

Experimental report

15/09/2023

Proposal: 7-02-216

Council: 10/2022

Title: Diffuse scattering and critical dynamics in alkali metal nitrates

Research area: Physics

This proposal is a resubmission of 7-02-210

Main proposer: Petr ONDREJKOVIC

Experimental team: Martin KEMPA
Petr ONDREJKOVIC

Local contacts: Andrew WILDES
Alexandre IVANOV
Andrea PIOVANO

Samples: RbNO₃

Instrument	Requested days	Allocated days	From	To
IN8 Flatcone	6	6	05/04/2023	12/04/2023
ORIENTEXPRESS	1	1	05/04/2023	06/04/2023

Abstract:

Alkali metal nitrates are examples of rare materials having symmetry-breaking structural phase transitions that give rise to polarity and chirality at the same time. These phase transitions are associated with the onset of a peculiar three-dimensional chiral modulation of the orientation of the NO₃ groups. We aim to trace a dynamical signature of their pretransitional correlations in the RbNO₃ single crystal in order to clarify the mechanism of this transition.

Diffuse scattering and critical dynamics in alkali metal nitrates

The experiment 7-02-216 was performed on the Laue neutron-diffractometer OrientExpress (5.4.2023) and the thermal triple-axis spectrometer IN8 (5.-12.4.2023). The main aim was to study critical dynamics in Rubidium nitrate (RbNO_3) single crystal. This was done via investigation of diffuse scattering in the vicinity of its phase transition ($T_C = 437$ K) to obtain information about correlated (rotational) vibrations of $[\text{NO}_3]^-$ anions which could be responsible for the non-trivial multiplication of the unit cell below T_C ($Pm-3m > P3_1/P3_2$) [1].

We used the OrientExpress in its standard configuration to realign a single crystal of RbNO_3 (volume of 120 mm^3) after its wrapping in an Al foil and fixed to an Al holder. The crystal was aligned to have the $[111]_{\text{pc}}$ (ferroelectric trigonal axis) and $[-110]_{\text{pc}}$ axes horizontal (see Fig. 1). Typical exposure time was 60 s and the accuracy of the relative alignment was less than 3 degrees which was sufficient for the principal experiment on the IN8.

The IN8 was operated in its standard configuration, with Si monochromator and the FlatCone multianalyzer (Si(111) with $k_f = 3 \text{ \AA}^{-1}$). The energy resolution was 1.4 meV (vanadium standard was used). The prepared RbNO_3 crystal was placed in a standard Orange cryofurnace. As proposed, the crystal was investigated at 298 K, 441 K (just above the T_C when heating up) and 464 K (high enough above T_C , but low enough below the next phase transition at 492 K), by taking global overview maps mostly at 0, 2, 4, and 6 meV in the equatorial scattering plane defined by $[111]_{\text{pc}}$ and $[-110]_{\text{pc}}$ axes (see Fig. 2). To understand various diffuse streaks which appeared above T_C (see Fig. 2c), we also mapped elastic and inelastic diffuse scattering out of the equatorial scattering plane. The IN8 allowed us to measure up to $1/6$ r.l.u along the $[11-2]$ direction which was enough to reach other non-equivalent Brillouin zone

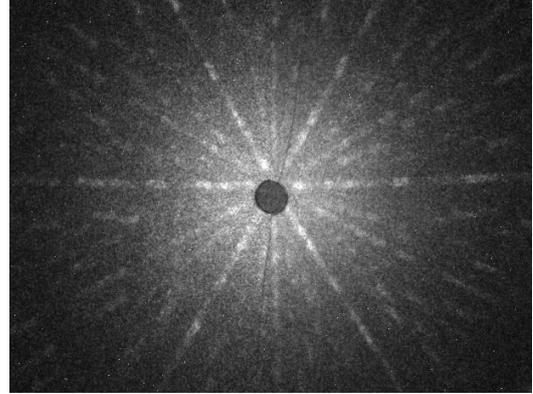


Fig. 1: Typical Laue diffraction pattern of RbNO_3 along its trigonal axis ($[111]$ pseudocubic axis).

