fcc solid solution of the Co–Pd system treated by SQS / DFT calculations

Supplementary materials of the paper:
"Hydrogen sorption properties of Pd-Co nanoalloys embedded into mesoporous carbons" (2015)

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Abstract

Electronic structures details and mixing energies are given for all compositions on the *fcc* solid solution of the Co–Pd system investigated by SQS and DFT calculations without and with spin polarization.

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Contents

1 Methodologies

The binary Co–Pd *fcc* solid solution has been treated by the SQS method[1]. It consists to consider the bulk *fcc* lattice by a random-like distribution of Co and Pd atom at a given composition and with a finite number of total atoms in a cell. The choice has been made by considering a 16-atom cell in Special Quasirandom Structure (SQS) for three compositions $(\frac{1}{4}, \frac{1}{2}, \frac{3}{4})$[2], and for infinite dilutions $(\frac{1}{16}, \frac{15}{16})$. These structures have been calculated in the frame of the DFT[3] within a pseudo-potential approach using the VASP package[4, 5]. The PBE functional has been used with a 400 eV cut-off energy[6] and a high k-mesh density. Preserving the original crystal symmetry, each structure has been fully relaxed, with and without the electronic spin-polarization. Charge transfers have been computed using Bader's prescription [7, 8]. Calculations have been done with the ZenGen task manager [9].

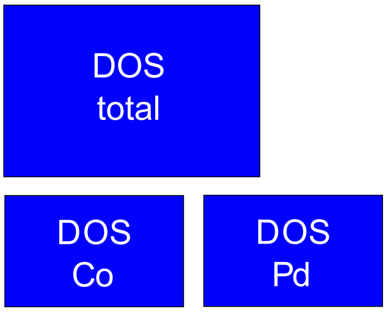
The mixing energy is simply given by the relation:

$$\Delta H^{fcc}_{\text{mix}}\text{Co}_x\text{Pd}_y = E^{fcc}\text{Co}_x\text{Pd}_y - xE^{fcc}(\text{Co}) - yE^{fcc}(\text{Pd}). \tag{1}$$

2 Without spin-polarization (NP)

2.1 Density of states(DOS)

Reading help:

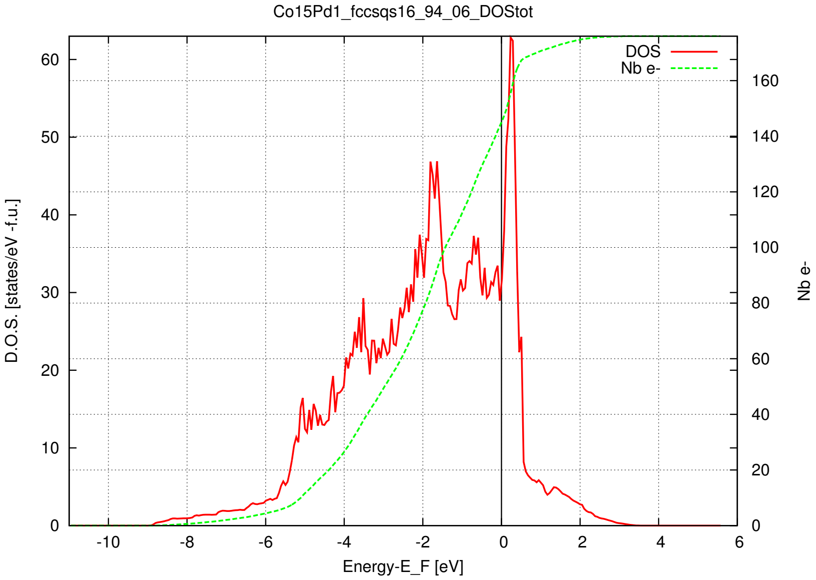


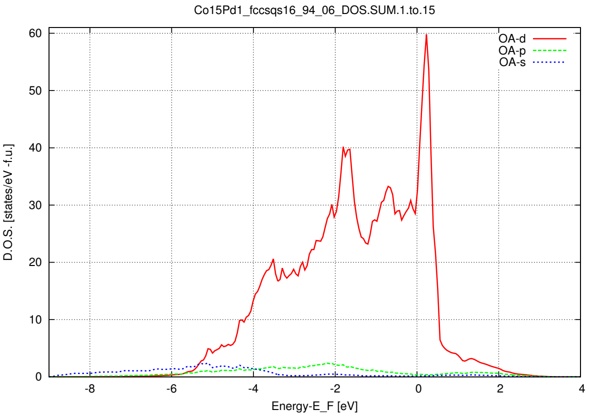
The Fermi level is shifted to the origin of energy.

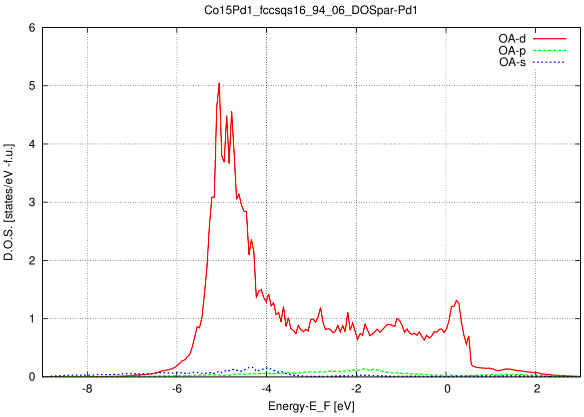
The total DOS is given for 16 atoms (red line, left scale) with the number of valence electrons (dashed green line, right scale).

The partial DOS, *i.e.* Co (left) and Pd (right) contributions are given for all atoms of the same type contained in a unit formula. The contribution of orbital s electrons ($l = 0$) is in blue, p ($l = 1$) in green and d ($l = 2$) in red.

