Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Al-Pt intermetallic compounds: HAXPES study

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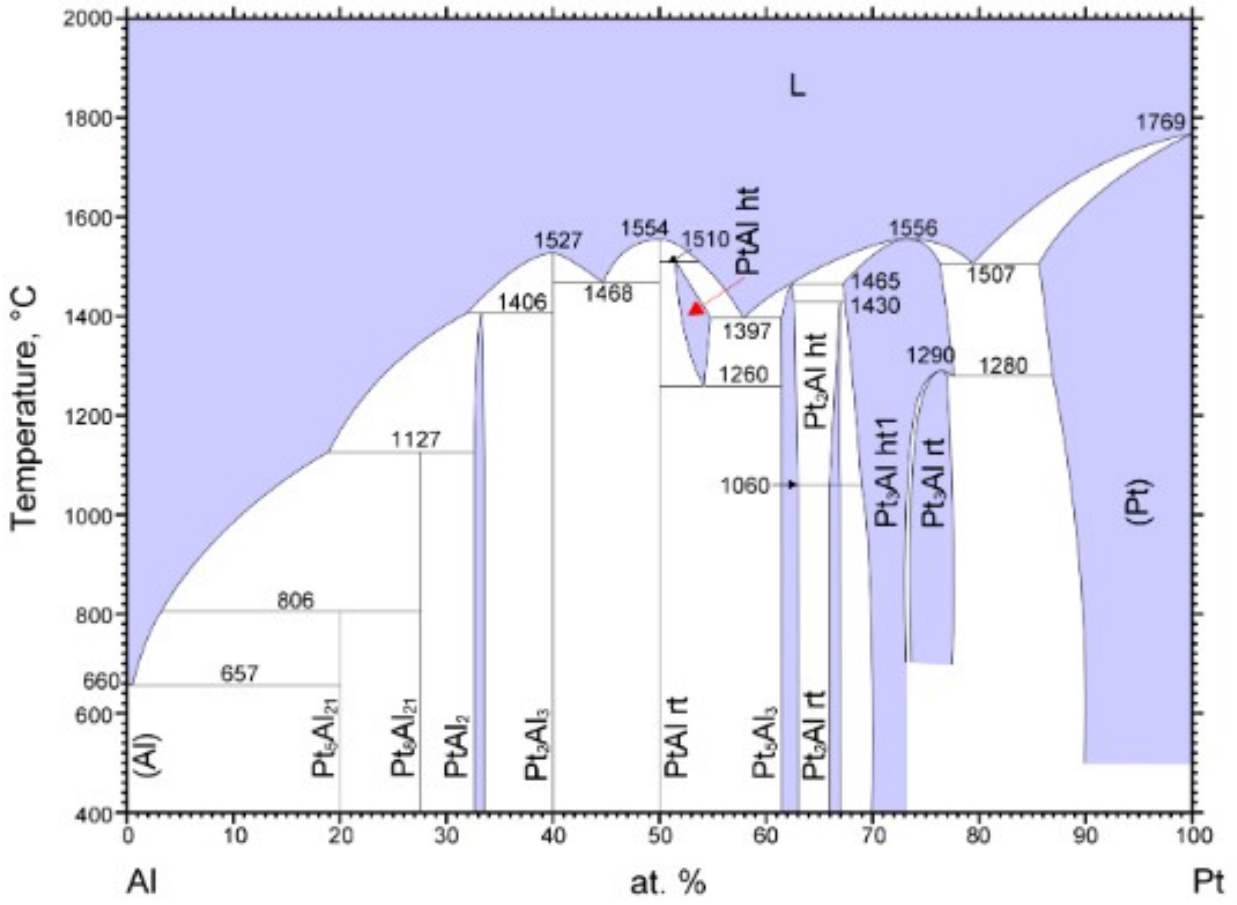


Figure S1. Phase diagram of binary Al-Pt system.[1]

