

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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.



	Experiment title: A high-pressure x-ray Raman scattering study of elemental silicon	Experiment number: HE3696
Beamline: ID16	Date of experiment: from: 26.10.2011 to: 01.11.2011	Date of report:
Shifts: 18	Local contact(s): Marco Moretti-Sala	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): K. Mende*, C. Sternemann*, A. Nyrow* Fakultät Physik / DELTA, Technische Universität Dortmund, D-44227 Dortmund, Germany J. Tse Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada		

Report: Silicon is one of the most common elements on earth. Because of its numerous technological applications and its presence in most geologically relevant minerals, many studies have been performed concerning the physical properties of silicon exposed to temperature and pressure. It is well known, that elemental silicon undergoes several phase transitions under the influence of high pressure. The face centered-cubic Si-I phase transforms to the tetragonal Si-II phase at 11 GPa. At 13 GPa, Si-II undergoes a transition to Si-XI which has an orthorhombic structure. This phase is followed by a transformation to the simple hexagonal structure of Si-V at 16 GPa, which remains stable until 38 GPa, where a transition to the “open” orthorhombic Si-VI phase occurs [1, 2]. At ambient conditions silicon is sp^3 hybridised. Under increasing pressure up to 42 GPa the hybridisation of the bonds changes to sp^2 , sp and then to a metal-like bond [1]. This drastic change from a semiconductor to a metal over a small pressure range qualifies silicon to investigate the rehybridisation of atomic orbitals under high pressure.

As shown in a previous study on the clathrate Ba_8Si_{46} [3], x-ray Raman scattering (XRS) at the Si $L_{2/3}$ -edge is particularly sensitive to the rehybridisation of atomic orbitals and thus a suitable technique to uncover silicon’s transition from semiconducting to metallic behaviour. Because of the high energy of the in- and outgoing x-rays, XRS is the only technique to obtain information of low absorption edges, such as the Si L-edge, under extreme conditions like diamond anvil cells.

The measurements were performed at beamline ID16 at ESRF using the multi analyser spectrometer in Rowland geometry with 9 Si(660) analyser crystals at a fixed analyser energy of 9.69 keV. The spectrometer covered a solid angle of 117° to 143° which results in a momentum transfer of the scattered photons of $q=8.46 \text{ \AA}^{-1}$ and $q=9.41 \text{ \AA}^{-1}$ respectively. The energy of the incident photons was tuned to obtain energy losses from 90 to 115 eV in the vicinity of the Si $L_{2/3}$ -edge at 100 eV.

Two diamond anvil cells were used. They were loaded with precharacterized Si powder and a ruby as pressure marker. The diamond anvil cells were specially designed to provide sufficient angular side-openings

to utilise all analyzer crystals. Due to technical reasons the cells were sent to ESRF with a primary pressure of about 3.4 GPa. The pressure has been determined by using an optical Raman spectrometer at the ESRF high pressure lab before and after each measurement. Spectra were taken at the Si $L_{2/3}$ -edge at several pressures ranging from the initial pressure at 3.4 GPa to 21 GPa.

Measured XRS spectra taken at varying pressures can be seen in figure 1. As reference, a previously measured spectrum of Si powder at ambient conditions is also shown. This spectrum shows a dominant white line which appears due to an excitonic excitation in pure Si. This exciton is a characteristic feature for the semi-conducting behaviour of silicon. The spectra in the low pressure regime practically resemble the shape of the reference sample. It appears, that up to pressures of around 5 GPa, no significant changes in the shape of the spectra can be observed. The spectra taken at 6.7 GPa and 11.1 GPa reveal a small decrease of the white line (region A) and thus a gain in spectral weight in the energy loss region from 103 to 110 eV (B). This indicates first changes in the chemical bonding of the Si structure although the commonalities indicate that the crystal structure at both pressure points still was fcc. This shift in the spectral weight may be associated to a smooth transition in hybridisation of Si with increasing pressure [4]. A strong reduction of the Si white line is clearly visible in the spectrum taken at 20.6 GPa. The excitonic feature disappeared, leaving a broad shoulder which clearly differs from the observed spectra in the low pressure regime. This gives direct evidence of the change in the hybridisation from a three-dimensional sp^3 in the fcc structure of Si-I and Si-II to the one-dimensional sp hybridised Si-V phase with a simple hexagonal structure. The disappearance of the excitonic excitation points out the transition from a semiconducting to a more metal-like state.

