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 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.

ESRF	**Experiment title:** Distribution of Ga/Ge in Thermoelectric clathrates	**Experiment number**: **01-02-691**
Beamline:	**Date of experiment**: from: 3/11 to: 6/11	**Date of report**: 6/2
Shifts: 3	**Local contact(s)**: Dr. Philip PATTISON	*Received at ESRF:*

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Report:

The compound $Ba_8Ga_{16}Ge_{30}$ has received increased attention due to its potential for thermoelectric waste heat recovery. The structure is a clathrate type I, which can be described as a covalent host structure with large voids build of Ga and Ge atoms. The Ba guest atoms are located in the centers of the voids. The eight Ba atom donate their two valence electrons to the host structure of 16 Ga^{3+} and 30 Ge^{4+}, giving a total of 184 electrons available for 92 bonds. The structure has five different crystallographic sites in space group Pm-3n: two Ba sites (*2a, 6d*) and three host structure sites (*6d*, *16i*, *24k*). In most of the literature appearing on the clathrates it is assumed that the Ga/Ge atoms are randomly distributed among the three framework sites,[i] even though MEM calculations has suggested preferential occupancies.[ii] The problem is that neighboring elements such as Ga and Ge have similar scattering power for x-rays. For neutrons the scattering length difference is somewhat larger Ga (7.28 fm) and Ge (8.19 fm), but Sales et al. concluded that occupancies could not be refined with the data they measured.[1] By measuring near the x-ray absorption edge it is possible to gain contrast between Ga and Ge as demonstrated by Y. Zhang et al.[iii] using powder diffraction. However, their refinements gave a p-type stoichiometry ($Sr_8Ga_{18.74(9)}Ge_{27.26(9)}$) in a sample known to be n-type.

Using single crystal resonant diffraction we aimed at obtaining sufficient contrast between Ga and Ge to refine occupancies of n- and p-type $Ba_8Ga_{16}Ge_{30}$ in accordance with our knowledge about the transport properties of the samples. The Ga and Ge edge was scanned using a fluorescence detector. The f' and f" of the two edges is shown in figure 1 as obtained by the program CHOOCH with the measured data.

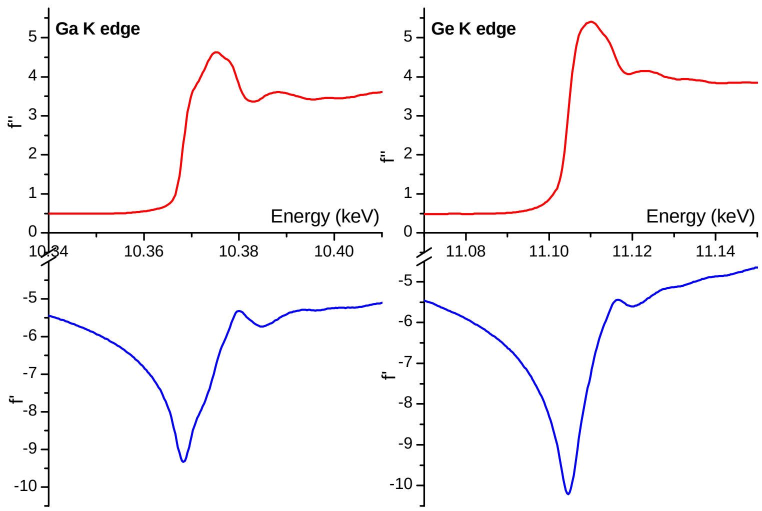

Figure 1: The Ga and Ge edges of $Ba_8Ga_{16}Ge_{30}$

In both cases small single crystals were chosen in order to reduce the effects of extinction and absorption. The p-type sample had approximate dimensions of 10x12.5x12.5µm while the n-type was 6x20x30µm, but with index able facets. Table 1 and 2, summarize the measurement performed on the p- and n-type samples.

Table 1: The data measured for the p-type sample.

mono (θ)	6.5008	10.2591	10.9965	10.9977
R_{merge}	8.66	5.42	5.71	5.00
$\#Ref_{total}$	21405	7038	4105	6921
$\#Ref_{used}$	17521	6567	3671	6328
#Unique	3670	1012	822	830

Table 2: The data measured for the n-type sample.

mono (θ)	6.5008	10.0412	11.0245	10.9968
R_{merge}	3.05	3.40	2.52	2.78
$\#Ref_{total}$	49196	11453	11505	9754
$\#Ref_{used}$	30934	6778	7611	5745
#Unique	4294	1196	997	1014

Preliminary refinements using SHELX have been performed. The data close to the Ga edge are considered to be the most informative with high contrast and low absorption. Refinement of the data yields the result shown in table 3.

Table 3: Results from refinements.

Sample	Mono (θ)	R1	Stoichiometry
p-type	109965	6.5%	$Ba_8Ga_{16.57(81)}Ge_{29.42(81)}$
n-type	109968	6.0%	$Ba_8Ga_{15.59(84)}Ge_{30.41(81)}$

The refinements are in good agreement with expected stoichiometry but unfortunately the uncertainties are fairly high. However, it should be possible to extract site occupancies of neighboring atoms from this single crystal resonant diffraction experiment.

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[i] B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson, D. Mandrus. *Phys. Rev.* B **63**, 245113 (2001)
[ii] A. Bentien, A. E. C. Palmqvist, J. D. Bryan, S. Latturner, G. D. Stucky, L. Furenlid, B. B. Iversen. *Angew. Chem. Int. Ed.*, **39**, 3613 (2000)
[iii] Y. Zhang, P. L. Lee, G. S. Nolas, A. P Wilkinson, *Appl. Phys Lett.* **80**, 2934 (2002)