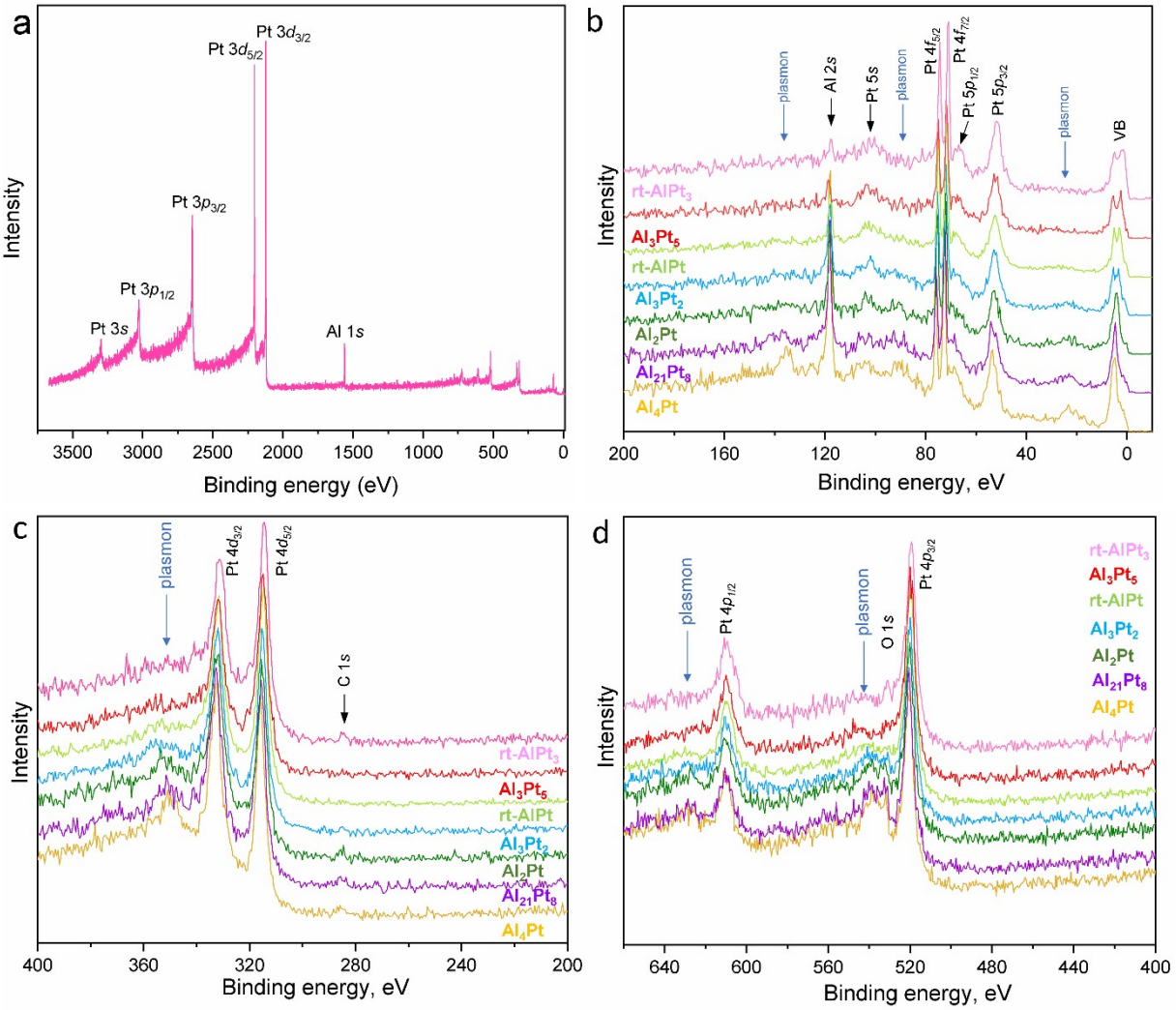


Figure S2. Exemplarily HAXPES wide scan for rt-$AlPt_3$ compound in the range of binding energies of 0-3600 eV (*a*). Fragments of the wide scans (normalized to 1 in the range of 0-650 eV) for all Al-Pt compounds in the ranges of 0-200 eV (*b*), 200-400 eV (*c*) and 400-650 eV (*d*).

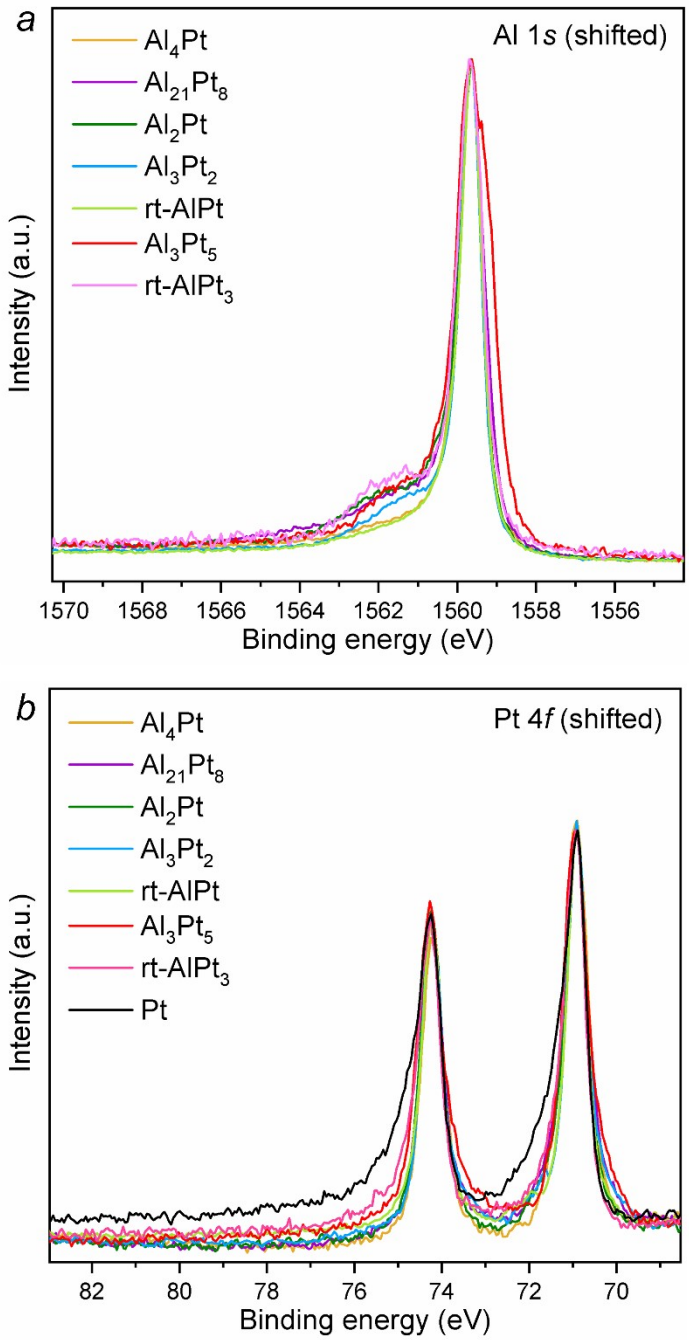


Figure S3. Shifted HAXPES spectra of Al 1*s* (*a*) and Pt 4*f* (*b*) core levels of Al-Pt compounds and elemental Pt for comparison of spectra line shapes.

