1090
doi:10.1017/S143192762001692X
Microsc. Microanal. 26 (Suppl 2), 2020

Stable Continuously Variable Temperature Cryo-STEM to Understand the Structurally Driven Phase Transition in the 2D Layered Magnet Nb_3Br_8

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Two-dimensional (2D) magnetic materials have recently emerged at the forefront of quantum materials research for their distinct thickness-dependent properties [1,2]. Niobium halides of form Nb_3X_8 are new class of 2D layered materials that exhibit a paramagnetic to non-magnetic transition upon cooling [3,4]. Loss of magnetism at low temperature in these geometrically frustrated materials has been coupled to a structural transition with re-stacking of the van der Waals layers from a 2-layer (α-phase, Fig. 2a) to a 6-layer (β-phase, Fig. 2d) unit cell [4]. The transition temperature to the β-phase occurs between 90-293 K depending on composition [5]. The precise mechanisms by which these types of phase transitions occur have remained elusive. Achieving atomic-scale imaging at a broad range of temperatures, cryogenic and intermediate, over multiple temperature cycles will advance our fundamental understanding of the magnetic transitions in these systems.

While sub-Ångström-resolution STEM has become routine in radiation-hard inorganic crystals, only recently has it been applied at cryogenic temperatures to study low-temperature physics such as charge ordering [6-9]. However, high-resolution STEM at intermediate temperatures to track the evolution of exotic states remains a serious challenge. With standard side entry cryo-holders modulating the sample temperature beyond the cryogenic baseline significantly disrupts the thermal equilibrium of the system, resulting in insurmountable sample drift for atomic-resolution studies. Here, we demonstrate a new side-entry, dual-tilt cryogenic holder (HennyZ) that combines liquid nitrogen cooling with fast, local heating via a 6-pin MEMS device, enabling intermediate temperature studies and the possibility for advanced experiments, such as *in situ* biasing [10]. Figure 1a shows an atomic-resolution HAADF STEM image of Nb_3Br_8 acquired at ~223 K in an FEI Titan Themis operated at 300 kV. The high signal-to-noise ratio and spatial resolution are enabled by consistently low drift rates of 0.3-0.4 Å/s (Fig. 1) at temperatures ranging from ~100 K to well above room temperature. Furthermore, the local heating allows the temperature to be cycled repeatedly and rapidly within a single experiment, affording novel dynamic studies. With the advent of this continuously variable temperature (CVT) cryo-STEM, we can now investigate the phase transitions in Nb_3Br_8 flakes at the temperatures where they occur.

The structure of exfoliated Nb_3Br_8, ~60 nm thick, was studied at atomic resolution with CVT cryo-STEM while cycling the temperature within the hysteresis of the full structural transition (~723 K to ~100 K to ~723 K) in ~10 K increments (Fig. 2). As shown in Figure 2a,d, the stacking sequences of the α- and β-phase structures are easily distinguished in plan-view. Our cryo-STEM temperature cycle experiments provide several significant insights into the nature of the structural phase transition from the α- to β-phase. First, the stacking changes do not occur abruptly. Rather, a series of unexpected, metastable intermediate stacking sequences are observed, as seen in Figure 2b,e, with transition phases of varying degrees of order (Fig. 2c). Second, the apparently stable intermediates encountered on heating *vs* cooling are distinct. Surprisingly, the full structural transition (from the starting α-phase, cooling to the β-phase, then heating to recovery of the α-phase) exhibits a wide hysteresis of ~400 K as opposed to < 20 K observed in the

magnetic transition of the bulk material [5]. Interestingly, we found that the hysteresis of this gradual structural transition grows as the exfoliated flakes become thinner, reaching >900 K in specimens thinner than 40 nm. This suggests the possibility of intermediate magnetic states as well. The tunable hysteresis observed here could be used as a handle to access a desired stacking sequence with specific magnetic properties. Additionally, there exists the possibility of preserving paramagnetism in this geometrically frustrated material to low temperature and accessing new physics, such as spin liquids. Understanding van der Waals stacking changes in 2D materials at the atomic scale is critical for rationally controlling quantum effects and tailoring their transition temperatures. To this end, we have demonstrated CVT cryo-STEM as an effective local probe for revealing novel structural phenomena in 2D layered materials within phase transitions, such as unexpected stacking sequences. [11]

