ESRF	**Experiment title:** **Combined X-ray diffraction and EXAFS using spatial resolution to study a pressure induced redox reaction in the Cs-Pd-(Cl/Br/I) system**	**Experiment number**: CH-1052
Beamline: ID09	**Date of experiment**: from: 6. April 2001 to: 10. April 2001	**Date of report**: 20.10.2006
Shifts: 12	**Local contact(s)**: Dr. Michael HANFLAND	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Gerhard WORTMANN, Universität Paderborn, Germany

Prof. Dr. Ronald FRAHM, Bergische Universität Wuppertal, Germany

Prof. Dr. Hans-Lothar KELLER*, Universität Dortmund, Germany

Matthias RICHWIN* Bergische Universität Wuppertal, Germany

Peter HEINES* Universität Dortmund, Germany

Hubertus GIEFERS, Universität Paderborn, Germany

Dr. Dirk LUETZENKIRCHEN-HECHT, Universität Wuppertal, Germany

Report:

The results of this experiment were published :

P. Heines, H.-L. Keller, P. Bouvier, M. Hanfland, *Z. Anorg. Allg. Chem.* 629 (2003) 545.

Abstract

$Cs_2[PdBr_4]I_2$ and $Cs_2[PdCl_4]I_2$ consist of isolated $[PdX_4]$–building–units (X = Cl, Br) which are supplemented by embedded neutral iodine molecules to form 'infinite' chains of the type -I-PdX_4-I- (Figure 1)[a]. Both compounds show a reversible pressure induced solid-state phase transition above 78 kbar and 199kbar, respectively (Figures 2 and 3).

A series of ca. 30 high pressure powder diffraction experiments was run in Le Toullec[b] type diamond anvil cells (300 mm /100 mm) using inconel gaskets, 0.200mm, pre-indented to aprox. 0.060 mm and a 0.120 mm spark eroded sample hole. Additional to the finely ground sample powders, pressure transmitting media (N_2 or Ar) and pressure markers (ruby, Sm_2+:SrB_4O_7)[c] were loaded into the inconel gaskets. The pressure was determined via the luminiscence method[d] and a mar345 detector plate was used to collect the diffraction patterns in transmission mode at a wavelength of 41.546 pm. The primary data was corrected for Lorentz polarization, detector non-linearities, and artefacts were removed prior to integration and conversion into 2Theta versus intensity plots with the progam suite FIT2D[e].

Profile fitting of the $Cs_2[PdBr_4]I_2$ model was sucessful up to 78 kbar, above a structural transition occurs which is the stable phase up to 218 kbar. The phase transition is reversible as indicated by the powder diffraction patterns collected after pressure release.

Profile fitting of the $Cs_2[PdCl_4]I_2$ model was sucessful up to 199 kbar (Figure 4), above a structural transition occurs which is the stable phase up to 410 kbar. The phase transition is reversible as indicated by the powder diffraction patterns collected after pressure release.

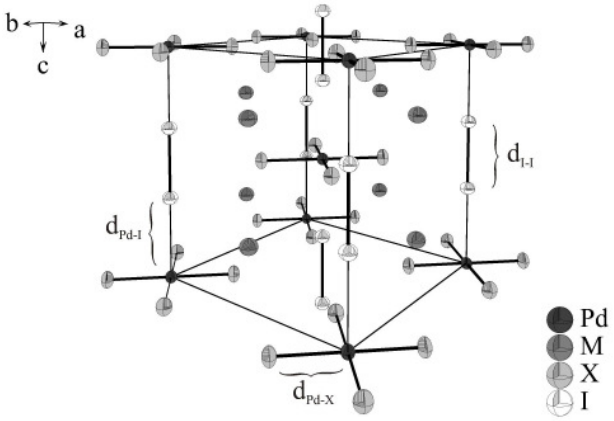

Figure 1: Crystal structure of $Cs_2[PdX_4]I_2$, Spacegroup I4/mmm (No 139)

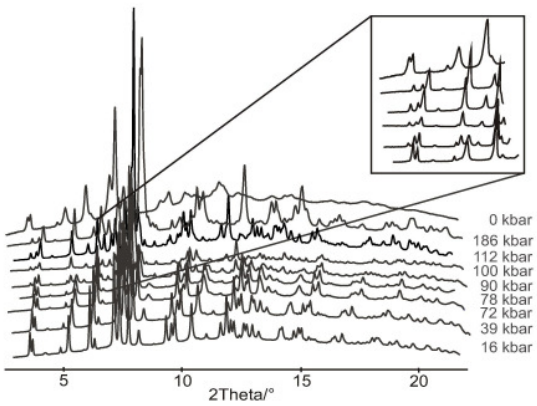

Figure 2: Selected diffraction patterns of $Cs_2[PdBr_4]I_2$

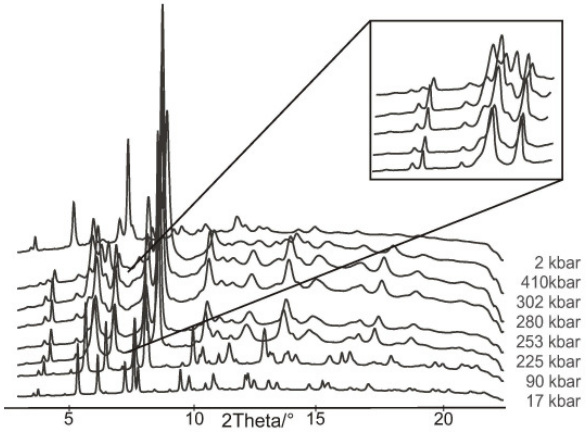

Figure 3: Selected diffraction patterns of $Cs_2[PdCl_4]I_2$

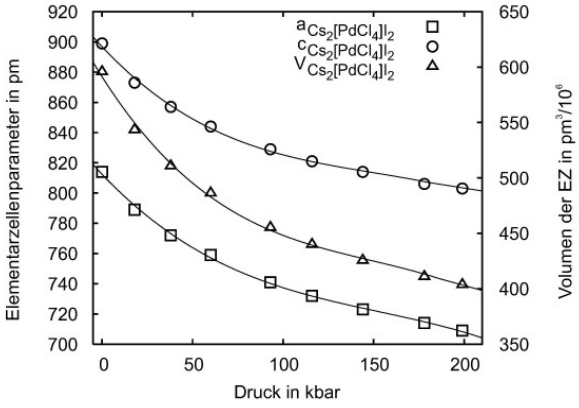

Figure 4: Unit cell parameters/volume versus pressure of $Cs_2[PdCl_4]I_2$

References:

[a] Heines, P; Keller, H.L.; Bouvier, P.,Hanfland, M.; *Z. Anorg. Allg. Chem.* ***629*** *(2003) 545.*

[b] Le Toullec, R.; Princeaux, J. P.; Loubeyre, P.; *High. Press. Res*. ***1*** (1988) 77.

[c] Mao, H. K.; Xu, J.; Bell, P. M.; *J. Geophys. Res.* ***B91*** (1986) 4673. Datchi, F.; Le Toullec, R.; Loubeyre, P.; *J. Appl. Phys.* ***81*** (1987) 3333.

[d] Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A.; *J. Appl. Phys.* ***46*** (1975) 2774.

[e] Hammersley, A; Svenson, S. O.; Hanfland, M.; Fitch, A. N.; Häuserman, D.; *High Press. Res.* ***14*** (1996) 235.