ESRF	**Experiment title:** Combined EXAFS and Energy Scanning XRD for the Investigation of a Pressure-Induced Solid-State Redox Reaction	**Experiment number**: CH-1301
Beamline:	**Date of experiment**: from: 26. Juni 2002 to: 1. July 2002	**Date of report**: 18.11.2006 *Received at ESRF:*
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Report:

The pressure-induced redox reaction within the system $Cs_2[Pd^{(II)}I_4]\cdot I_2$ / $Cs_2[Pd^{(IV)}I_6]$ was investigated by means of EXAFS spectroscopy and energy dispersive X-ray powder diffraction. Pressures were generated with a motor driven large volume cell of the Paris-Edinburgh (type V) using pill-shaped boron epoxy resin sample containers with drilled holes of 2 mm diameter. The powdered samples were diluted with hexagonal BN (1:4) to optimize absorption ratios and transferred to the pressure cell. The automatic procedures at BM29 were used to allign the sample within the beam. Pressure-dependent X-ray powder patterns were recorded using a seven channel energy dispersive detector system described by Filipponi et al.[1,2] Lattice parameters of h-BN were refined using least-squares methods and the Holzapfel[3] and Birch-Murnaghan[4] equations of state were to derive the pressures. Single K-edge EXAFS spectra of Pd (24350 eV), I (33164 eV), and Cs (35985 eV) were recorded between 24.0 keV and 36.4 KeV in 1 eV steps with typically 1100 data points per spectrum. Due to monochromator instabilities at high energies, slightly narrower Cs spectra were recorded. Glitches were removed from the data and Fourier transformed ($k \in [1.5\ \text{Å}^{-1};\ 18.0\ \text{Å}^{-1}]$, k-weight = 1, Hanning window sills = 0). External references were CsI, PdI_2 and Pd-foil. The collected spectra were fitted using the program package FEFF/FEFFIT.[5,6]

The absorption edge spectra of palladium and iodine were recorded at ten pressure steps. Before and after each recorded EXAFS spectrum, energy dispersive powder diffraction patterns were collected. Unit cell parameters of h-BN (as a pressure marker) and the sample were refined by least-squares methods. Interatomic distances of the tetragonal phase at ambient pressure were used as starting points and refined successively. The absorption edges of palladium and iodine were refined simultaneously using this crystal structure model. The free parameters were the Debye-Waller factors, the EXAFS amplitudes and the bond distances, keeping the unit cell parameters fixed to the values extracted from the energy-dispersive diffraction data. The results from the EXAFS analysis (Figures 1,2) exhibit obvious deviations from the distances determined by Rietveld refinements. The disparities are attributed to discrepancies in the fitting procedures of the EXAFS data. The crystallographic and chemically dissimilar iodine atoms I(1) and I(2) in Cs2[PdI4]·I2 (Figure 3) are indistinguishable in the EXAFS fitting process applied. The constraints employed in the fitting procedure cause a shift of the value for the bond length Pd-I(2) towards longer distances in comparison to the results of the full profile refinements. In agreement with the diffraction data, both experimental series depict the phase transition above 19 kbar which is in very good agreement with earlier results.

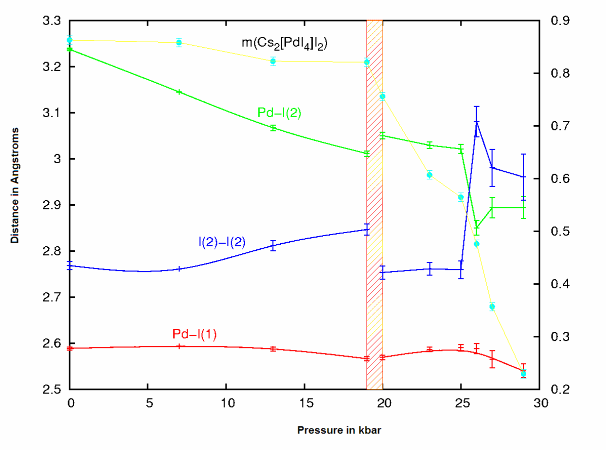

Figure 1: Disitances Extracted from X-Ray Data

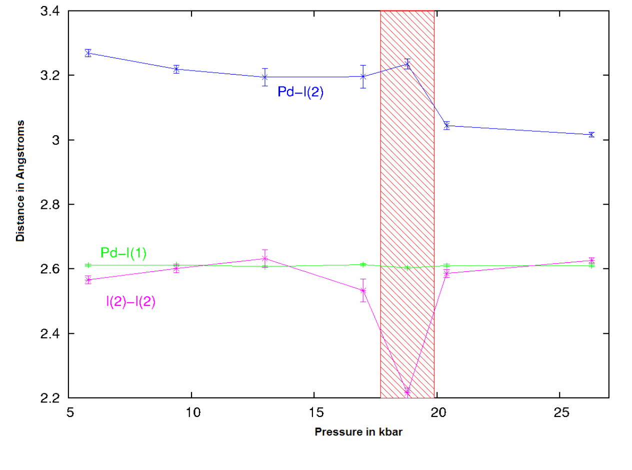

Figure 2: Distances extracted from EXAFS fit

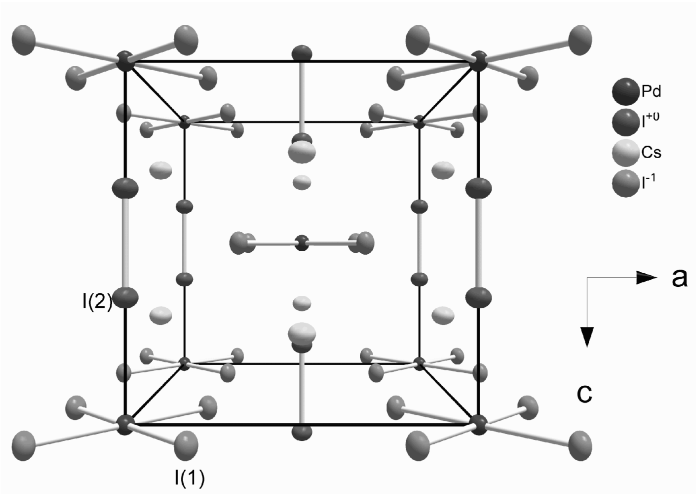

Figure 3: Crystal structure of $Cs_2[PdI_4]\cdot I_2$ indicating the different iodine atoms I(1) and (I2)

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