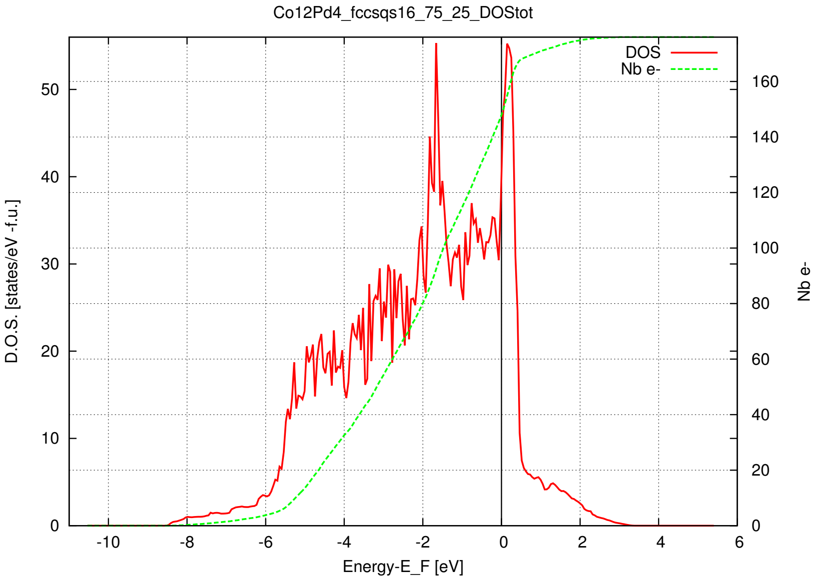
2.1.1 Co15-Pd1, $x_{\mathrm{Co}} = 0.94$, $x_{\mathrm{Pd}} = 0.06$







2.1.2 Co12-Pd4, $x_{\mathrm{Co}} = 0.75$, $x_{\mathrm{Pd}} = 0.25$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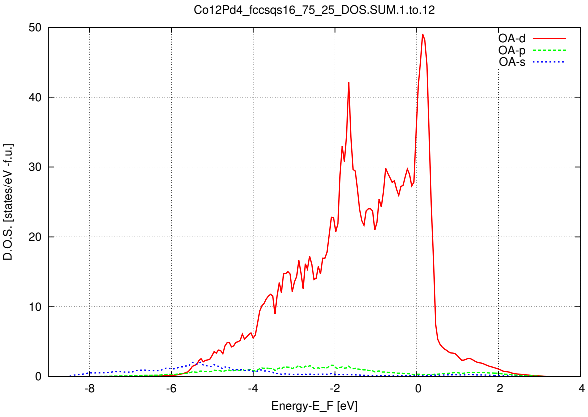
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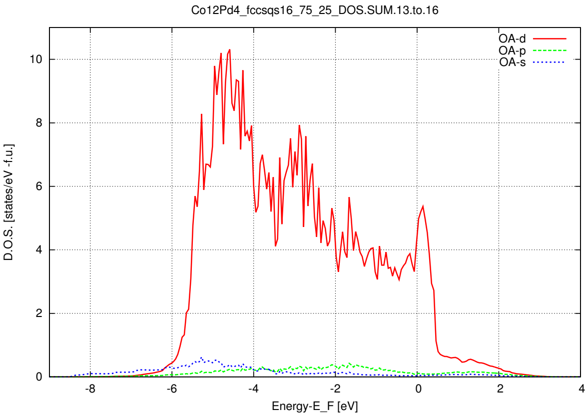
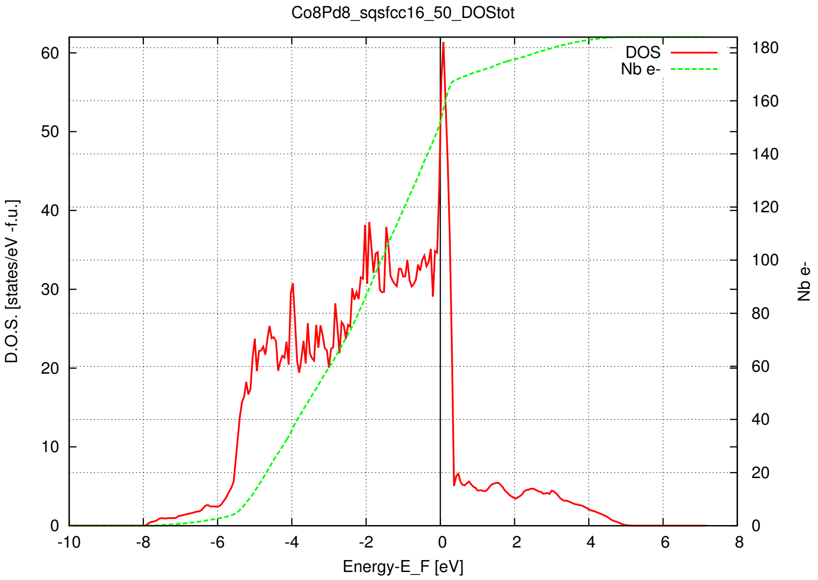
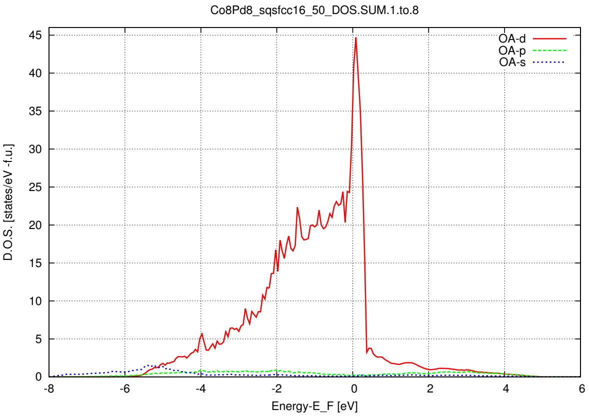
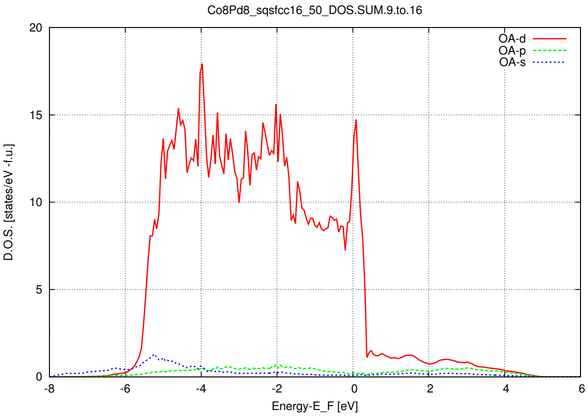

