ESRF	**Experiment title:** Rattling modes in new thermoelectrics	**Experiment number**: HS 4530
Beamline: ID28	**Date of experiment**: from: 16.11.2011 to: 22.11.2011	**Date of report**: 26.2.2012
Shifts: 18	**Local contact(s)**: Dr Elena Borissenko	*Received at ESRF:*

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Report:

Sodium cobaltate (Na_xCoO_2) has emerged as a material of exceptional technological interest due to its potential for thermoelectric applications [1,2], and our neutron diffraction studies have demonstrated the central role played by superstructures [3].

A single crystal of $Na_{0.8}CoO_2$ in the ordered stripe phase [4] was mounted on ID28 on a glass needle in two orientations: with (*h*0*l*) and (*hhl*) horizontal scattering planes. The phonon dispersion was measured along several symmetry directions and at many general wave-vector transfers, ***Q***. Figure 1 shows typical data, in this case for the dispersion measured along ΓK. The agreement with a calculation for $NaCoO_2$ using the CASTEP code is very promising.

Preliminary calculations for $Na_{0.8}CoO_2$ with the ordered stripe phase indicate that there is a ***Q***-independent rattler mode at $E \sim 12$ meV. Figure 2 shows experimental evidence for this extra mode in our data, with the correct temperature factor. This is an important result since the rattling of cations is expected to disrupt the propogation of phonons, leading to low thermal conductivity, as required for optimum thermoelectric performance.

Figure 3 shows the temperature dependence of an acoustic phonon at $T \sim 200$ K in the ordered stripe phase, at $T \sim 320$ K in a partially disordered stripe phase, and at $T \sim 400$ K in the disordered phase. There is some broadening and softening of this phonon at elevated temperatures, but the effects are subtle.

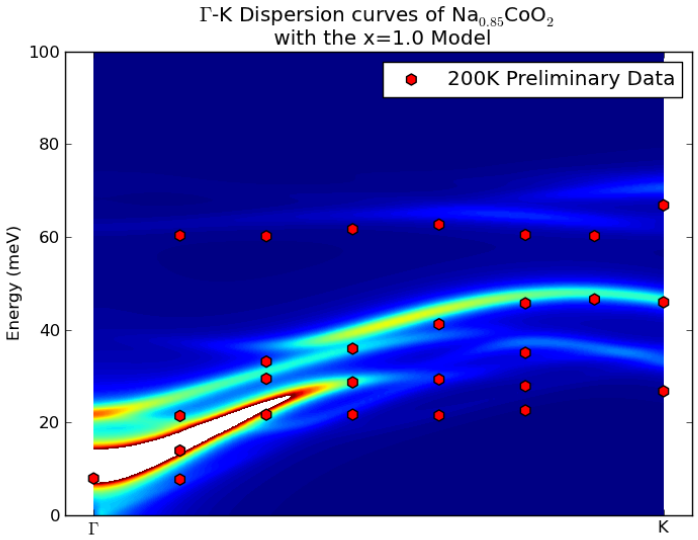
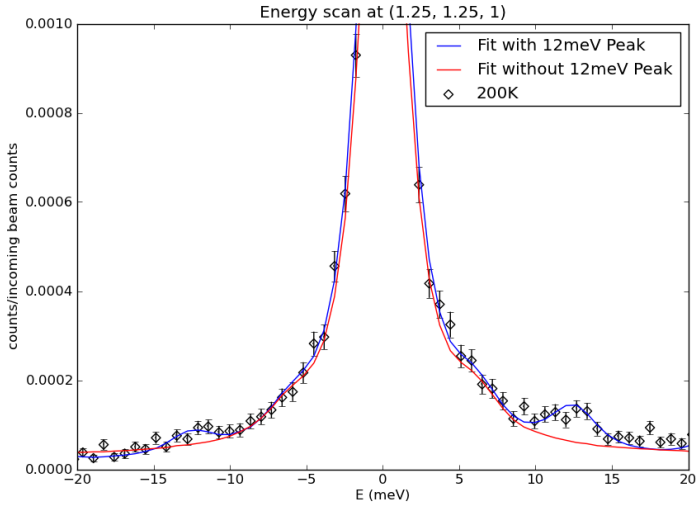


Fig. 1. One of the phonon dispersions along ΓK measured on ID28 (red circles). The data agree well with calculations for $NaCoO_2$ using the CASTEP code (intensity contour diagram).

Fig. 2. A rattler mode was observed at E ~ 12 meV, in agreement with preliminary CASTEP calculations using the ordered stripe phase superstructure for $Na_{0.8}CoO_2$.



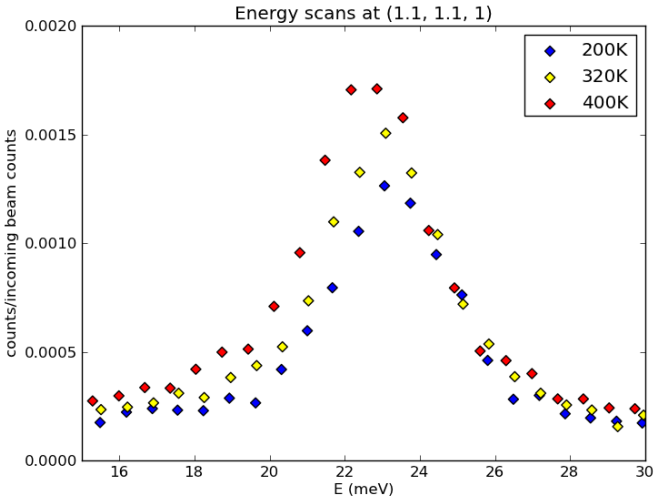


Fig. 3. An acoustic phonon in the ordered stripe phase (blue), a partially disordered stripe phase (yellow) and the disordered phase (red), showing broadening and softening as a function of temperature.

References

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[4] D.J.P. Morris *et al.*, *Phys. Rev. B* **79**, R100103 (2009)