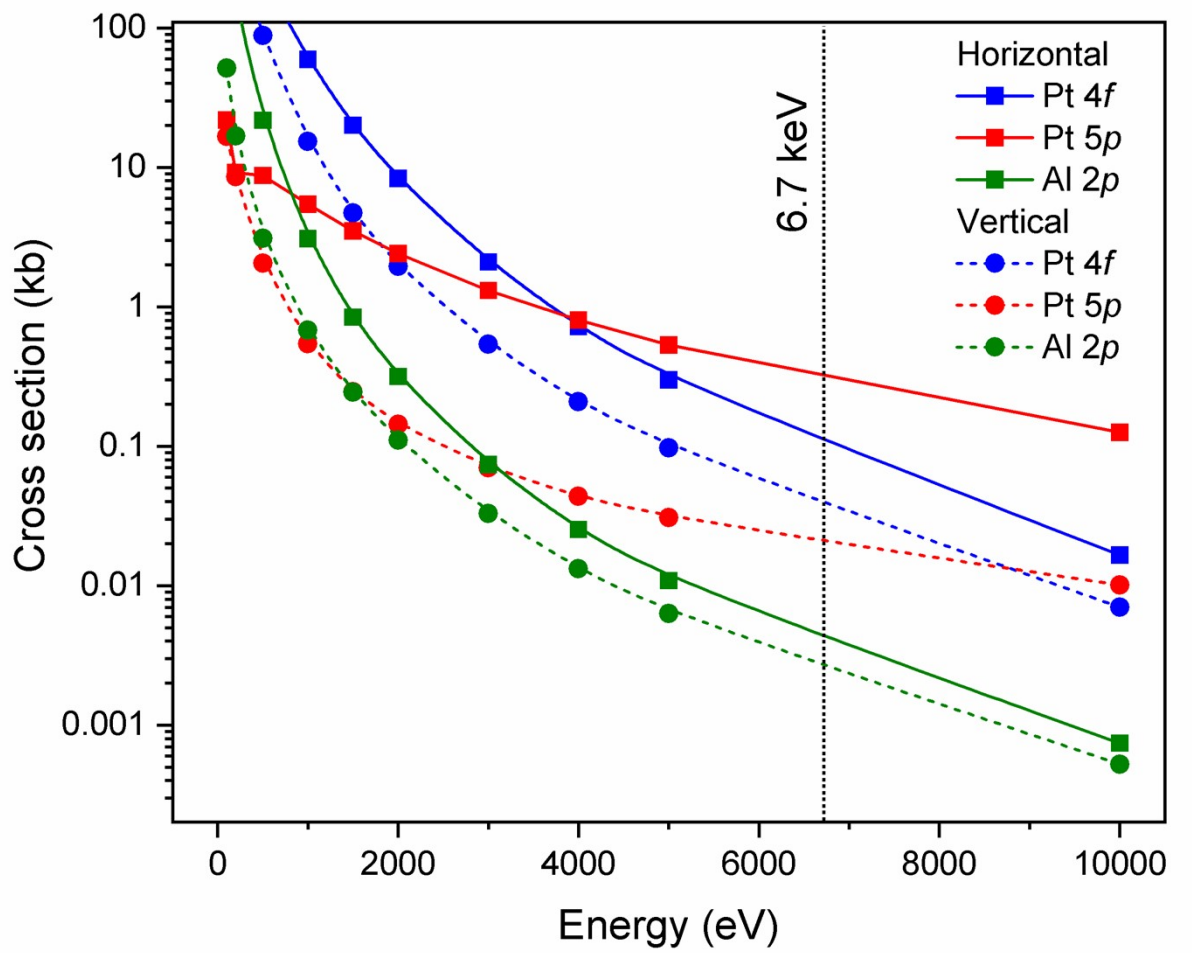


Figure S4. Atomic subshell photoionization cross sections of Pt 4*f*, Pt 5*p* and Al 2*p* core levels (in kb = 10^3 barns) as a function of the photon energy (in eV). Dashed line is used to guide the eye to the photon energy of the presented HAXPES studies. The values were taken from tabulated values.[2-4]

