Experimental report

28/12/2021

Proposal: **7-02-190**

Council: 10/2019

Title: Soft phonon mode in quantum paraelastic $BaZrO_3$

Research area: Materials

This proposal is a continuation of 7-02-180

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Experimental team: Andrea PIOVANO

Local contacts: Andrea PIOVANO

Samples: $BaZrO_3$

Instrument	Requested days	Allocated days	From	To
IN8	6	6	01/02/2021	07/02/2021

Abstract:

The aim of the project is to demonstrate and characterize the phenomenon of "quantum paraelasticity" in the cubic perovskite $BaZrO_3$. For that purpose, we propose to measure its "soft" phonon mode, the associated branch, and its evolution with temperature, with the aim to elucidate the role of quantum fluctuations in the phonon frequencies.

A test experiment was carried out on IN22 and has enabled us to identify the mode of interest, and partly characterize its dispersion and its temperature-dependence. Here, we propose a follow-up experiment to complete the dispersion of the tilt mode(s) and the acoustic modes along the directions of interest at room and low temperatures.

Report on proposal 7-02-190

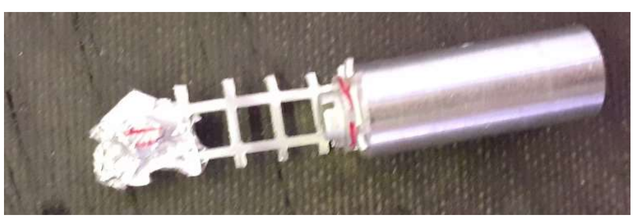
The objective of the project is to study the octahedra "tilt" phonon mode in $BaZrO_3$, which is predicted to be unstable by DFT but remains stable in experiments at all investigated temperatures[1,2,3]. We want in particular to determine its dispersion, and check his expected softening at low temperatures. This problem can in principle be addressed by inelastic neutron scattering, but the main experimental challenge has been for a long time the small size of the available crystals. Here, we take advantage of our recent synthesis of larger single crystals by the floating zone technique to study this special case of lattice dynamics.

In a previous proposal (7-02-180), 3 days were allocated on IN22 for a test measurement. This was a success and gave us significant results. We could identify a low-energy mode at the R point as anticipated. The selection rules observed for this mode are consistent with the tilt mode with symmetry R_4^+. This mode softens strongly with decreasing temperatures. Both at room temperature and at 2 K, we got hints that the mode disperses very strongly in the vicinity of the R point, but the low intensity did not allow us to determine the dispersion.

This proposal is a follow-up where we made use of the higher flux at IN8 to measure more precisely the dispersion of the tilt mode(s) and the acoustic modes along the Γ-R-M directions both at room temperatures and low temperatures.

Experimental details

The experiment was performed on the same $BaZrO_3$ single crystal (~200 mg) that was already used on IN22. Sample preparation was minimal in order to keep as much sample volume as possible. The crystal was oriented with respect to natural faces that could be identified as [001] due to their respective orientations at right angles. The crystal was fixed in the holder using an Al foil (Fig. 1) and placed in an Orange Cryostat.

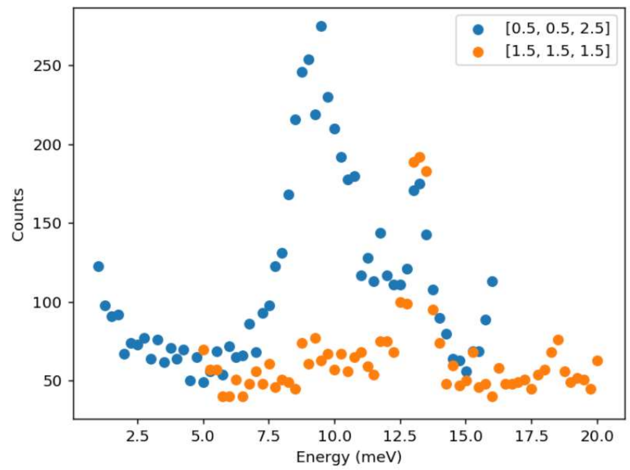


<u>Figure 1:</u> Sample mounted on the Al holder.

The experiment was conducted remotely, with Andrea Piovano (ILL) on site and Mael Guennou and Constance Toulouse (Univ. of Luxembourg) attending remotely via VISA. No technical problem is to be reported, except a leak in the cryostat in the very last hours of beam time that produced strong background signal.