Co12Pd4_fccsqs16_75_25_DOS.SUM.13.to.16

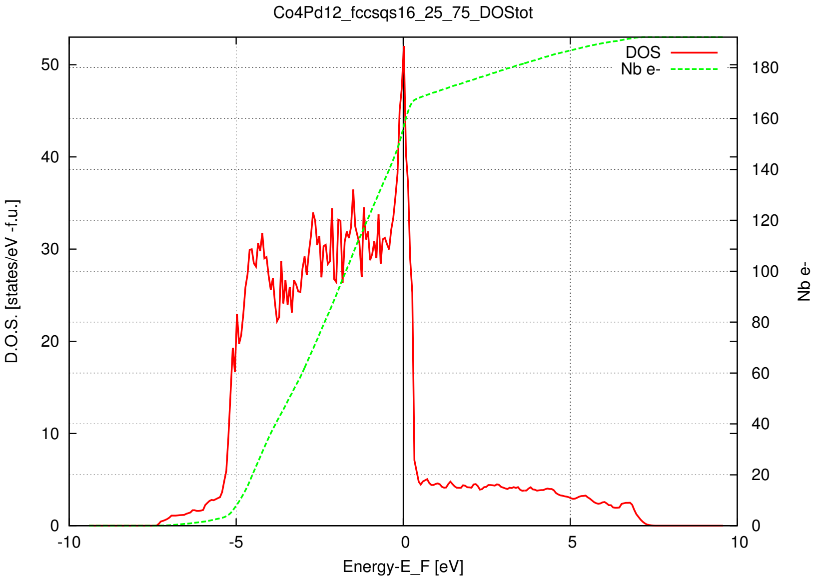
2.1.3 Co8-Pd8, $x_{\mathrm{Co}} = 0.50$, $x_{\mathrm{Pd}} = 0.50$

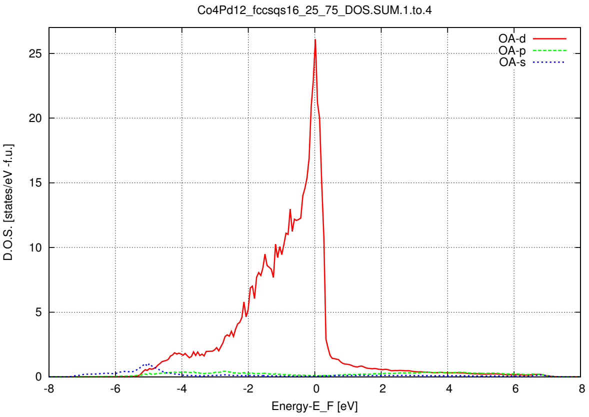


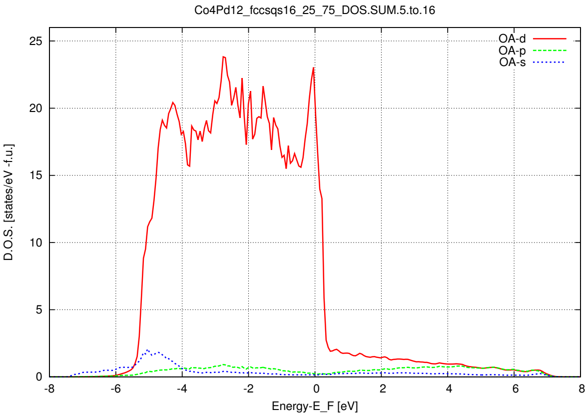




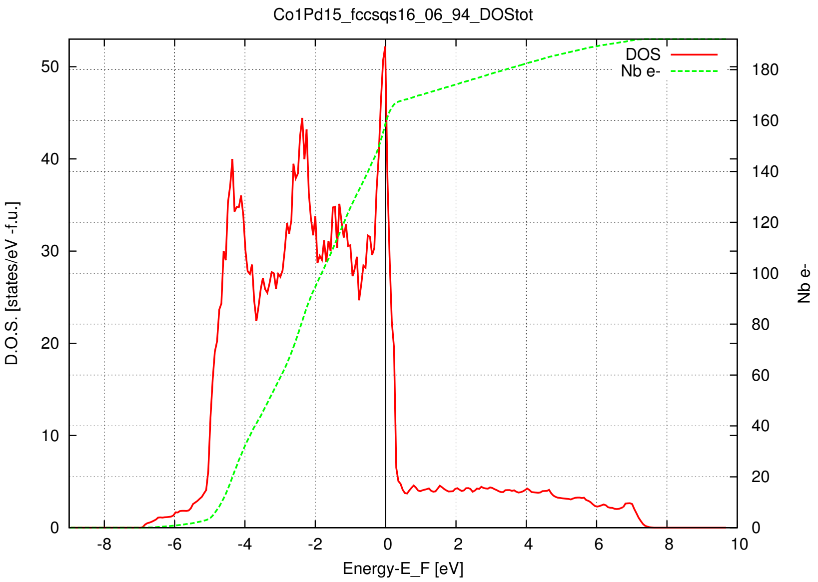
2.1.4 Co4-Pd12, $x_{\mathrm{Co}} = 0.25$, $x_{\mathrm{Pd}} = 0.75$



