

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: $d(\text{Pd-Ga}) = 2.54 \text{ \AA}$ and $d(\text{Pt-Ga}) = 2.57 \text{ \AA}$ (derived from x-ray single crystal structure refinements). Analysis with the electron localization function (ELF) reveal ring-like attractors on these short bonds similarly to the hypothetical 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.

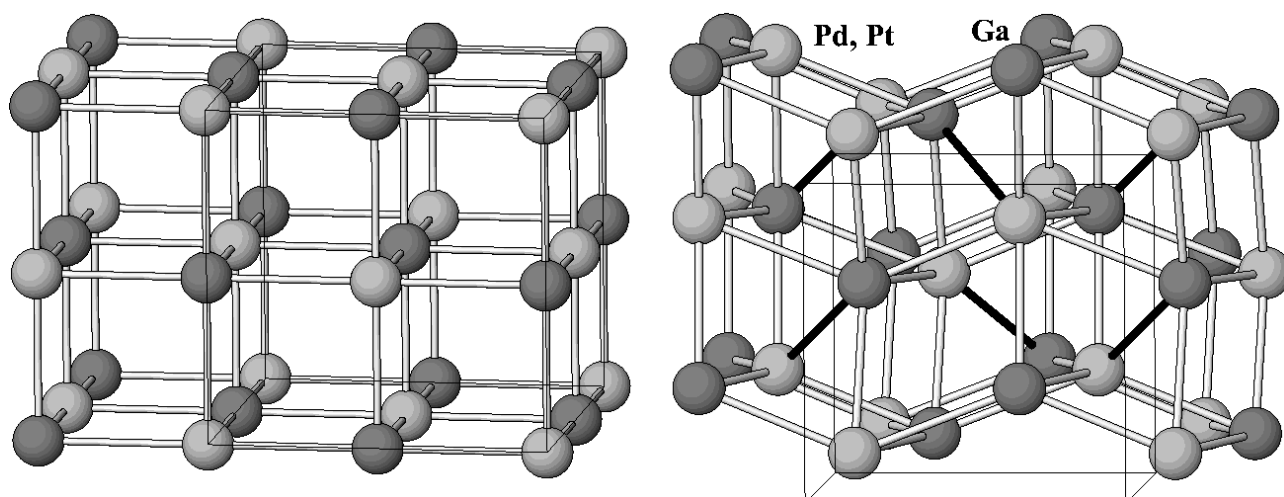


Figure 1: Crystal structure of PdGa and PtGa (right) in comparison to NaCl (left). The shortest distances along the three-fold axes are marked black: $d(\text{Pd-Ga}) = 2.54 \text{ \AA}$ and $d(\text{Pt-Ga}) = 2.57 \text{ \AA}$.

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 L_{III} edges, the occupancy of Pd $4d$ -states and Pt $5d$ -states was obtained, respectively. For comparison we measured absorption edges of the Pd valence compounds PdO, K_2PdCl_6 , the coordination compound $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pd}$ and the Pt valence compounds PtCl_2 and PtCl_4 .

Pd L_{III} and Pt L_{III} 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 L_{III} 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_2PdCl_6 (0, +2, +4), the Pd L_{III} edge is shifted by 1.3 eV from Pd to PdO and by 2.4 eV from Pd to K_2PdCl_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_2PdCl_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_2O [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 $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pd}$ 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 PtGa₂ 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.

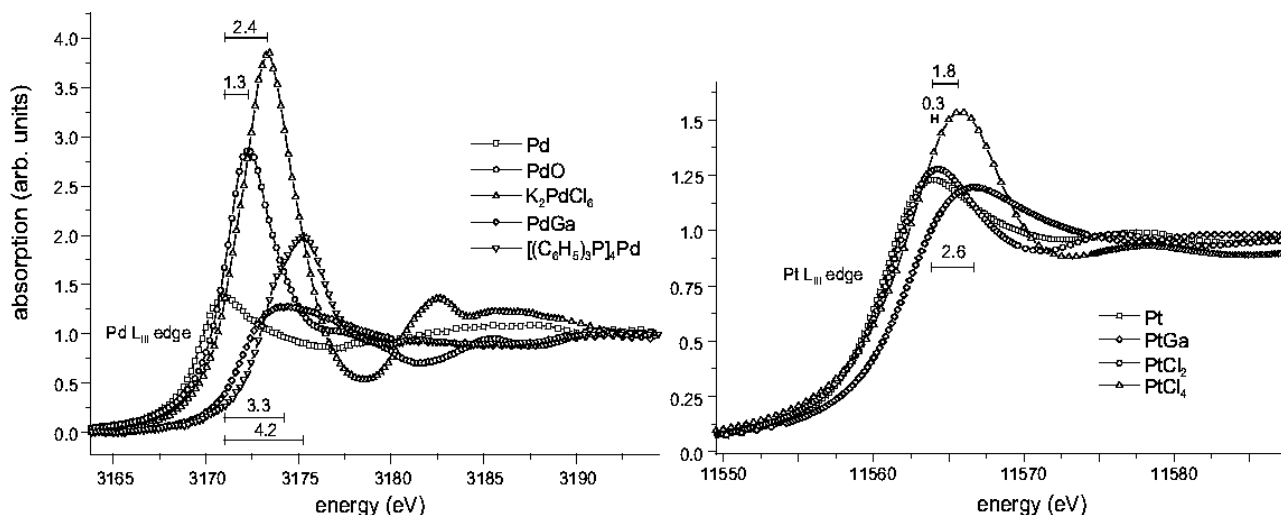


Figure 2: Pd L_{III} (left) and Pt L_{III} (right) x-ray absorption spectra of PdGa in comparison with Pd, PdO, K₂PdCl₆, $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Pd}$ and PtGa, respectively, in comparison with Pt, PtCl₂ and PtCl₄.

References

- [1] E. Hellner, F. Laves, Z. Naturforsch. 2a, 177 (1947).
- [2] M. K. Bhargava, A. A. Gadalla, K. Schubert, J. Less-Comm. Met. 42, 69 (1975).
- [3] L. Pauling, A. M. Soldate, Acta Crystallogr. 1, 212 (1948).
- [4] M. Kohout, F. R. Wagner, Yu. Grin, Theor. Chem. Acc. 108, 150 (2002).
- [5] Z. Hu, H. von Lips, M. S. Golden, J. Fink, G. Kaindl, F. M. F. de Groot, S. Ebbinghaus, A. Reller, Phys. Rev. B 61, 5262 (2000).
- [6] O. Yu. Khyzhun, J. Alloys Comp. 305, 1 (2000).
- [7] M. Grioni, J. B. Goedkoop, R. Schoorl, F. M. F. de Groot, J. C. Fuggle, F. Schäfers, E. E. Koch, G. Rossi, J.-M. Esteve, R. C. Karnatak, Phys. Rev. B 39, 1541 (1989).
- [8] C. Bourg, S. Gamblin, D. S. Urch, J. of Electron Spectroscopy and Related Phenomena 73, 163 (1995).
- [9] L.-S. Hsu, G. Y. Guo, J. D. Denlinger, J. W. Allen, Phys. Rev. B 63, 155105 (2001).