Experimental report

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Proposal: 7-03-145 **Council:** 4/2015

Title: Na diffusion in Na0.7CoO2 at high temperature

Research area: Physics

This proposal is a resubmission of 7-03-128

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Samples: Na0.7CoO2

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	23/10/2015	26/10/2015

Abstract:

Understanding of Na-ion mobility in the layered NaxCoO2 family is very important for both applied as well as fundamental sciences. For x=0.7 we have found two structural phase transitions at about 290 and 400K, strongly coupled to Na diffusion. Above 400K a quasielastic signal could be measured at MARS, PSI. The data analysis is however ambiguous. High quality diffraction experiment suggests, that in this temperature range 2D Na diffusion occures on its hexagonal sublattice. But it is also possible that Na motion is complexer as thought and local motion is measured at MARS. We would like to investigate the quasielastic scattering above 400K with an energy resolution of 1 (or maximum 10) microeV. First choice for this study is IN16b, where we apply for 3 days of beam time. Alternatively IN5 could be also considered.

Na diffusion in $Na_{0.72}CoO_2$ at high temperature

The aim of the beam time was to measure the Na^+ ion diffusion in $Na_{0.7}CoO_2$. It represents a promising family of Na-battery cathods, but also intresting from many other different points of view, where Na^+ ion mobility plays a crucial role.
We knew from previous experiments and literature that

- Na^+ ion is mobile above ∼200K.
- the crystal structure is basically hexagonal, there are alternating CoO_2 and Na_x layers.
- there are 2 phase transition temperatures around 300 and 400K. In the middle temperature range the crystal lattice is distorted in a way that Na-Na distance is shortened along a 1D zig-zag path, which allows Na+ diffusion at this moderate temperatures. This diffusion is probably supported by phonons.
- the hexagonal structure is reached only above the second phase transition, where QENS signal suddenly appears on a spectrometer with $13\mu eV$ energy resolution (MARS, PSI).
- close to certain Na contents, like x=0.7 where Na is selforganised in small clusters, the diffusion coefficient may change drastically.
- samples are very reproducible qualitatively (but not quantitatively), even if the nominal composition is not the same.

Unfortunately at MARS the limited number of Q values and the poore data quality did not even allow to distinguish whether the QENS signal is caused by a longrange or a localised diffusion process. In the literature different methods reported to lead to diffusion coefficients wich differs by 4-5 orders of magnitudes. One of the possible explanations is that they are measuring different processes.
Now, the big improovement of IN16b compared to the old IN16 made it possible to conclude that we do see translational diffusion. The diffusion coefficient is sample dependent, but the variation is far from being orders of magnitudes. Furthermore, we observed QENS signal already in the middle temperature range, which is highly relevant for applications. Details are provided below.

The sample amount and geometry was optimised: 4 g of $Na_{0.7}CoO_2$ powder was distributed on a thin rectangular Al support, packed in Al foil, and rolled into a cylinder. This was then placed in a 22mm diameter sample holder, resulting in a whollow cylinder geometry of 35mm height. Although the maximum intensity is unfortunately very limited due to the Co absorbtion, it was possible to record FWS, IFWS and QENS spectra of sufficient quality.
Two sample has been studied, both being x≈0.7, although the nominal compositions were slightly different (x=0.72 and 0.8, as named later in the report). For both samples FWS and IFWS at 6μeV has been measured between 280 and 430K (Figure 1.). During heating with 0.5K/min 0.5 min/point FWS and 4.5min/point IFWS was measured in an alternating manner. FWS was also recorded during the rapid cooling, which showed a hysteresis of up to 20K. The following QENS spectra have been measured: 5h @ 280K and 12h @ 430K for sample x=0.8, and 24h @ 430K and 6h @ 380 K for sample x=0.72. Empty can and vanadium has been also measured. The statistics of the Vanadium resolution function did profit from the data of the previous user group.