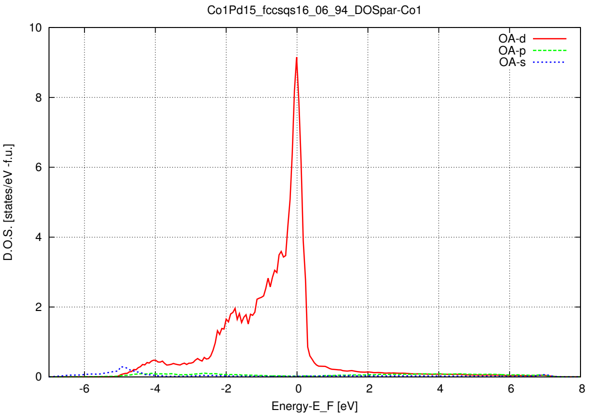




2.1.5 Co1-Pd15, $x_{\mathrm{Co}} = 0.06$, $x_{\mathrm{Pd}} = 0.94$



Co1Pd15_fccsqs16_06_94_DOStot



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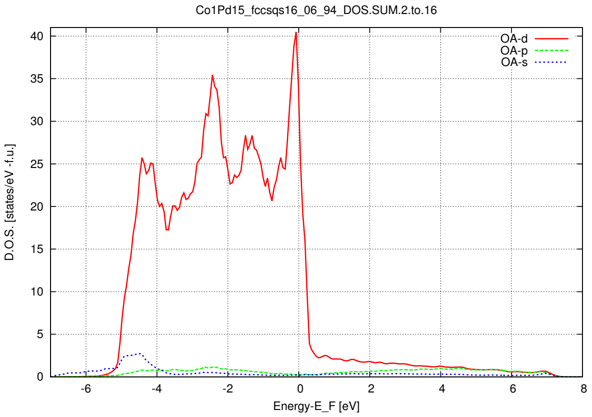
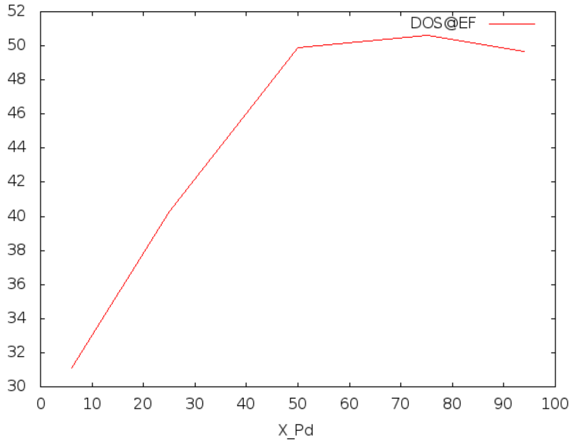


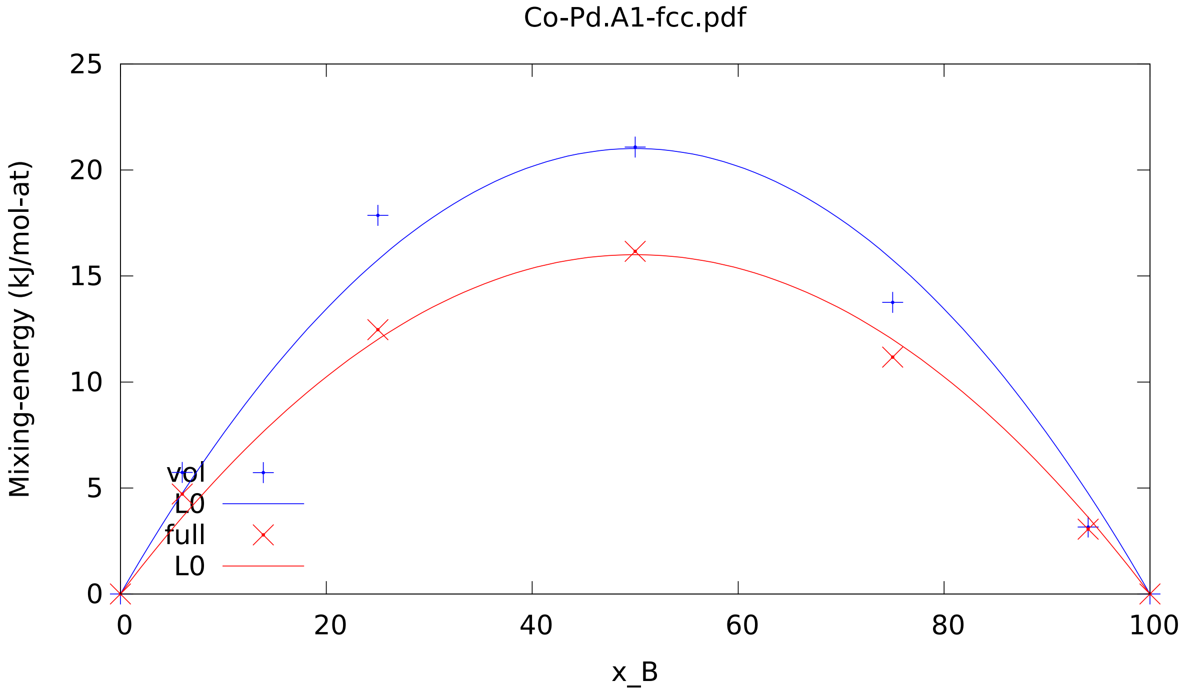
Co1Pd15_fccsqs16_06_94_DOS.SUM.2.to.16

2.2 Density of states at Fermi level



2.3 Mixing energy

2 steps have been considered : `vol` for an unique volume relaxation, and `full` for a full relaxation (*i.e.* volume and internal position)



