doi:10.1017/S1431927622006870
Microsc. Microanal. 28 (Suppl 1), 2022

Atomic-Scale Phase Transformation of $CrCl_3$ Elucidated by Cryo-STEM

Hsin-Yun Chao[1*], Miaofang Chi[1*]

[1] Oak Ridge National Laboratory, Center for Nanophase Materials Sciences, Oak Ridge, Tennessee, United States
* Corresponding authors: chaoh@ornl.gov, chim@ornl.gov

With the development of quantum spintronic devices, the ability to control both spin and charge degrees of freedom in nano-electronics is a forefront necessity [1]. Characterization of two-dimensional (2D) semiconducting magnetic materials is an important area of research due to their low-dimensionality and versatility. However, the atomic scale transformations for quantum materials have yet to be thoroughly explored. Quantum systems often have phase transitions at low temperatures, altering their atomic ordering and electron spin. The competition of phases can often lead to changes in magnetic states and structural heterogeneity [2]. Scanning Transmission Electron Microscopy (S/TEM) is an advantageous way to perform atomic-scale imaging and spectroscopy measurements. In order to explore the low-temperature phase phenomena, cryogenic STEM (cryo-STEM) has been developed in recent years to provide a technique that probes the complex states of quantum materials at liquid nitrogen temperatures from atomic to mesoscopic scales.

Chromium trihalides (CrX_3) form a group of 2D quantum materials with exemplary properties in which the magnetic state can depend sensitively on stacking and temperature. $CrCl_3$, a chromium trihalide semiconductor with a Curie temperature at 16 K, above which it transitions from ferromagnetic to paramagnetic, has yet to be thoroughly investigated using STEM techniques. Previously, CrX_3 materials have been reported to undergo phase transformation from a high-temperature monoclinic to low-temperature rhombohedral by X-ray powder diffraction [3,4]. In particular, $CrCl_3$ is reported to have this transition around 230 K. Though $CrBr_3$ is demonstrated to experience the expected structural transition via 4D-STEM, STEM imaging by Ray et al. suggests CrI_3 does not undergo phase transformation to rhombohedral at low temperatures, but there exists 0 ° and ±120 ° monoclinic variants that can appear to have three-fold symmetry resembling the rhombohedral phase due to stacking [5]. This fascinating structural disparity could be applicable to other CrX_3 materials, altering previously established preconceptions. In this work, we elucidate the structural changes for low-dimensional $CrCl_3$ both at room temperature and cryogenic temperatures.

We obtain low-dimensional $CrCl_3$ flakes 10 to 20 nm in thickness via mechanical exfoliation. The sample is deposited on a holey carbon copper TEM grid and coated with ≈ 2 nm of amorphous carbon to improve contrast. Subsequently, the sample is imaged in STEM mode at 200 kV with a convergence semi-angle of 27.4 mrad and an annular dark field (ADF) collection angle of 68 to 280 mrad. Atomic resolution STEM ADF images are obtained both at 295 K and 99 K, with the latter temperature well below the predicted structural transition temperature of 230 K. Furthermore, selected area diffraction (SAD) is used to confirm structural changes and variations observed. Notably, the structure for $CrCl_3$ at the two temperatures studied (295 K and 99 K) are structurally congruous, which deviates from previous phase predictions. Our experiments show structural similarities between CrI_3 and $CrCl_3$ in retaining the monoclinic structure with rotational variants creating a three-fold-like symmetry in the diffraction pattern when stacked. Distinct structural transformations of $CrCl_3$ as well as its implications for future device integration will also be discussed. [6]

References:

[1] A Hirohata, H Sukegawa, H Yanagihara, I Žutić, T Seki, S Mizukami and R Swaminathan, EEE Transactions on Magnetics **51** (2015), pp. 1-11. doi: 10.1109/TMAG.2015.2457393.
[2] Y Cui and L Kourkoutis, Accounts of Chemical Research **54** (2021), p. 3619-3620. doi: 10.1021/acs.accounts.1c00373
[3] B Morosin and A Narath, The Journal of Chemical Physics **40** (1964), p. 1958-1967. doi: 10.1063/1.1725428
[4] M Mc Guire, Crystals **7** (2017), p. 1-25. doi: 10.3390/cryst7050121.
[5] A Ray, Y Shao, Y Xu, N Sivadas, T Li, Z Wang, K Mak, J Shan, C Fennie, and D Muller, Microscopy and Microanalysis **26** (2020), p. 636-638. doi: 10.1017/s1431927620015366.
[6] Microscopy research was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, which is a US Department of Energy (DOE), Office of Science User Facility. This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC0500OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).