

## 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 using the **Electronic Report Submission Application**:

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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.



	<b>Experiment title:</b> <b>The high-pressure, high-temperature phases of lithium sulphate</b>	<b>Experiment number:</b> HS-1883
<b>Beamline:</b> ID30	<b>Date of experiment:</b> from: 9/11/2002 to: 12/11/2002	<b>Date of report:</b> 24/02/2005
<b>Shifts:</b> 12	<b>Local contact(s):</b> Mohamed Mezouar, Wilson Crichton	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>David A Keen* and David C Parfitt*, Physics Department, Oxford University, Clarendon Laboratory</b> <b>Stephen Hull*, ISIS Facility, Rutherford Appleton Laboratory</b>		

## Report:

The aim of this experiment was to determine the structures of the high pressure, high temperature phases of  $\text{Li}_2\text{SO}_4$  and to use the results to understand the ionic conductivity mechanisms in the material. In particular, increasing pressure within the superionic high temperature  $\alpha$ -phase was expected to allow us to decouple the dynamic effects of sulphate group rotation and lithium ion mobility effectively. This is important given the controversy over the nature of the conduction mechanism in this superionic material; different groups have advocated mechanisms based on simple ion diffusion; assisted by 'paddle-wheel' sulphate group rotations or combinations of the two. Additionally, any ionic motion within the more dense higher pressure phases at high temperature would provide further insight on the conduction process.

The experiments were carried out during the allocation period above, and completed during July 2003. It was found that the finely ground powder grains of the cubic superionic  $\alpha$ -phase very readily fused to form a sample consisting of a small number of crystallites. This made interpretation of these data impossible. However, good quality data from the high-pressure  $\varepsilon$ -phase was successfully refined and the structural model was used as the basis for further molecular dynamics simulations as a function of temperature and pressure. The structure remains essentially ordered with no measurable lithium ion diffusion at high temperature. However, the MD simulations reveal a small number of locally diffusive events at temperatures just below the melting point. These are not mediated by significant sulphate group rotations.

This work has been written up and will be submitted to *Physical Review B* in the very near future. The abstract of the paper follows:

*High pressure forms of lithium sulphate: structural determination and molecular dynamics simulation*

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Powder X-ray diffraction has been performed on lithium sulphate,  $\text{Li}_2\text{SO}_4$ , in the temperature range 300K to 1000K and at pressures up to 7.5GPa. The ambient pressure  $\beta$ -phase appears stable up to 3GPa whereupon a slow transformation begins into a new phase,  $\delta$ - $\text{Li}_2\text{SO}_4$ . This phase is characterised by broad, very low intensity Bragg peaks. Above 7GPa and with slight heating, another phase,  $\varepsilon$ - $\text{Li}_2\text{SO}_4$ , is formed which shows sharp Bragg peaks. Rietveld refinement of the structure of the  $\varepsilon$ -phase has shown it to be isostructural to the high-temperature phase  $\text{Na}_2\text{SO}_4$ -III. Molecular dynamics simulations of the  $\varepsilon$ -phase using an established potential indicate that at high temperatures  $\text{Li}_2\text{SO}_4$  may show disordering of the lithium ions and rotations of the sulphate groups, but not at a level approaching the extreme disordering shown in the superionic  $\alpha$ -form of  $\text{Li}_2\text{SO}_4$ .

