Experimental Report

27/03/2014

Proposal: **7-01-369** **Council:** 10/2012

Title: Phonon lifetimes of the thermoelectric material sodium cobaltate

This proposal is a new proposal

Researh Area: Physics

Main proposer: **GOFF Jonathan P.**

Experimental Team: GOFF Jonathan P.
VONESHEN David

Local Contact: PIOVANO Andrea

Samples: Sodium cobaltate / Na0.8CoO2

Instrument	Req. Days	All. Days	From	To
IN8	8	5	02/05/2013	07/05/2013

Abstract:

Sodium cobaltate has excellent thermoelectric properties, including low thermal conductivity. We have measured its phonon dispersion using inelastic x-ray scattering, and we find that it has well defined modes unlike a phonon glass. First-principles density-functional calculations are in excellent agreement with the data, and we identify a rattling mode. We now propose to use the better energy resolution of inelastic neutron scattering on IN8 to measure the energy line widths of selected modes as a function of temperature. This will allow us to determine the phonon lifetimes and estimate the lattice contribution to the thermal conductivity.

Suppression of thermal conductivity by rattling modes in thermoelectric sodium cobaltate

D.J. Voneshen, K. Refson, E. Borissenko, M. Krisch, A. Bosak, A. Piovano, E. Cemal, M. Enderle, M.J. Gutmann, M. Hoesch, M. Roger, L. Gannon, A.T. Boothroyd, S. Uthayakumar, D.G. Porter, J.P. Goff, *Nature Materials* **12**, 1028 – 1032 (2013).

Abstract

The need for both high electrical conductivity and low thermal conductivity creates a design conflict for thermoelectric systems, leading to the consideration of materials with complicated crystal structures. Rattling of ions in cages results in low thermal conductivity, but understanding the mechanism through studies of the phonon dispersion using momentum-resolved spectroscopy is made difficult by the complexity of the unit cells. We have performed inelastic x-ray and neutron scattering experiments that are in remarkable agreement with our first-principles density-functional calculations of the phonon dispersion for thermoelectric $Na_{0.8}CoO_2$, which has a large-period superstructure. We have directly observed an Einstein-like rattling mode at low energy, involving large anharmonic displacements of the sodium ions inside multi-vacancy clusters. These rattling modes suppress the thermal conductivity by a factor of six compared to vacancy-free $NaCoO_2$. Our results will guide the design of the next generation of materials for applications in solid-state refrigerators and power recovery.