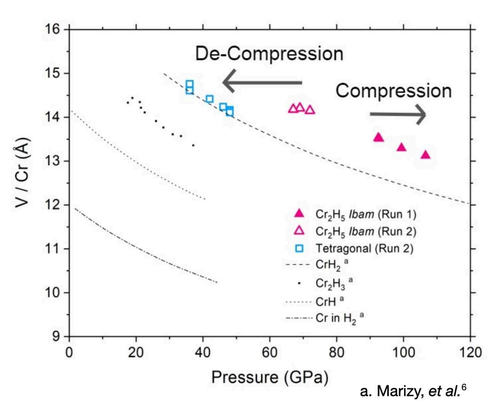

Figure 7: Pressure/Temperature path yield novel phases.

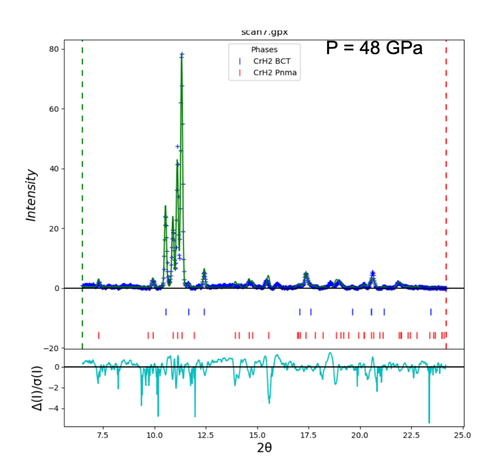

Figure 8: XRD Intensity vs 2θ reveals a novel phase of CrH_2.

CONCLUSIONS

We have successfully synthesized chromium polyhydride phases CrH_2, Cr_2H_5, and another tetragonal CrH_2 phase using the high temperature and pressure approach. CrH_2 was synthesized after heating to 1862 ± 200 K and Cr_2H_5 was synthesized after heating to 2380 ± 200 K, while at high pressure. Another predicted phase, CrH_3, was not observed at the pressure range of our experiments. Moreover, a tetragonal CrH_2 phase was observed upon decompression, which is a new phase that was not predicted by previous theoretical models. Indeed, the synthesis path using decompression should provide an additional direction for future on synthesis of other new metal hydrides. The discovery of these new phases should provide crucial information for improving theoretical models at high pressures, and could potentially lead to finding new functional materials.

ACKNOWLEDGMENTS

The research team is very appreciative of all of the advice, efforts and hard work of Muhtar Ahart, Maddury Somayazulu, and the entire HPCAT Staff, as well as the APS User Office and Argonne Educational Programs.

The team would also like to acknowledge LTHS Science Teachers, Mr. Rich Fullriede, Mr. Brian Lessner, Dr. John Greenan, and Dr. Robert McBride.

REFERENCES

Laser micro-machining system: Hrubiak, R., S. Sinogeikin, E. Rod, G. Shen. (2015) The laser micro-machining system for diamond anvil cell experiments and general precision machining applications at the High Pressure Collaborative Access Team. *Review of Scientific Instruments*, 86, 072202.
Dioptas program: *DIOPTAS*: a program for reduction of two-dimensional X-ray diffraction data and data exploration. Clemens Prescher and Vitali B. Prakapenka High Pressure Research Vol. 35 , Iss. 3,2015. DOI: 10.1080/08957959.2015.1059835
Fityk program: M. Wojdyr, J. Appl. Cryst. 43, 1126-1128 (2010)
Vesta program: K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *J. Appl. Crystallogr.*, 44, 1272-1276 (2011).
Dubrovinsky, L., Dubrovinskaia, N. , Prakapenka, V. B. & Abakumov, A. M. Implementation of micro-ball nanodiamond anvils for high-pressure studies above 6Mbar. Nat. Commun. 3, 1163 (2012).
Henderson, B. (2019) *The Stuff of Dreams.* Scientific American.
Van Zee, R., DeVore, T. & Weltner Jr, W. CrH and CrH2 molecules: ESR and optical spectroscopy at 4K. J. Chem. Phys. 71, 2051–2056 (1979).
Xiao, Z., Hauge, R. & Margrave, J. Reactions and photochemistry of chromium and molybdenum with molecular hydrogen at 12K. J. Phys. Chem. 96, 636–644 (1992).
Yu, S., Jia, X., Frapper, G., Li, D., Oganov, A. R., Zeng, Q., & Zhang, L. Sci. Rep. 5, 17764 (2015)
Marizy, A., Geneste, G., & Loubeyre, P. Synthesis of bulk chromium hydrides under pressure of up to 120 GPa. Phys. Rev. B, 184103 (2018).

U.S. DEPARTMENT OF ENERGY
Argonne National Laboratory is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC.
LOCKPORT PORTERS
Argonne NATIONAL LABORATORY