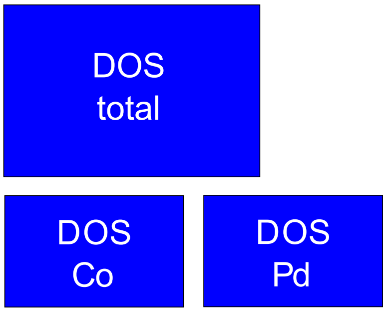
Conclusion

The high density of state of the Co-based alloys suggests a more stable stable by a ferromagnetic ordering (Stoner criterion). In fact for all compositions, Fermi level is centered in a dense structure corresponding to $3d$ states of Co.

3 With spin-polarization (SP)

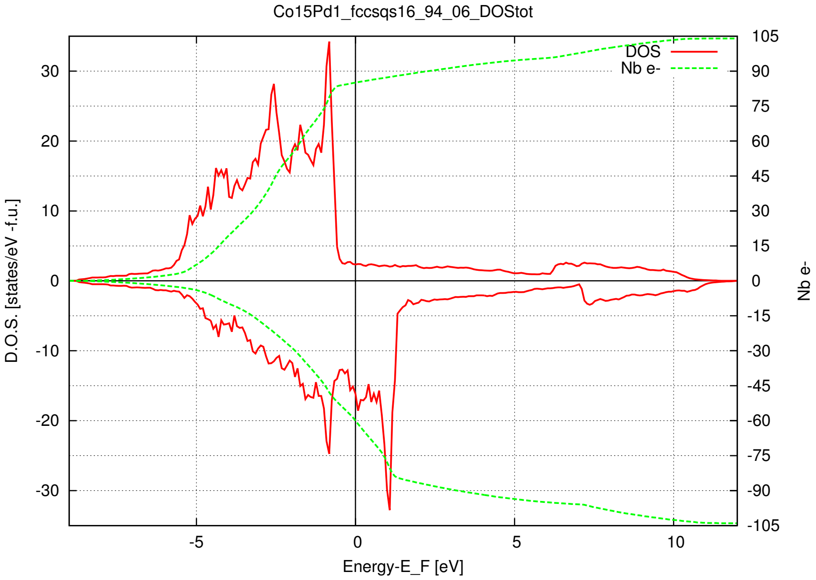
3.1 Density of states(DOS)

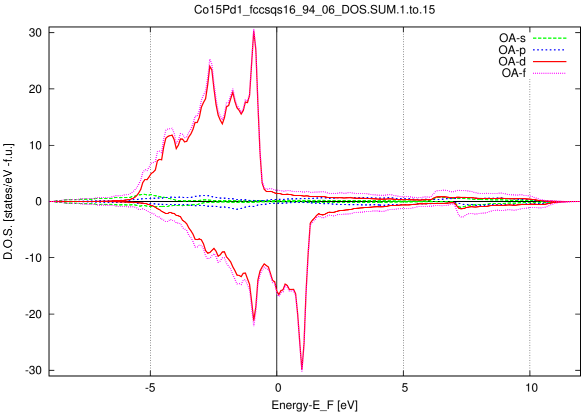
reading help:

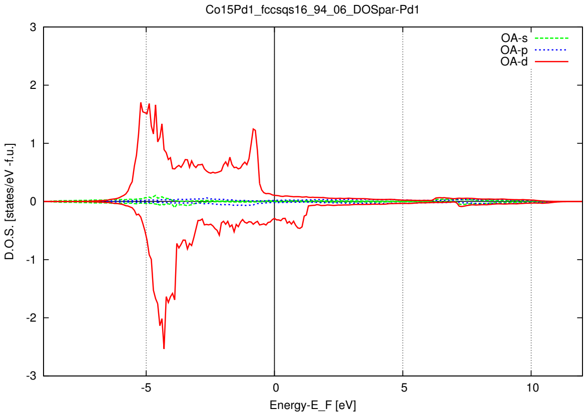


Same conventions as those given in the previous section are used, with contributions in both directions of spin.
There is a bug for displaying partial DOS, read "OA-f" as the total DOS of the atom. The reader had obviously understand :)

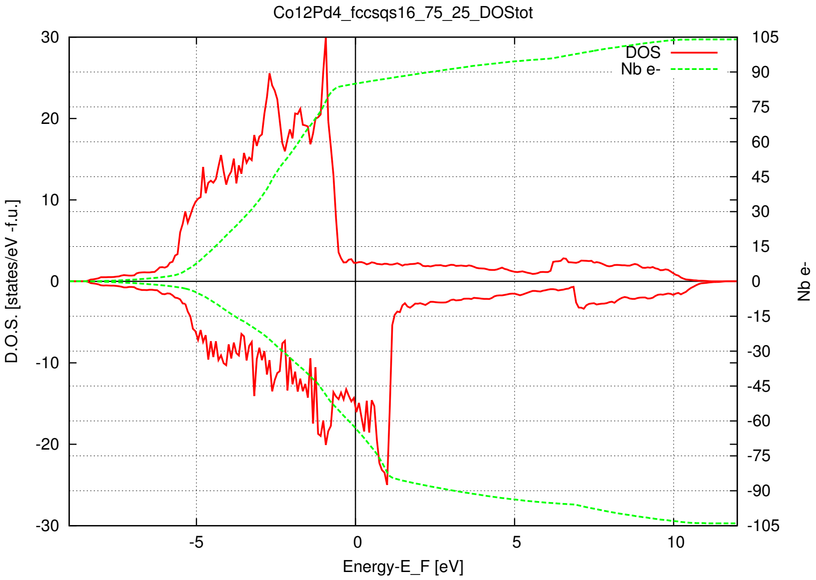
3.1.1 Co15-Pd1, $x_{\mathrm{Co}} = 0.94$, $x_{\mathrm{Pd}} = 0.06$