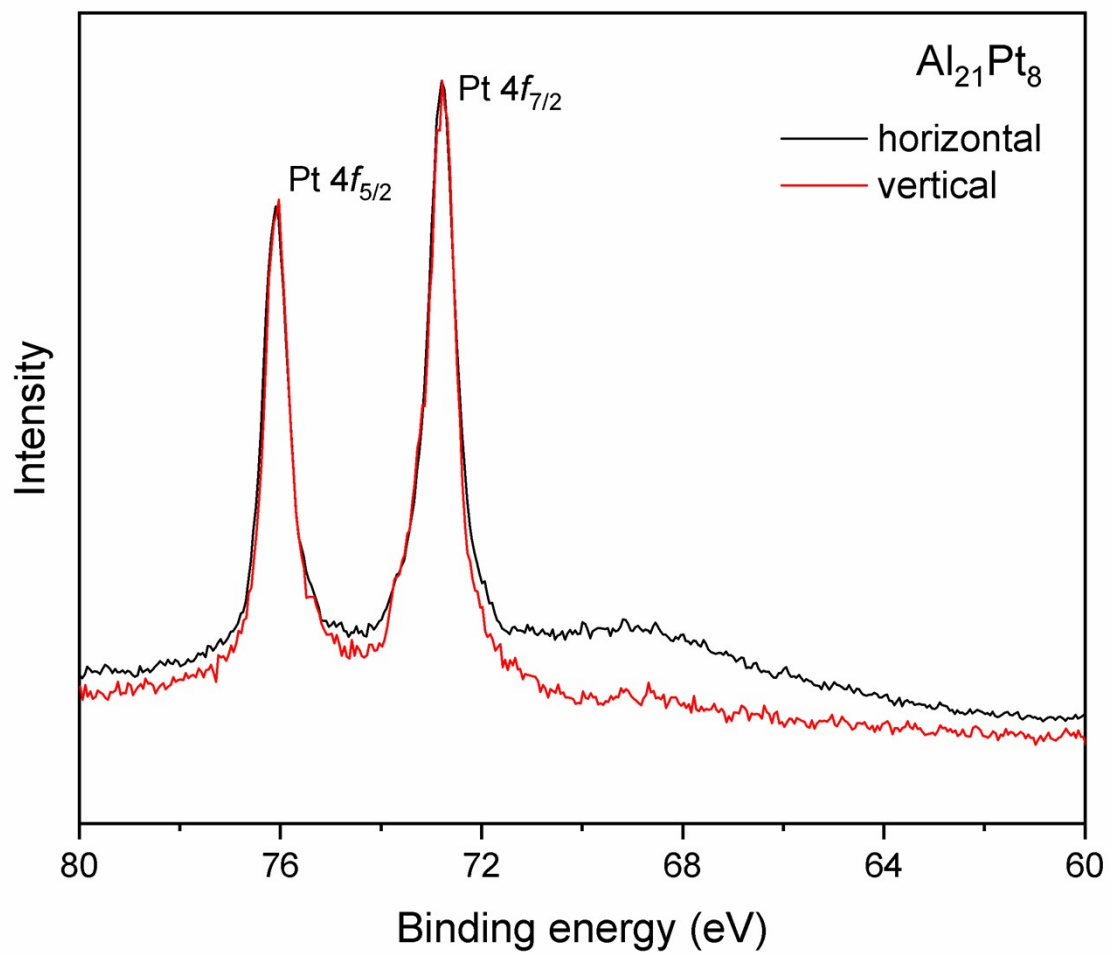


Figure S5. HAXPES spectra of Pt 4*f* core levels of $Al_{21}Pt_8$, measured in horizontal and vertical modes. The intensities are normalized to 1.

