



	Experiment title: Pressure induced phase transitions in the Cs-Pd-I-System	Experiment number: CH-786
Beamline: BM29	Date of experiment: from: 07. Dec. 1999 to: 12. Dec. 1999	Date of report: 30. Aug. 2000
Shifts: 15	Local contact(s): Bowron, Daniel	<i>Received at ESRF:</i>
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Report:

The aim of the experiment was to study pressure induced redox reaction in the $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ system. From X-ray diffraction it is known that in this compound, Pd is present in a divalent state as Pd^{2+} , coordinated with four I^- anions in a square planar arrangement and an I_2 molecule perpendicular to each side of this plane [1]. By applying pressures of about 2 GPa, a transition towards Cs_2PdI_6 occurs, where two additional iodine atoms are incorporated into the first Pd coordination shell, forming an octahedral iodine coordination around the Pd sites. During this process, a charge transfer from Pd^{2+} to the I_2 molecule should take place, leading to a Pd^{4+} cation and 2 I^- anions.

To investigate this transition, EXAFS spectra were recorded of the Cs, Pd and I-K edges, respectively. Pressure in the range from 0 to 6 GPa was applied using a high pressure cell from the Paderborn group with boron carbide (B_4C) anvils [2]. Approximately 190 spectra were recorded.

The energy shifts of the K absorption edges of palladium, iodine and cesium in the sample were measured using palladium metal foil and CsI as references. Their values have been calculated by fitting arc tangens functions to both the sample and the reference absorption data that were recorded simultaneously. The difference in energy between the two absorption edges as a function of element and pressure is shown in fig. 1, left side. The transition can clearly be detected in the range of 2-2.5 GPa, as indicated by the iodine edge shift. However, the edge shift of the palladium also shows that there is no abrupt transition as relatively strong changes can be observed in the low pressure region.

The preliminary data analysis, using the UWXAFS package - feff code, version 6.01a, and feffit, version 2.54 - was performed by fitting a theoretical structural model to the recorded data, with four main structural parameters allowed to vary: both crystallographic axes a and c to monitor the size of the unit cell, and the distances between palladium and iodine in the fourfold planar coordination (named 'Pd-I1') as well as the distance from palladium to one side of the iodine dumbbell, denoted 'Pd-I2'.

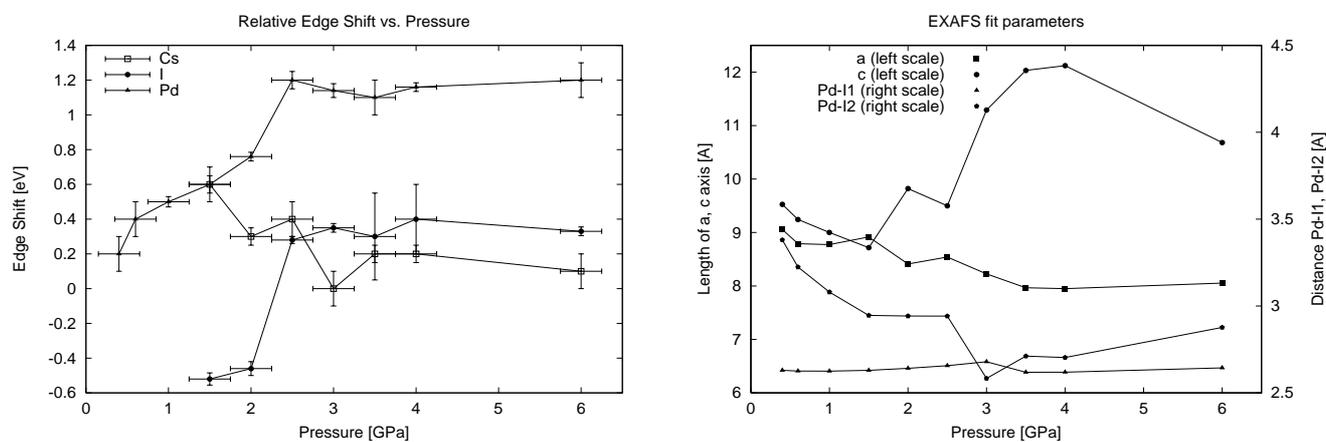


Figure 1. Left: measured K-edge shifts of the sample in relation to references given in the text; right: parameters from the EXAFS data analysis, see text.

From the data analysis, one can conclude that with increasing pressure the size of the unit cell decreases along the a -axis, and increases along the c -axis with the obtained values being in well agreement with the data obtained from previous diffraction experiments. Furthermore, the distance between Pd and I in the I_2 dumbbell strongly decreases as the I_2 dumbbell expands, which again is in agreement with previous experiments, while the interatomic distance in the square planar Pd-I coordination ('Pd-I1') increases up to a certain pressure, which is due to the charge transfer from the iodine dumbbell to the palladium. These two last mentioned changes occur not at once at a well-defined transition pressure, but continuously with rising pressure.

However, the analysis of several features suffers from ambiguities in the fitting procedure, for which to resolve more information is necessary to gain further insight into the local structure during the transition, especially to determine the interaction between charge transfer and structural change; therefore two new compounds ($Cs_2PdCl_4 \cdot I_2$ and $Cs_2PdBr_4 \cdot I_2$) have been prepared, to simplify data analysis by reducing the number of iodine sites.

References

- [1] B. Schüpp, P. Heines, H.-L. Keller et.al., HASYLAB Annual Report 1998, 621
- [2] ESRF Highlights 1997/98, p. 36