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Unraveling the Relationship Between Layer Stacking and Magnetic Order in Nb_3X_8 Systems via Controlled-Temperature Cryo-STEM

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Achieving sub-Ångström resolution in cryo-STEM has enabled precise mapping of structural responses related to underpinning low-temperature physics, such as periodic lattice displacements and associated charge density waves [1-3]. Most high-resolution cryo-STEM, however, is performed at the absolute temperature of the holder, precluding access to intermediate temperatures, and thus limiting the ability to track structural transformations and the emergence of correlated phases over temperature. Here, we use controlled-temperature cryo-STEM to explore the effects of temperature and composition on the layer stacking of van der Waals Nb_3X_8 (X=Cl or Br) and its relationship to magnetic order measured *ex situ*.

Nb_3X_8 are insulating, cluster-based, layered materials that exhibit an antiferromagnetic to non-magnetic transition [4]. In Nb_3Cl_8, the loss of magnetic order occurs at temperatures below 90 K and has been coupled to a symmetry-lowering crystallographic distortion and layer stacking change from a 2-layer (α-phase) to a 6-layer (β-phase) unit cell [5]. Figure 1a shows a cryo-STEM image of the 2-layer unit cell of α-Nb_3Cl_8 imaged at 93 K using a Gatan 636 liquid-N_2 specimen holder, but the lower temperature β-phase is inaccessible. The transition temperature, however, depends strongly on composition with Nb_3Br_8 exhibiting the β-phase at 293 K (Fig. 1b). While tuning of the magnetic ordering temperature through composition is appealing, the mechanism by which the layer stacking reorganizes is not understood. In order to unravel this at temperatures accessible through cryo-STEM, we analyzed specimens of the doped system $Nb_3Cl_2Br_6$. Plan view imaging demonstrates the transformation of $Nb_3Cl_2Br_6$ from an apparent α-phase at 293 K to β-phase at 93 K (Fig. 2). Cryo-STEM imaging of cross-sectional specimens, however, reveals that the reorganization of layer stacking does not occur. Rather, persistent stacking faults are observed accompanying a 2-layer unit cell (Fig. 1c). This may explain the apparent restacking observed in plan view or possibly indicates that the transition in cross-sectional TEM samples is suppressed.

Pinpointing the emergence of these structural changes and their relationship to magnetic order necessitates atomic-resolution imaging at more than two temperatures. Thus, to achieve controlled-temperature cryo-STEM on an aberration-corrected Titan Themis 300, we have employed the novel HennyZ liquid-N_2 specimen holder equipped with a 6-pin MEMS system for local heating [6]. This expands the realm of cryo-STEM to any desired intermediate temperature from room temperature down to near liquid-N_2 temperature. With this advancement we have observed the structural phase transformation onset in $Nb_3Cl_2Br_6$ with atomic-resolution at ~225 K (Fig. 2b). This new capability allows us to investigate the implications of composition and temperature on layer stacking in a single materials system. Understanding the mechanism of stacking changes and their effect on magnetic ordering will afford handles for new materials with tailored transition temperatures [7].

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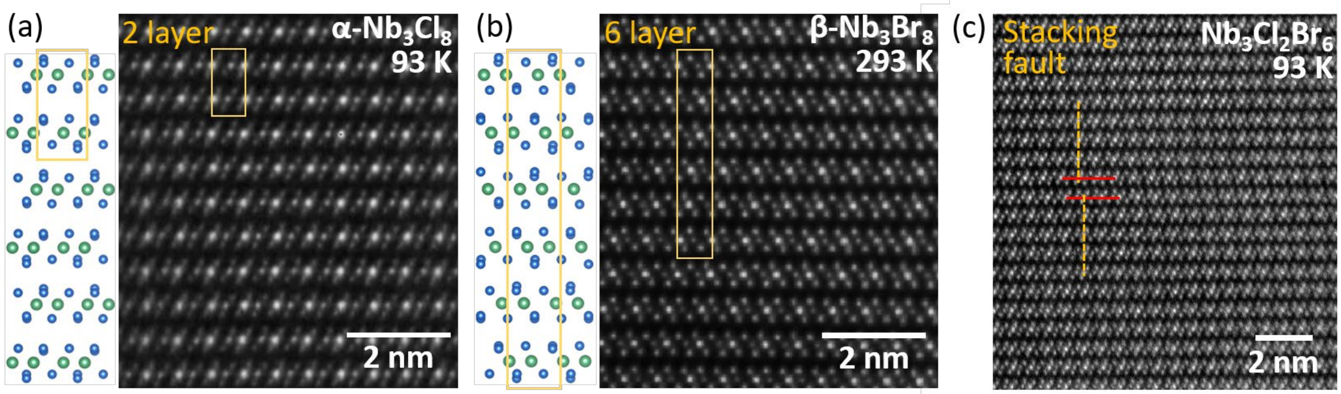