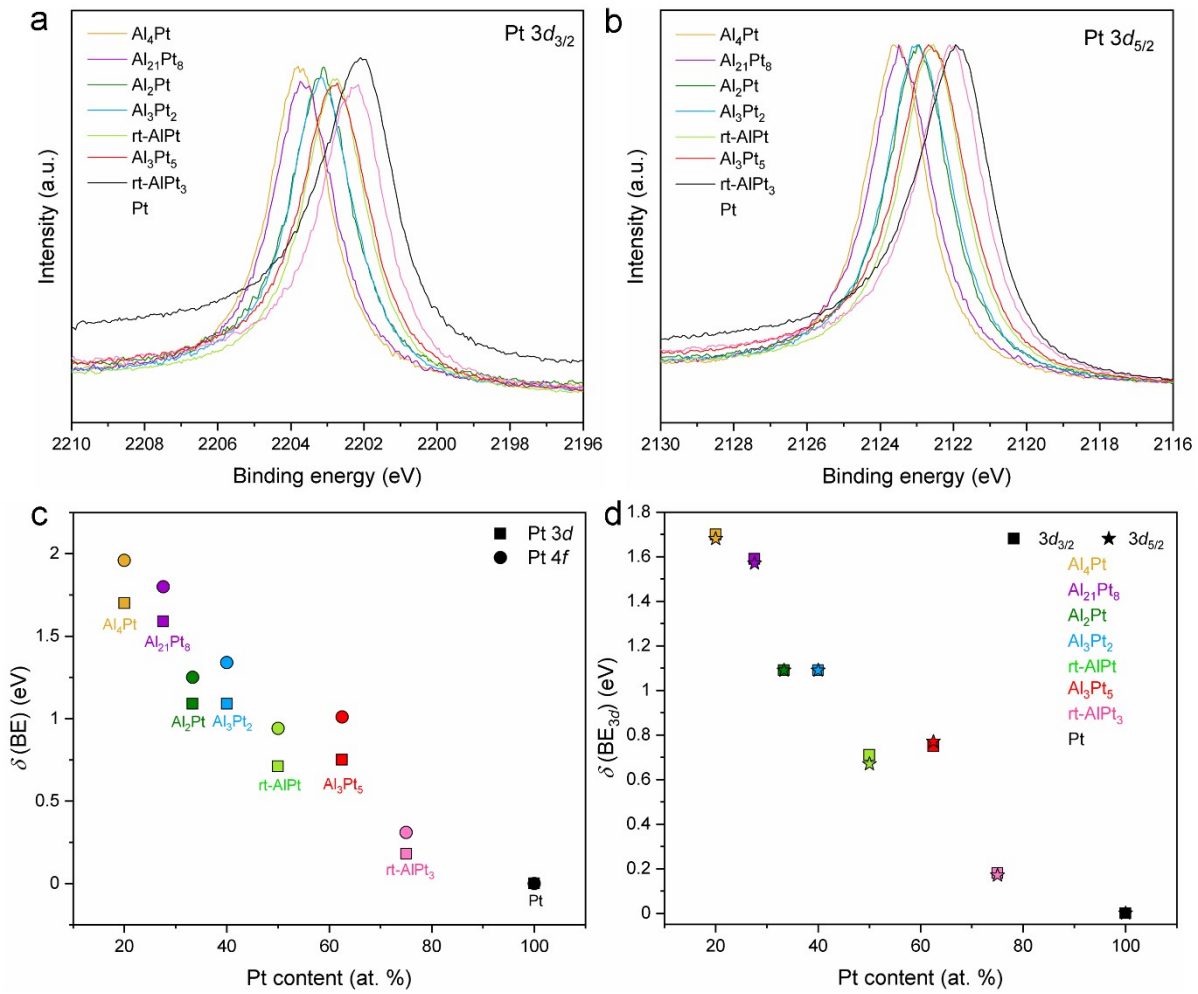


Figure S6. HAXPES spectra of Pt 3*d* core levels (*a* - Pt $3d_{3/2}$, *b* – Pt $3d_{5/2}$) and shifts of their binding energies (in relation to elemental Pt, $\delta(BE_{3d})$) as a function of Pt content in Al-Pt compounds (*c* – in comparison with Pt 4*f* core levels, *d* – Pt $3d_{3/2}$ and Pt $3d_{5/2}$ lines of the doublet).

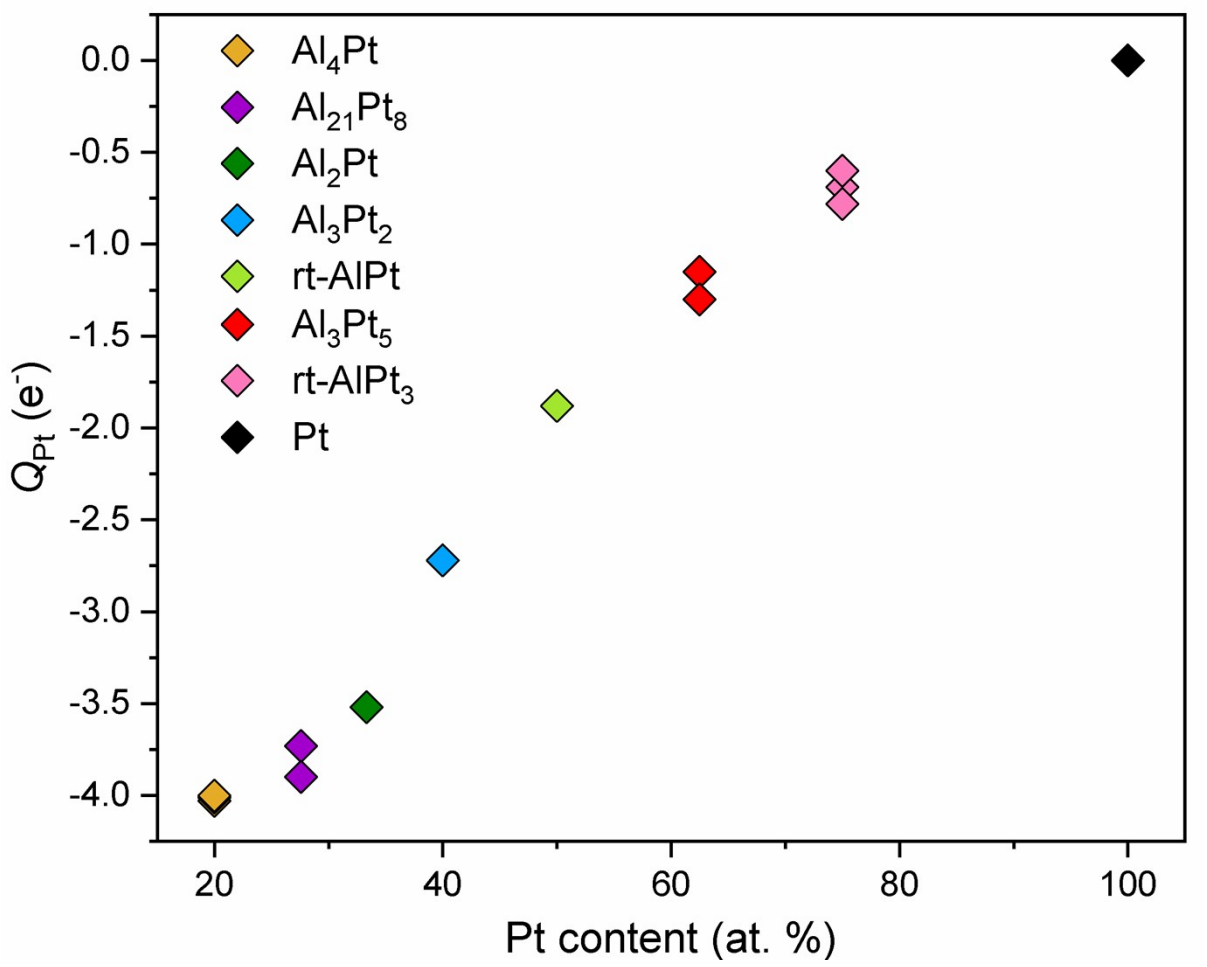


Figure S7. Effective charges of Pt atoms in Al-Pt binary compounds as a function of Pt content. The values for the symmetrically inequivalent Pt atoms are shown separately.