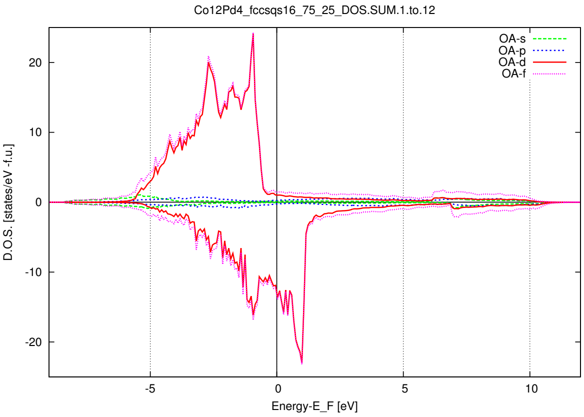


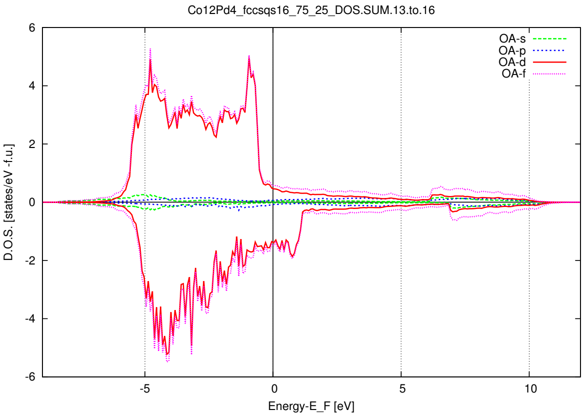




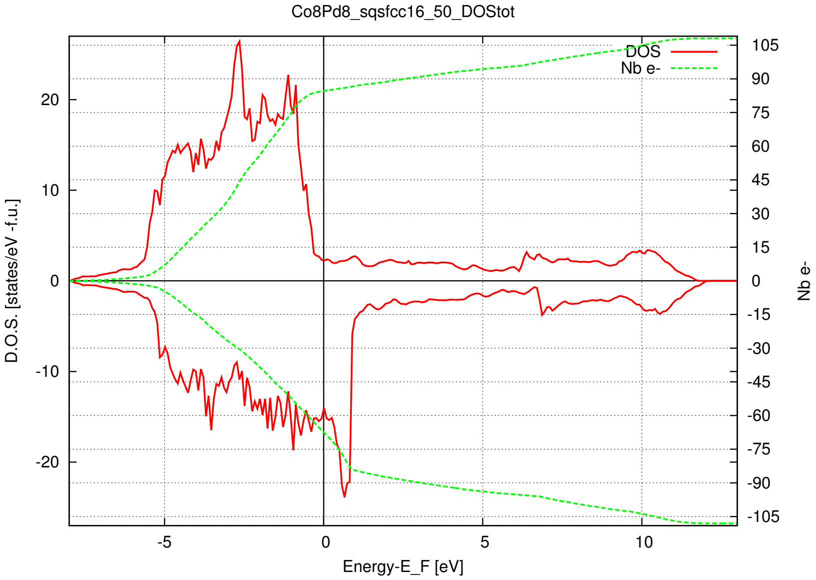
3.1.2 Co12-Pd4, $x_{\mathrm{Co}} = 0.75$, $x_{\mathrm{Pd}} = 0.25$