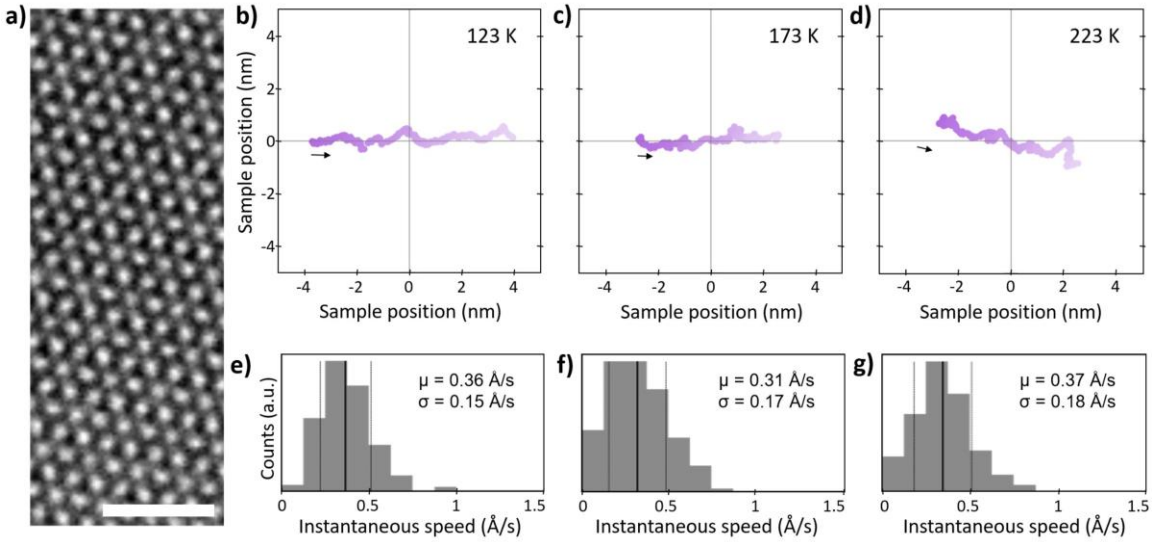

Figure 1. Stable high-resolution imaging at intermediate temperatures. (a) Atomic-resolution HAADF-STEM image of Nb3Br8 at ~223 K. Scale bar=1 nm. Drift performance of the continuously variable temperature cryo-STEM holder at various low temperatures measured by sample positions plotted over a time of 250 s at (b) 123 K, (c) 173 K, and (d) 223 K. (e-g) Corresponding instantaneous drift speed histograms. Mean speed (μ) and standard deviations (σ) marked by solid and dotted vertical lines, respectively. Figure adapted from reference [10].

https://doi.org/10.1017/S143192762001692X Published online by Cambridge University Press

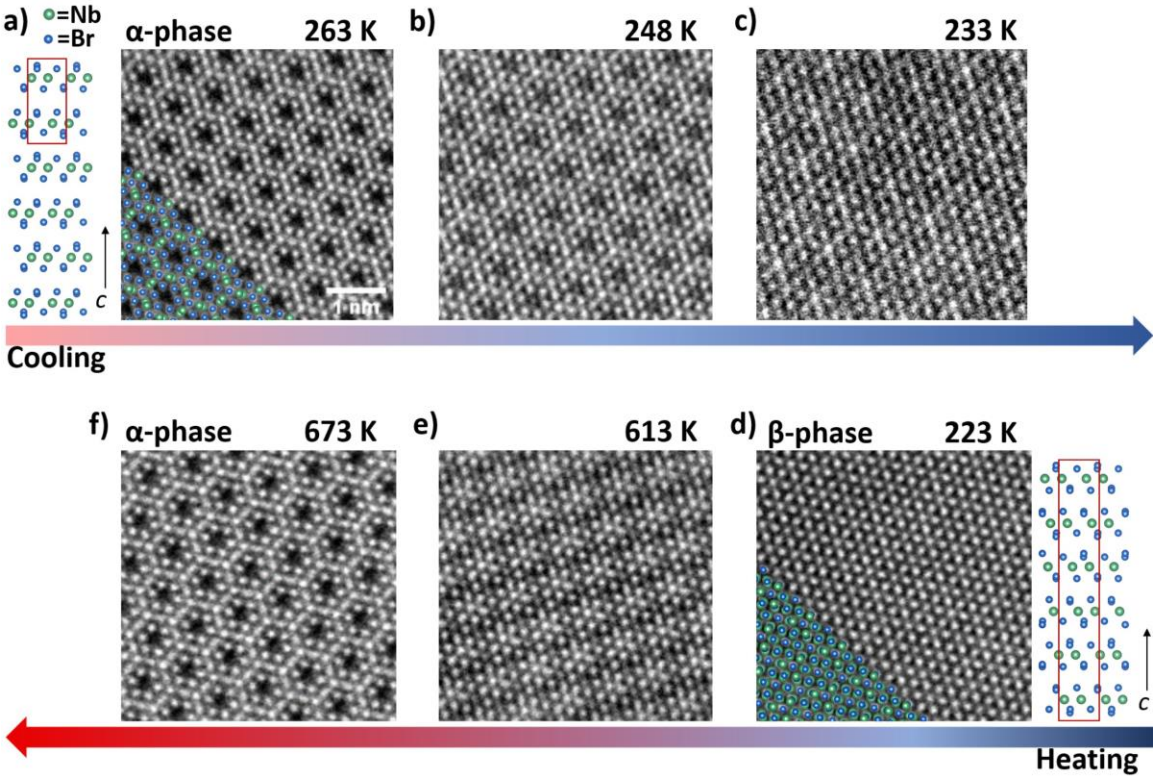

Figure 2. Atomic-scale visualization of a phase transition at intermediate temperatures. Plan-view HAADF STEM images of (a) α-Nb3Br8 at 263 K, (b) an intermediate phase at 248 K, (c) a disordered transition phase at 233 K, (d) β-Nb3Br8 at 223 K, (e) an intermediate phase at 613 K, and (f) recovery of α-Nb3Br8 at 673 K. Images were taken sequentially on the same flake during temperature cycling in a single experiment. Predicted α-Nb3Br8 and β-Nb3Br8 structures as viewed down the c axis are overlaid on corresponding images and models of cross-section views are shown next to each image (red box denotes the unit cell). Scale bar=1 nm; all images are same scale.

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[11] This work is supported by PARADIM, an NSF-MIP (DMR-1539918), and NSF DMR-1429155 & DMR-1719875.

https://doi.org/10.1017/S143192762001692X Published online by Cambridge University Press