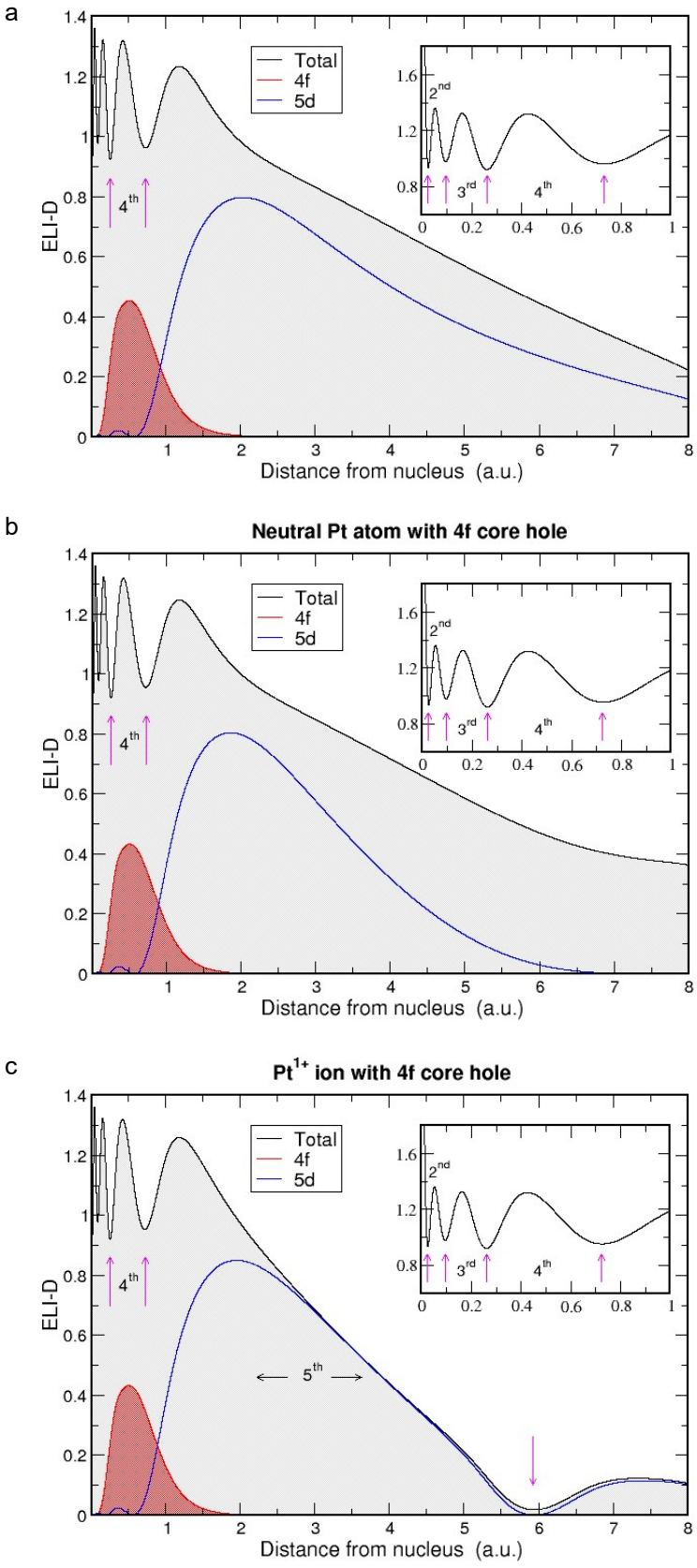
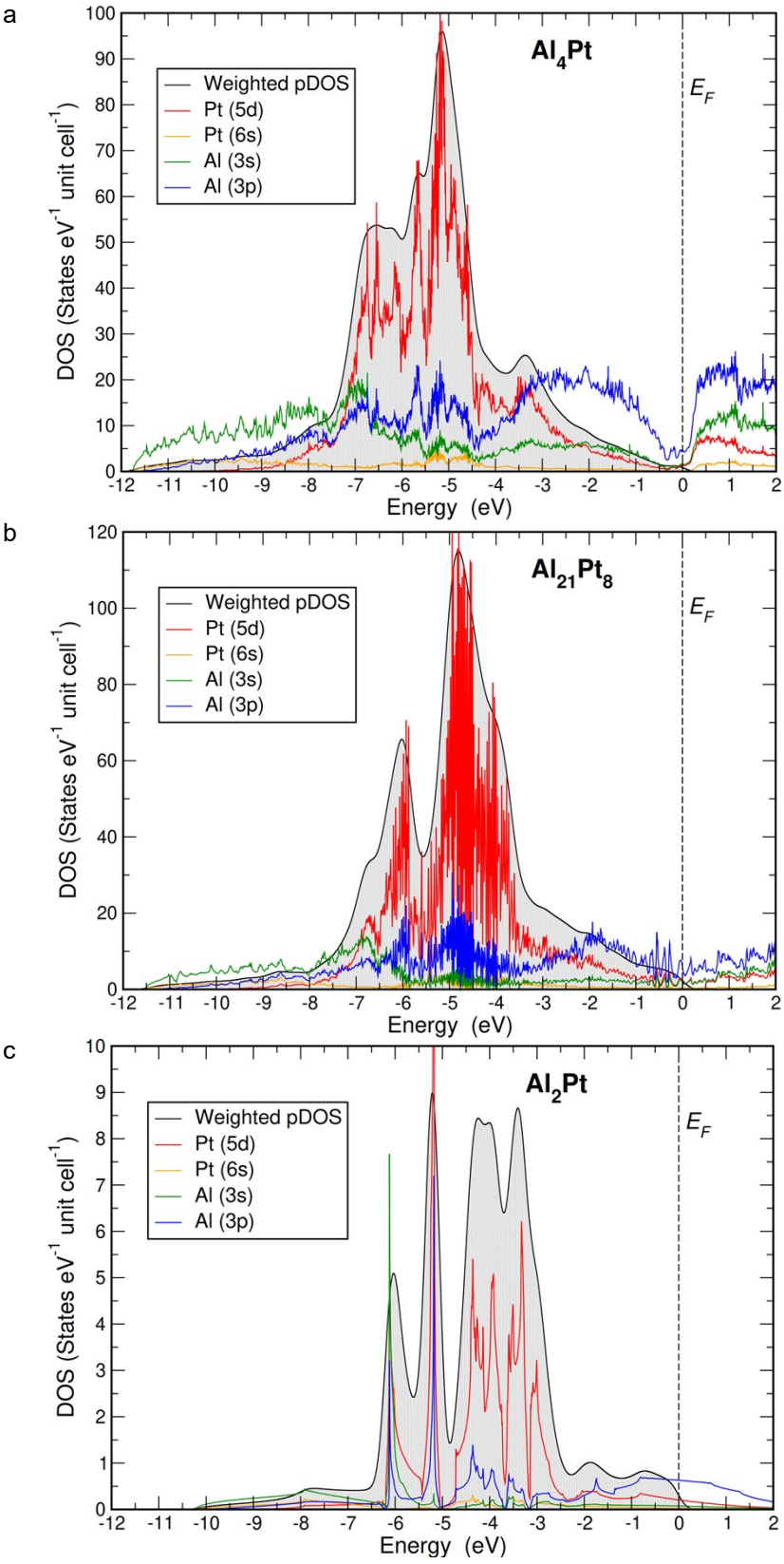