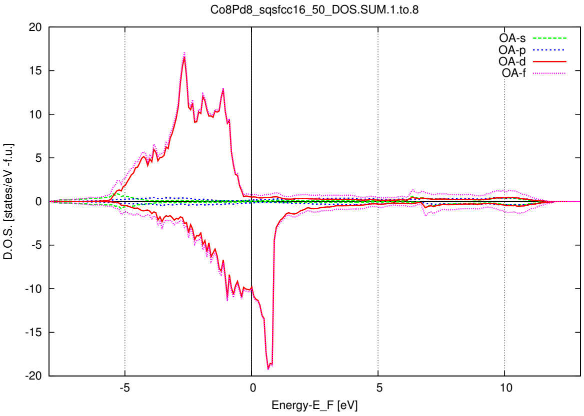


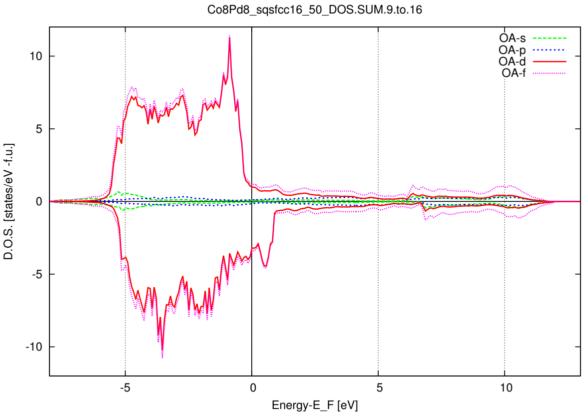




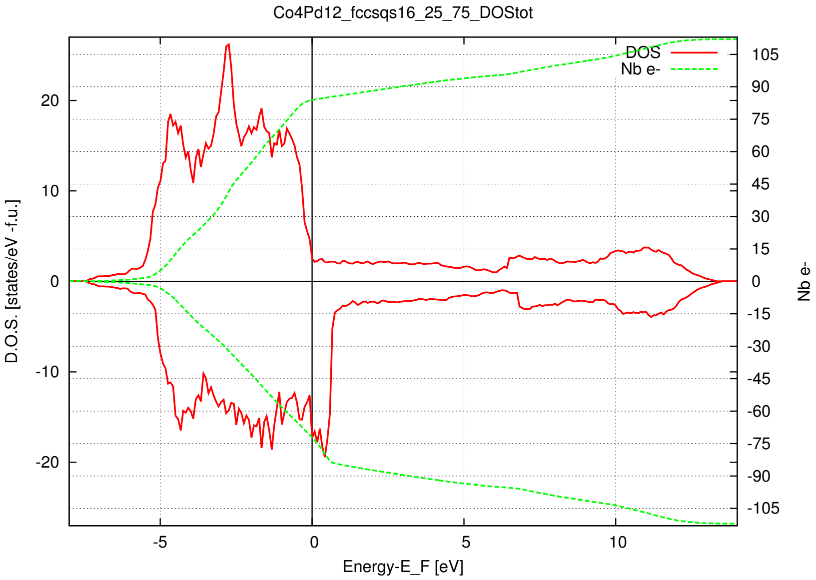
3.1.3 Co8-Pd8, $x_{\mathrm{Co}} = 0.50$, $x_{\mathrm{Pd}} = 0.50$

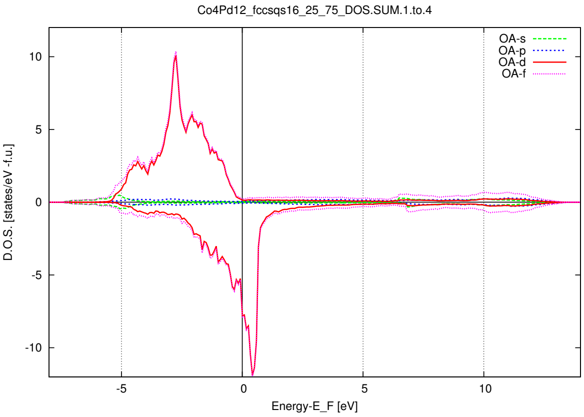


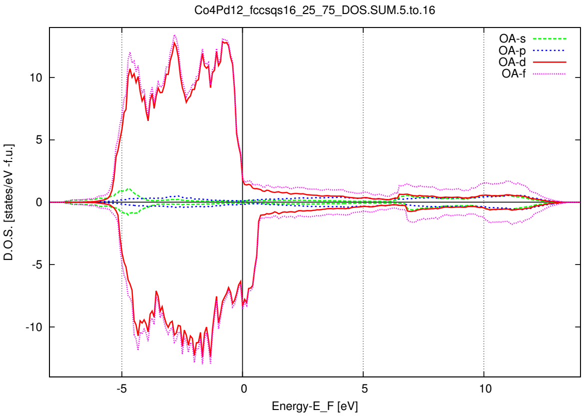




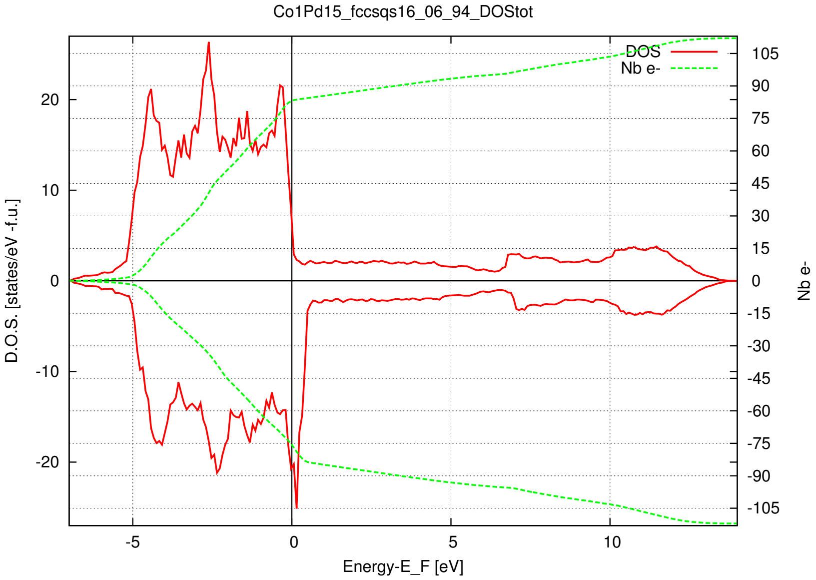
3.1.4 Co4-Pd12, $x_{\mathrm{Co}} = 0.25$, $x_{\mathrm{Pd}} = 0.75$

