EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Investigation of negative thermal expansion mechanism in $Cd(CN)_2$	**Experiment number**: HC 2437
Beamline: BM01A	**Date of experiment**: from: 25 Mar 2016 to: 29 Mar 2016	**Date of report**: 2.3.2020
Shifts: 6	**Local contact(s)**: Dmitry Chernyshov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

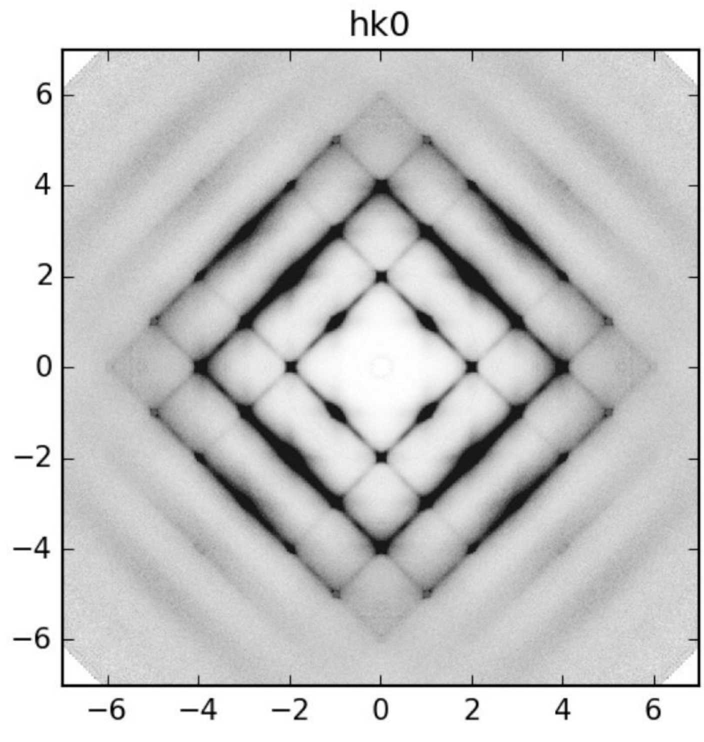
Arkadiy Simonov*[1,2], Hanna Boström*[1], Amber Thompson*[1], Andrew L. Goodwin[1]

1 Department of Chemistry, University of Oxford

2 Materials Department ETH Zurich

Report:

Cd(CN)2 is the material with the record large negative bulk thermal expansion (NTE). The original idea of our experimenta was to investigate the mechanism of the NTE in $Cd(CN)_2$ and in particular to determine to which extent disorder of the cyanide ion is reponsible for this property.



During the measurement we have collected excellent single crystal diffuse scattering datasets (see figure on the right) at various temperatures. For this we would like to thank Dmitry Chernyshov for his help and all of his experience with the measurement of the single crystal diffuse scattering and also all the staff of SNBL, which made sure the beamline is up for the task including the excellent measurement software, the stability of the beam and effortless operation for us as users.

Analysis have shown that the physics of local order of cyanide ions in $Cd(CN)_2$ is very rich, and resembles the behaviour of spin-ice materials. Unfortunately single crystal diffuse scattering alone was not sufficient to characterise these phenomena fully, so over the last years we have also used extensive DFT and Monte-Carlo modelling, powder neutron PDF investigations, as well as solid-state NMR. These investigations were the foundation of the PhD thesis of Chloe Coates and Mia Baise.

The final publication explaining the findings is still on review, but the preprint is available online [1]. Following is its abstract:

“Spin-ices are frustrated magnets that support a particularly rich variety of emergent physics. Typically, it is the interplay of magnetic dipole interactions, spin anisotropy, and geometric frustration on the pyrochlore lattice that drives spin-ice formation. The relevant physics occurs at temperatures commensurate with the magnetic interaction strength, which for most systems is 1-5K. This low energy scale poses severe challenges for experimental studies of spin-ices and the practical exploitation of their unusual properties. Here, we show that non-magnetic cadmium cyanide (Cd(CN)2) exhibits analogous behaviour to magnetic spin-ices, but does so on a temperature scale that is nearly two orders of magnitude greater. The electric dipole moments of cyanide ions in Cd(CN)2 assume the role of magnetic pseudospins, with the difference in energy scale reflecting the increased strength of electric \emph{vs} magnetic dipolar interactions. As a result, spin-ice physics influences the structural behaviour of Cd(CN)2 even at room temperature.”

References:

[1] Coates, Chloe S., Mia Baise, Arkadiy Simonov, Joshua W. Makepeace, Andrew G. Seel, Ronald I. Smith, Helen Y. Playford et al. "Room temperature spin-ice physics in cadmium cyanide." *arXiv preprint arXiv:1904.05749* (2019).