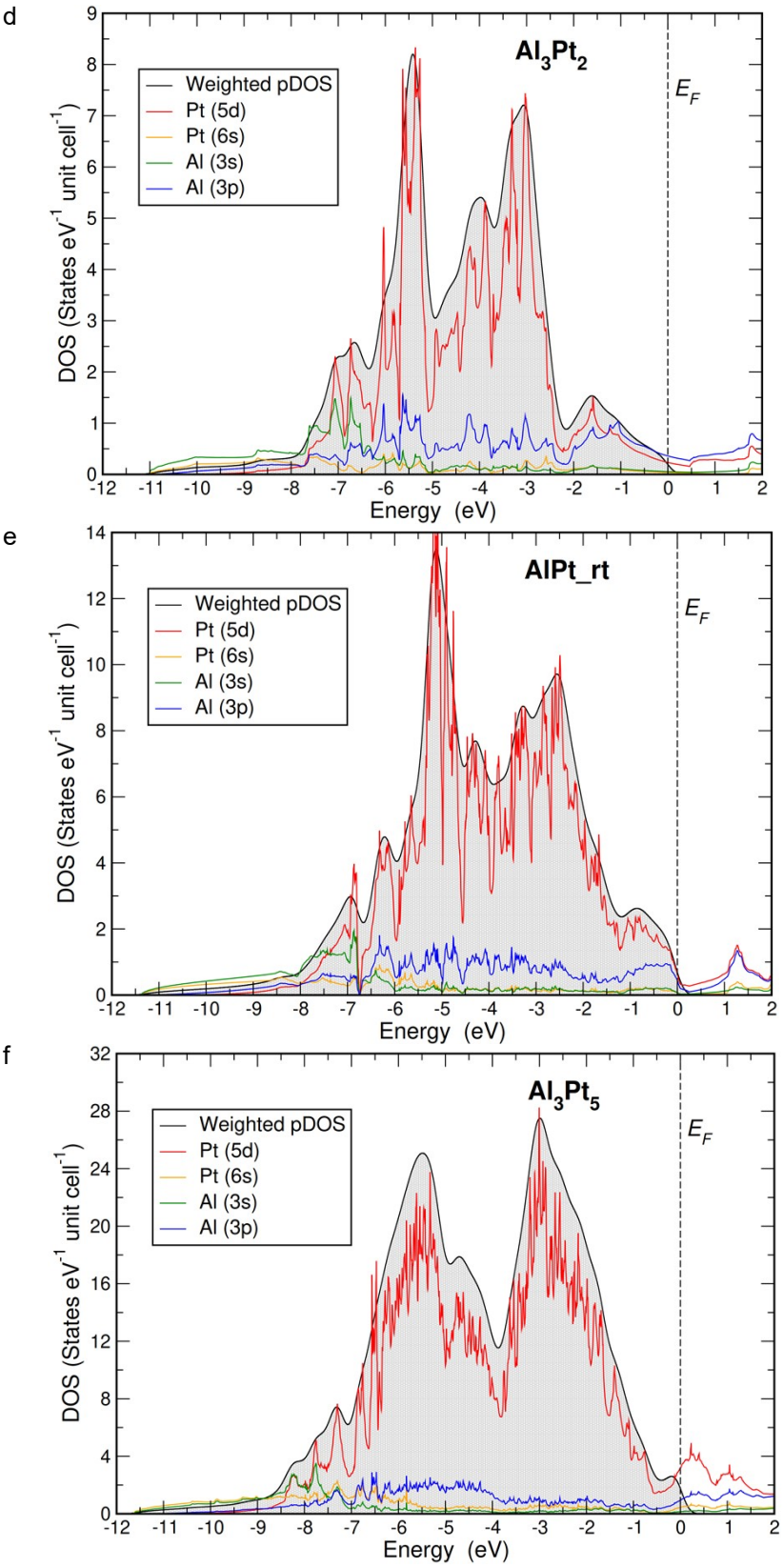
Figure S8. The total ELI-D and the partial ELI-D (pELI) due to 4*f* and 5*d* orbitals. (a) Normal Pt atom, (b) Neutral Pt atom with a core hole in 4*f*, (c) Pt^{+1} ion with a core hole in 4*f*. The minima of the total ELI-D define the boundaries between the shells. In the main figure, the boundaries of the 4^{th} shell are indicated. The insets show the region within 1 au of the nucleus so that all shells up to $n = 4$ can be easily identified.

