Square-Plane Rotation in $K_2MnCl_2I_2$

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Background and aim. This proposal targeted the origin of large uniaxial negative thermal expansion (NTE) in mixed-halide layered perovskites $K_2MCl_2X_2$. Synchrotron X-ray diffraction had established the lattice parameter evolution, but the low-temperature symmetry remained uncertain because the distortion is dominated by subtle halide displacements. High-resolution neutron powder diffraction (NPD) was therefore required to distinguish candidate structures and clarify the microscopic mechanism. We report here the 200 K result for $K_2MnCl_2I_2$, which shows *c*-axis NTE below at low temperatures.

Experiment. Air-sensitive polycrystalline $K_2MnCl_2I_2$ was sealed in a 6-mm-diameter vanadium sample holder. Variable-temperature NPD data were collected on HERMES using constant-wavelength neutrons (λ = 2.195 Å) and a closed-cycle refrigerator. The 200 K pattern, measured below the transition, was analyzed by Rietveld refinement with GSAS-II. A supercell generated by cooperative rotation of $MnCl_4$ square planes fitted the data well, which is described by an orthorhombic *Aeam* space group.

Results. The *Aeam* model reproduces the observed profile satisfactorily (**Fig. 1,** R_w = 7.05%), compared to other candidate models. The refined lattice parameters are *a* = 7.1063(11) Å, *b* = 7.1139(13) Å, and *c* = 17.5869(23) Å. Its agreement is better than that of the *c*-axis-doubled $I4_1/acd$ alternative (R_w = 7.37%), and the diffraction pattern provides no evidence for *c*-axis doubling.

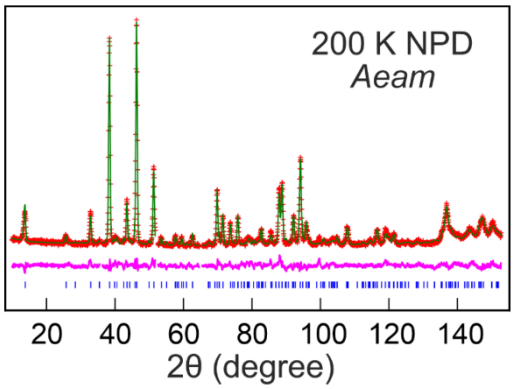

Fig. 1. Observed (red crosses), calculated (green line), and difference (magenta line) profiles for the *Aeam* refinement of HERMES NPD data from $K_2MnCl_2I_2$ at 200 K, blue ticks mark Bragg positions.

Conclusion. The 200 K NPD result assigns the low-temperature phase to *Aeam* and identifies in-plane rotation of rigid $MnCl_4$ squares as the origin of the superstructure. Together with the temperature-dependent lattice data, it links the rotation below the transition to the large uniaxial NTE. The experiment thus achieved the central objective of the proposal: resolving a chloride-driven distortion that was ambiguous by X-ray diffraction and establishing the structural basis for a strain-relief mechanism in the mixed-anion lattice. This result constitutes a key component of our manuscript, which is currently under review.