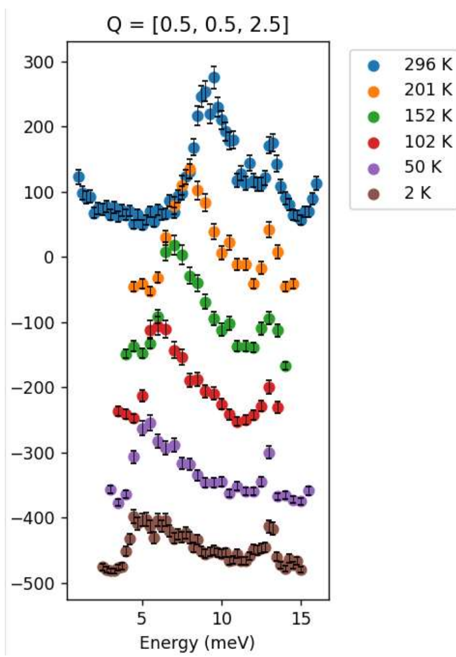
Main results

<u>Result n°1:</u> We confirm the observations on IN22, i.e. the presence of the tilt mode at the R point, its energy and its selection rules (Fig. 2).



<u>Figure 2:</u> Inelastic E-scans at room temperature at different R-points. The mode at 8.5 meV is assigned to the soft mode of interest. The sharp mode at 13 meV is the acoustic mode.

<u>Result n°2:</u> This mode softens with temperature, from ~8.5 meV at room temperature to ~5 meV at 2 K (Fig. 3). The mode becomes also much more asymmetric, which we attribute to an increase in dispersion at low temperatures. A proper fitting of the spectra using the instrumental response and dispersion hypotheses is currently in progress.



<u>Figure 1:</u> Scans at [0.5, 0.5, 2.5] at different temperatures, from room temperature down to 2K.

Result n°3: The dispersions from Γ to R and from R to M could be measured at 2K (Fig. 4). The main acoustic branch is clearly visible, as well as the soft mode around the R point. Like in the test experiment on IN22, we observe that the mode intensity decreases quite strongly as we move away from the R point, but here we could nonetheless follow it to a much better extent. In particular, it can be tracked all the way to the M point where it reaches a rather high energy above 20 meV. There is no indication of any mode at lower energy.

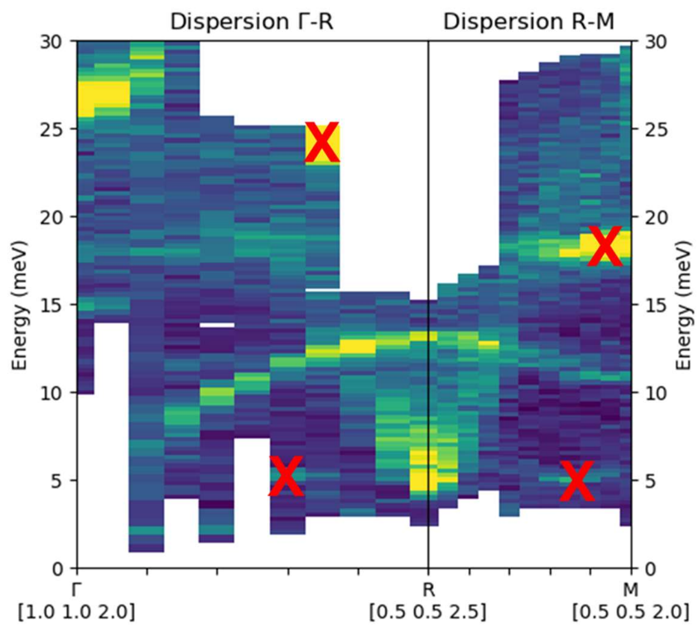


Figure 2: Dispersion from Γ to R and from R to M at 2 K. The red crosses indicate spurions.

Conclusions

The experiment was altogether successful. We could answer the main questions namely confirm the strong dispersion of the tilt mode in the vicinity of the R point and collect data of sufficient quality for an accurate temperature dependence of its frequency. This supports our recent interpretation of the Raman spectrum of $BaZrO_3$ that states that this mode is not visible as an overtone in the Raman spectrum and does not appear in any phonon combination[3].

At this stage, the data collected at IN22 and IN8 looks sufficient to produce a publication on the low-frequency lattice dynamics of $BaZrO_3$ and specifically on the renormalization of the tilt mode frequency at the R point, and thereby make a significant addition to the recent literature on the phonons in $BaZrO_3$[4].

Some questions still remain unanswered, such as the detailed temperature dependence of the modes at the M point. This might be considered for future proposals.

[1] Akbarzadeh *et al.*, Phys. Rev. B 72, 205104 (2005)
[2] Bennett *et al.*, Phys. Rev. B 73, 180102 (2006)
[3] Toulouse *et al.*, Phys. Rev. B 100, 134102 (2019)
[4] Perrichon *et al.*, Chem. Mater. 32, 2824 (2020)