The local minima of the total ELI-D define the boundaries between adjacent shells. The first three boundaries do not change across the different cases, 0.024, 0.094 and 0.260 a.u. The upper boundary of the 4th shell changes very little, 0.732 (normal) versus 0.726 au (with core hole). According to the results of these LDA calculations, the electronic configurations obtained by integrating the 5*d* electron density are (1) 9.417 (5*d*), 0.583 (6*s*); (2) 10.0 (5*d*), 1.0 (6*s*); (3) 10.0 (5*d*). Note that only in the ionized case (c), the 5th shell is formed (upper boundary at 5.942 au, because in this case practically there is no 6th shell; the number of electrons above r = 5.942 au is only 0.0005!

The shape of the pELI due to 4*f* does not seem to change, although of course integration of the 4*f* electron density over all space gives 14, 13 and 13 electrons, respectively, for the three treatments. However, note that in all cases pELI-4f leaks into the 5th shell, but reaches to zero at about 2 au.

The pELI due to 5*d* runs almost parallel to the total ELI-D above r ~ 2 au in the normal case (a). Here, the 5th and 6th shell cannot be differentiated. The same is also true for the neutral Pt atom with a 4*f* core hole. However, in this case the 5*d* subshell is fully occupied, thus pELI-5*d* becomes zero at about 7 au.


a
b
c
Al4Pt
Al21Pt8
Al2Pt
Weighted pDOS
Pt (5d)
Pt (6s)
Al (3s)
Al (3p)
EF
DOS (States eV-1 unit cell-1)
Energy (eV)


d
Al_3Pt_2
Weighted pDOS
Pt (5d)
Pt (6s)
Al (3s)
Al (3p)
E_F
DOS (States eV^{-1} unit cell^{-1})
Energy (eV)
e
AlPt_rt
Weighted pDOS
Pt (5d)
Pt (6s)
Al (3s)
Al (3p)
E_F
DOS (States eV^{-1} unit cell^{-1})
Energy (eV)
f
Al_3Pt_5
Weighted pDOS
Pt (5d)
Pt (6s)
Al (3s)
Al (3p)
E_F
DOS (States eV^{-1} unit cell^{-1})
Energy (eV)

g

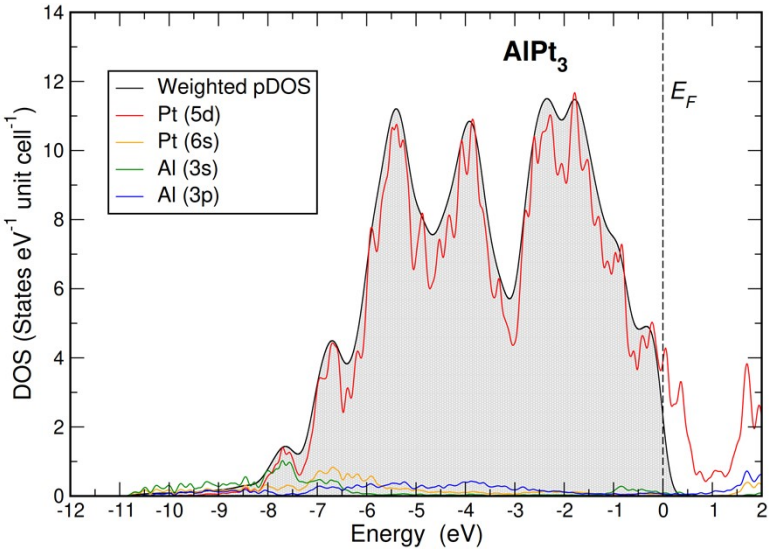


Figure S9. The sum of broadened and photoionization-cross-section weighted pDOS for Al_4Pt (a), $Al_{21}Pt_8$ (b), Al_2Pt (c), Al_3Pt_2 (d), rt-AlPt (e), Al_3Pt_5 (f) and rt-$AlPt_3$ (g) compounds.

References:

[1] A.J. McAlister, D.J. Kahan in *Binary alloy phase diagrams* (Ed. T.B. Massalski), ASM International, Materials Park, Ohio, USA, **1990**, pp. 195-197.

[2] M.B. Trzhaskovskaya, V.I. Nefedov, V.G. Yarzhemsky, *At. Data Nucl. Data Tables* **2001**, 77, 97.

[3] M.B. Trzhaskovskaya, V.I. Nefedov, V.G. Yarzhemsky, *At. Data Nucl. Data Tables* **2002**, 82, 257.

[4] M.B. Trzhaskovskaya, V.K. Nikulin, V.I. Nefedov, V.G. Yarzhemsky, *At. Data Nucl. Data Tables* **2006**, 92, 245.