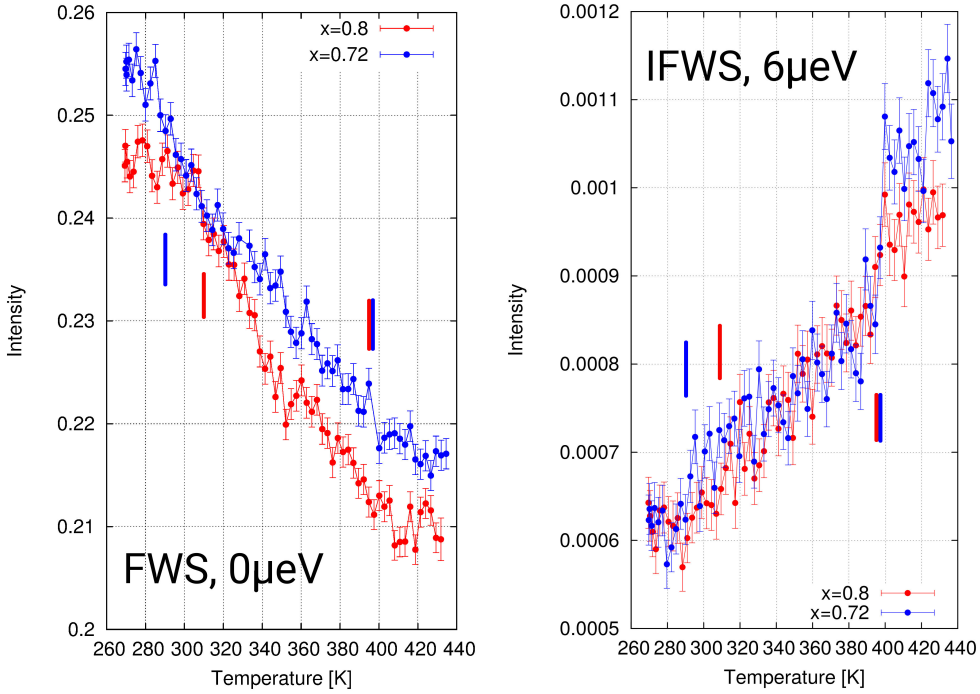

Figure 1: Elastic and inelastic fixed window scans on two slightly different samples (see text for more details). The structural phase transitions at about 300 and 400K (indicated with bars) are much clearer visible in the IFWS data. The intensity increase is due to Na ion diffusion and low energy phonons.

Contrary to MARS, the IFWS spectra are not constant in the middle temperature range. The step around 300K at MARS was caused by low energy phonons, but at this lower energy QENS is also contributing to the intensity increase, as it is evidenced on Fig-

ure 2. The QENS spectra has been fitted preliminarily by an elastic and a Lorentzian component. The Lorentian line with of sample x=0.72 @ 430K clearly indicate a long range translational diffusion. The same sample @ 380K and the second sample @ 430K exhibits slower, but still detectable dynamics. Data analysis is in progress.

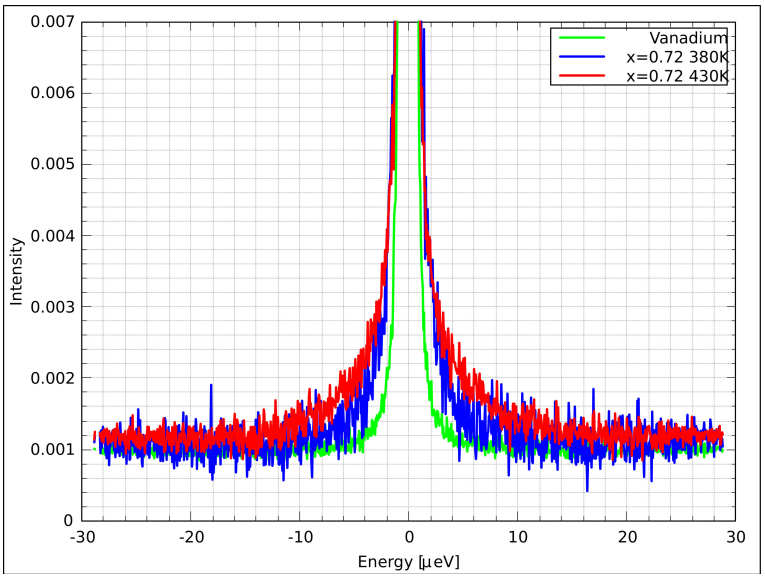

Figure 2: QENS signal is detected not only above the second phase transition (≈400K), but already in the middle temperature range.

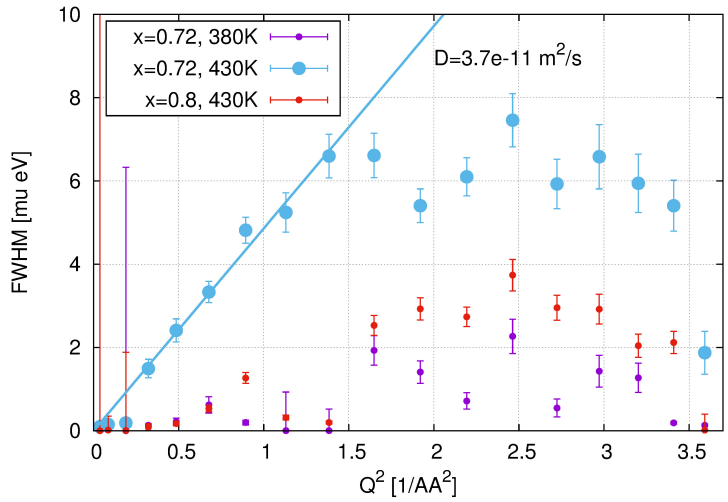

Figure 3: Preliminary fit of the QENS spectra with an elastic component and single Lorentzian suggest long range translational diffusion.