XANES study on the intermetallic compounds PdGa and PtGa, two representatives of the FeSi structure

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PdGa [1] and PtGa [2] crystallize in the FeSi structure type with space group $P2_13$. The FeSi structure can be described as a strongly distorted NaCl structure with an increase of the coordination number from 6 to 7 for both atomic types [3] (Figure 1). In the crystal structures of PdGa and PtGa, the shortest contacts between transition metal and gallium run along the three-fold axes: $d$(Pd–Ga) = 2.54 Å and $d$(Pt–Ga) = 2.57 Å (derived from x-ray single crystal structure refinements). Analysis with the electron localization function (ELF) reveals ring-like attractors on these short bonds similarly to the hypothetic molecule Sc–Ge [4]. Additionally, each gallium atom participates in three three-centre bonds Pd–Ga–Pd and each palladium atom contributes to six of these three-centre bonds.

Figure 1: Crystal structure of PdGa and PtGa (right) in comparison to NaCl (left). The shortest distances along the three-fold axes are marked black: $d$(Pd–Ga) = 2.54 Å and $d$(Pt–Ga) = 2.57 Å.

To investigate the contribution of the transition metal $d$-electrons to the bonding in the nominated compounds, x-ray absorption near edge spectroscopy (XANES) was performed. From the Pd and Pt LIII edges, the occupancy of Pd 4$d$-states and Pt 5$d$-states was obtained, respectively. For comparison we measured absorption edges of the Pd valence compounds PdO, $K_2$PdCl$_6$, the coordination compound $[(C_6H_5)_3P]$$_4$Pd and the Pt valence compounds PtCl$_2$ and PtCl$_4$.

Pd LIII and Pt LIII XANES spectra were recorded in transition arrangement at the EXAFS beamlines E4 and A1 of HASYLAB. The radiation was monochromatized with a Si(111) double-crystal at beamline E4 and a four-crystal monochromator at beamline A1.

According to the dipole-transition selection rule, the Pd LIII White Line (WL) features correspond to the transition Pd $2p_{3/2} \rightarrow 4d_{5/2}$ (Figure 2). Reflecting the change of the Pd oxidation state in Pd, PdO and $K_2$PdCl$_6$ (0, +2, +4), the Pd LIII edge is shifted by 1.3 eV from Pd to PdO and by 2.4 eV from Pd to $K_2$PdCl$_6$ (according to Ru [5] and W [6] compounds). In contrast to valence compounds, for PdGa, the edge shift of 3.3 eV can not be related with a Pd oxidation state; we expect a value near zero.

According to the ground-state rule, for the valence compounds PdO and $K_2$PdCl$_6$ the intensity of the WL increases with oxidation state. The observation of a small intensity maximum in the WL of
Pd indicates, that 4d-states are not fully occupied, due to Pd s-d hybridization as known from Cu$_2$O [7]. The intensity of the WL of PdGa is as small as of Pd. Therefore, the Pd 4d-states of PdGa are not filled up. The high intensity of the WL for the coordination compound [(C$_6$H$_5$)$_3$P]$_4$Pd is not compatible with a 4d$^{10}$ configuration. This result is supported by x-ray emissions spectroscopy [8] and by analysis with ELF.

Analogous to PdGa, the intensity of the WL of PtGa is very similar to that of Pt. Therefore, PtGa has non-filled Pt 5d-states. Similar results for PtGa$_2$ were obtained from XANES and angle-resolved photo-electron spectroscopy [9].

Our results of XANES support the bonding analysis with ELF, suggesting the participation of the Pd d-electrons in the chemical bonding.

![Figure 2: Pd LIII (left) and Pt LIII (right) x-ray absorption spectra of PdGa in comparison with Pd, PdO, K$_2$PdCl$_6$, [(C$_6$H$_5$)$_3$P]$_4$Pd and PtGa, respectively, in comparison with Pt, PtCl$_2$ and PtCl$_4$.](image)

References