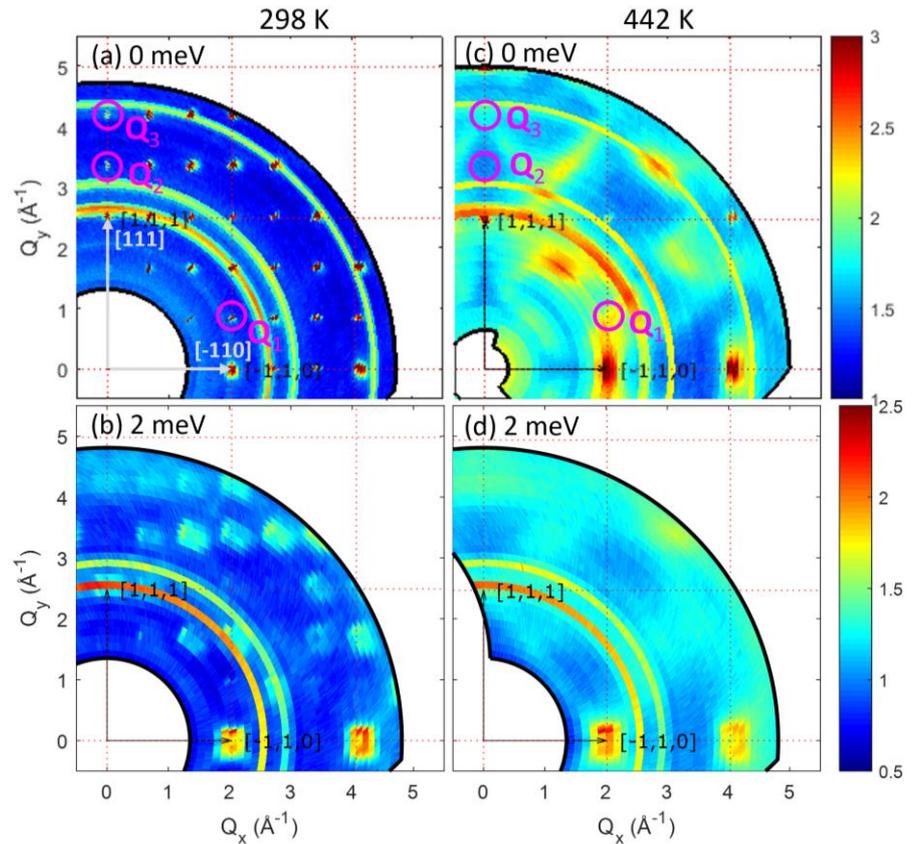


Fig. 2: Neutron scattering maps at 0 and 2 meV: (a,b) in the ferroelectric phase at 298 K and (c,d) in the paraelectric phase at 442 K.

centers (e.g., 100 and 101) from which transverse diffuse scattering streaks also come to the equatorial plane, similarly as the transverse diffuse scattering seen in the -110 zone in Fig. 2c. Because of these extensive measurements, we finally did not switch to the single detector as originally proposed. Examples of measured spectra at selected Γ points of the ferroelectric phase are plotted in Fig. 3. An optical phonon polarized along the ferroelectric trigonal axis was observed (see Fig. 3b).

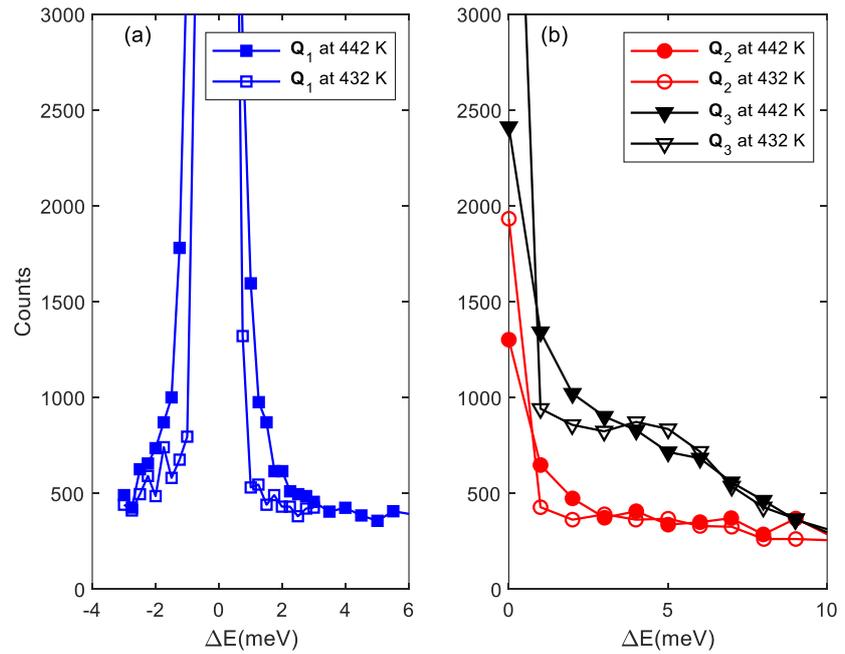


Fig. 3: Neutron scattering spectra at 442 K (above T_C) and 432 K (below T_C) taken on cooling. The selected \mathbf{Q} are also marked in Fig. 2a,c: $\mathbf{Q}_1=(-2/3,4/3,1/3)$, $\mathbf{Q}_2=(4/3,4/3,4/3)$, and $\mathbf{Q}_3=(5/3,5/3,5/3)$.

We found that the strong streaks of diffuse scattering, which appear above T_C , are mostly resolution-limited on the IN8 (see Fig. 2d and Fig. 3a). This scattering remains strong at least up to 20 K above T_C in agreement with total synchrotron scattering [2]. However, neutron scattering gives a stronger contrast of different features due to strong scattering from $[\text{NO}_3]^-$ anions. When cooling down from 465 K to the ferroelectric phase, its scattering remains constant and disappears abruptly at 432 K (note the considerable thermal hysteresis). At the same time, we observed that the phase transition is destructive, in the sense that the single crystal is split in domains which cannot be removed when heating it back to its paraelectric phase.

In conclusion, we found strong mostly resolution-limited diffuse scattering in the paraelectric phase of RbNO_3 on the thermal three-axis spectrometer IN8. This scattering remains strong high above the $T_C = 437$ K in agreement with the total synchrotron scattering [2].

References:

- [1] J. Liu *et al.*, *J. Solid State Chem.* **160**, 222 (2001).
- [2] M. Paściak, P. Ondrejko, J. Fabry, *et al.* (2022), unpublished results.