Investigation of Ammonium Dynamics in Layered Halide Perovskites

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Layered halide perovskites have garnered significant research interest recently due to their outstanding photovoltaic performance. These materials can incorporate a variety of organic or inorganic polyatomic cations. Unlike conventional oxide perovskites, which typically contain only monoatomic cations, the inclusion of polyatomic cations in halide perovskites provides additional structural flexibility, potentially enhancing functionalities not found in oxide perovskites.

While much research has focused on the practical applications of halide perovskites, the fundamental structural chemistry and dynamic behavior of polyatomic ions remain underexplored. To address this gap, we synthesized and investigated ammonium-based halide perovskites.

Our study concentrated on an n = 1 Ruddlesden-Popper perovskite, $(NH_4)_2MnCl_4$. Our additional measurements, including specific-heat, synchrotron X-ray diffraction, and neutron powder diffraction on deuterated samples, revealed complex phase transitions, showing four distinct symmetries as the material cooled from room temperature to 2 K. Additionally, we observed significant uniaxial negative thermal expansion. Understanding the structural chemistry and thermal behavior of this material may provide insights for designing similar materials.

Although synchrotron and neutron diffraction provided information on the average symmetry, they failed to clarify the behavior of ammonium cations, such as potential order/disorder transitions or their relationship to bulk symmetry changes. To probe ammonium dynamics, we employed quasi-elastic neutron scattering (QENS), taking advantage of hydrogen's large incoherent neutron scattering length. Using the AGNES spectrometer at JRR-3, we collected high-quality QENS data, which was used to determine the mean-square displacement of hydrogen $\langle U^2 \rangle$ (Figure 1).

Interestingly, data collected between 80 K and 200 K showed a linear trend, spanning all three phase transitions, indicating no clear evidence of a conventional order/disorder or static/dynamic transition. Instead, ammonium freezing appears to be a continuous process. However, slope changes at ~200 K and ~80 K suggest a correlation between bulk symmetry changes and ammonium dynamics at these two temperatures. We are continuing to analyze the QENS data to develop a comprehensive interpretation of these findings.

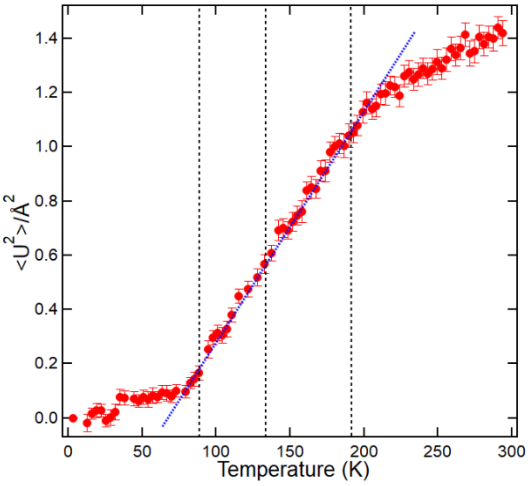

Fig. 1. Mean-square displacements of hydrogen $\langle U^2 \rangle$ as a function of temperature for $(NH_4)_2MnCl_4$, derived from raw data collected using the AGNES neutron spectrometer at JRR-3. The dashed lines indicate the three phase transitions identified through specific-heat measurements and diffraction data.