Figure 1. HAADF STEM imaging of cross-sections of (a) α-Nb_3Cl_8 at 93 K and (b) β-Nb_3Br_8 at 293 K. Yellow boxes on images and corresponding schematics indicate the 2- and 6-layer unit cells of the α and β phases, respectively. To access the low temperature β-phase in Nb_3Cl_8 cooling below 90 K is required. (c) $Nb_3Cl_2Br_6$ exhibiting the 2-layer unit cell and a stacking fault (red lines) at 93 K.

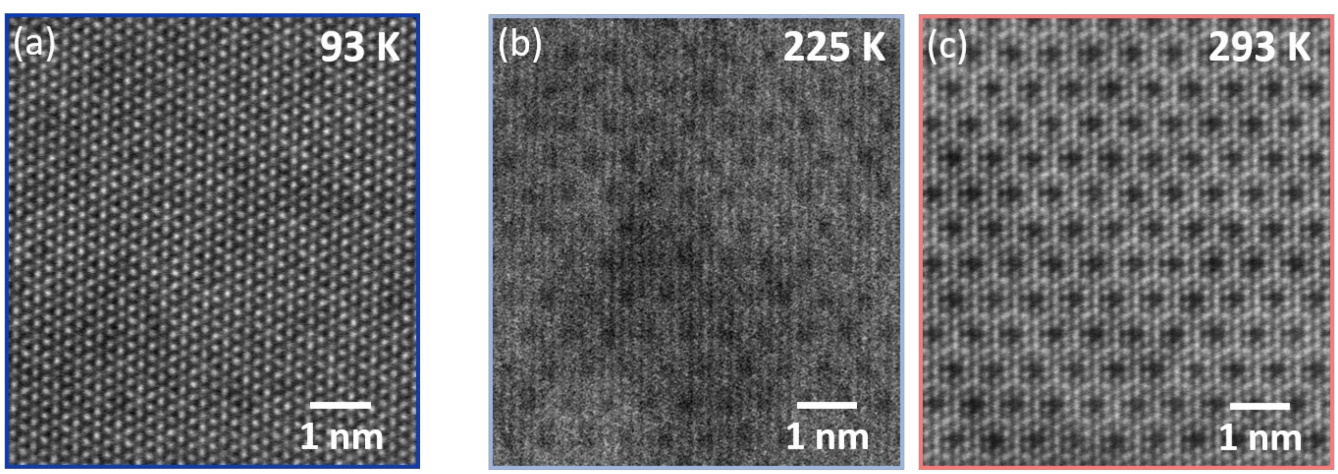

Figure 2. Tracking phase changes in $Nb_3Cl_2Br_6$ by controlled-temperature cryo-STEM: Plan view HAADF-STEM images of $Nb_3Cl_2Br_6$ at (a) 93 K (holder absolute temperature), (b) 225 K exhibiting a transformation onset, and (c) 293 K (b,c using the cryo+MEMS HennyZ holder). The reduced contrast in (b) is largely due to a decrease in crystalline order rather than to instabilities at the sample from the cooling holder. Note: (a) taken from different region than (b,c).

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