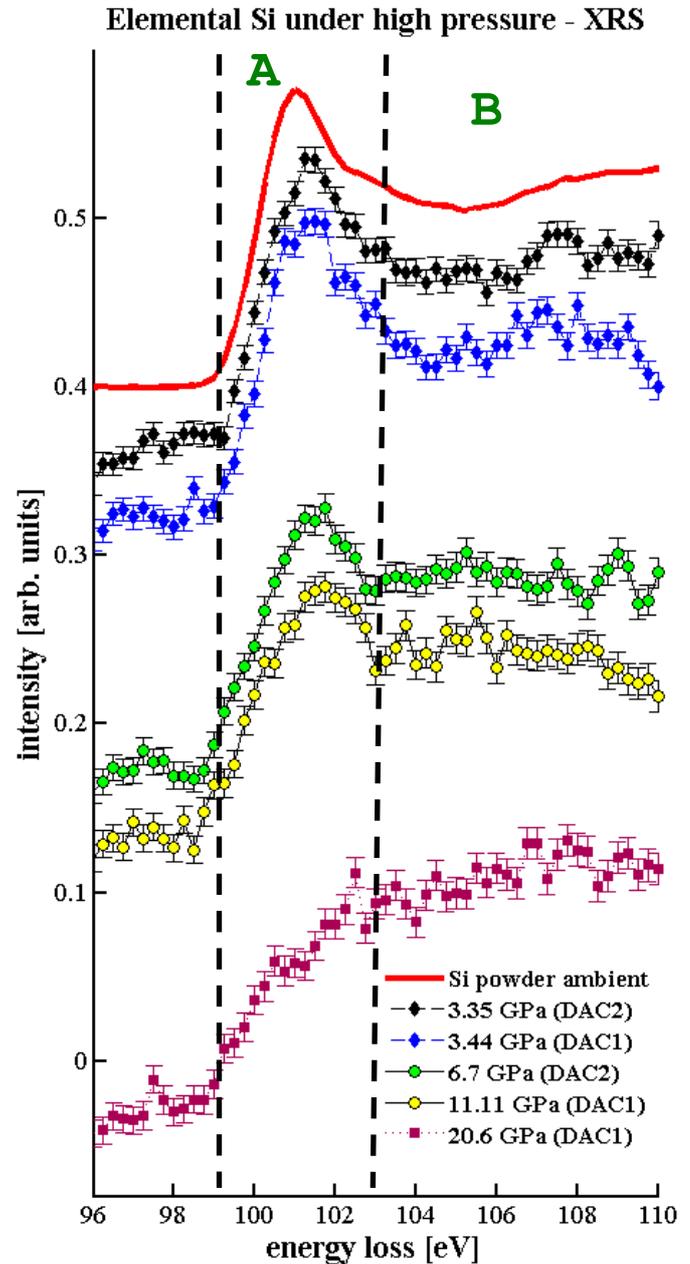


figure 1: Measured spectra of the Si $L_{2/3}$ -edge at varying pressures, arranged according to similar shapes.

Calculations are currently in the works to further understand the rehybridisation of silicon under pressure. Since there is only one spectrum with sufficient statistics in the high pressure regime, further measurements are needed to confirm the observed changes in spectral shape. Moreover, spectra for the intermediate Si phases Si-II and Si-XI should be measured to approve the trend of metallisation. These results present the first direct evidence that the Si phase transitions are triggered by changes of the electronic structure of the material.

- [1] J. S. Tse, Y. Ma, and H. M. Tutuncu, *J. Phys.: Condens. Matter* **17**, S911 (2005), and references therein.
- [2] M. Hanand, U. Schwarz, K. Syassen, and K. Takemura, *Phys. Rev. Lett.* **82**, 1197 (1999).
- [3] J. S. Tse, L. Yang, Ch. J. Sahle, C. Sternemann, et al. *Phys. Rev B* **84**, 184105 (2011)
- [4] J. S. Tse, in *Modern Charge-density Analysis*, ed. C. Gatti and P. Macchi, Springer Verlag (2012).