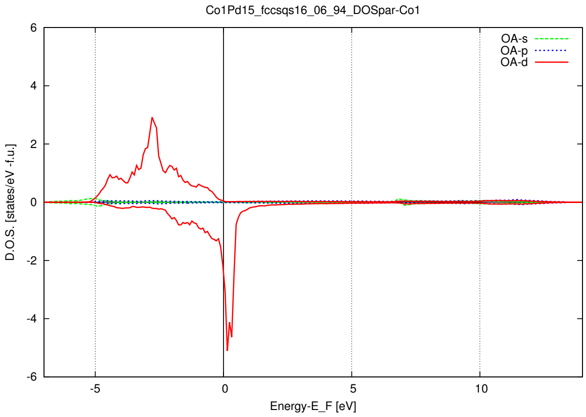


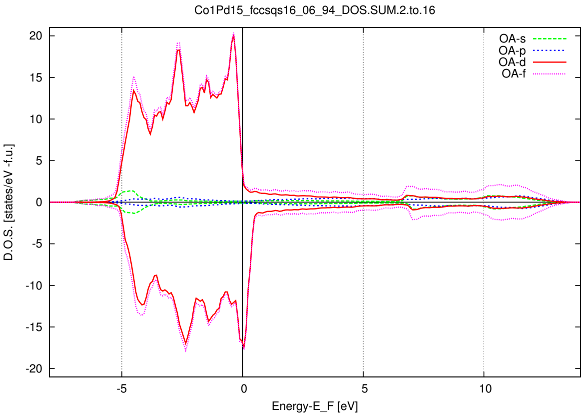




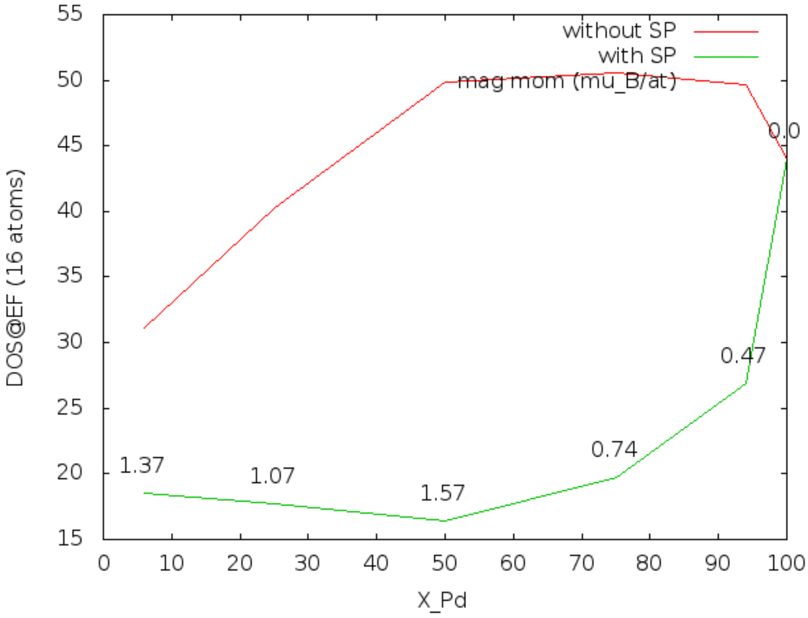
3.1.5 Co1-Pd15, $x_{\mathrm{Co}} = 0.06$, $x_{\mathrm{Pd}} = 0.94$







3.2 Density of states at Fermi level



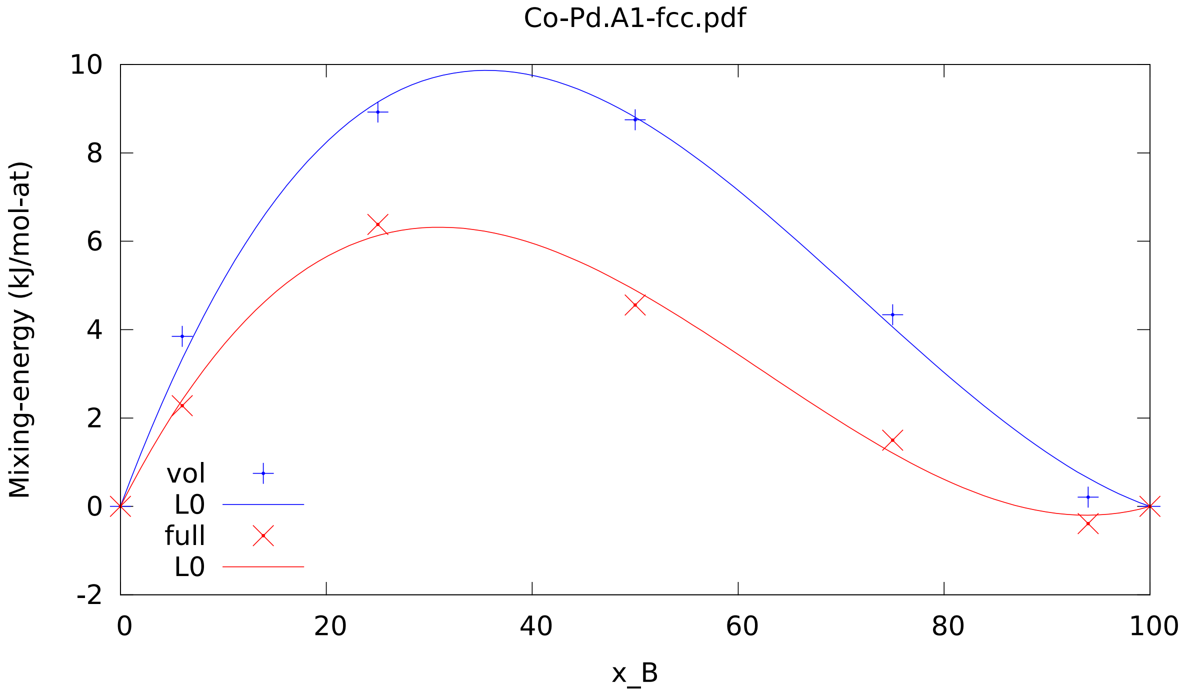
At all composition, there is a Bader charge transfer from Co to Pd. Values are given in the following table.

x_{Pd}	e- (Co)	e- (Pd)
0.06	0.03	0.47-
0.25	0.12	0.35-
0.50	0.24	0.24-
0.75	0.40	0.13-
0.94	0.50	0.03-

This charge transfer lead to fulfill the $4d$ states of Pd. In this way, the main electronic structure of the majority spin is fully filled and the Fermi level (E_F) falls in a valley of states in the electronic structure of the minority spin, located in front of a localized $3d$ peak of Co. This combined effect leads to a reduction of the density of states at E_F with SP in comparison with pure *fcc*-Pd. To satisfy the Stoner criterion, system is thus more stable with ferromagnetic ordering at 0 K and the density of states at E_F decreases with Co content. The magnetic moment by Co atom is indicated below SP points (in μ_N), and are in good agreement with experiments [10].

3.3 Mixing energy

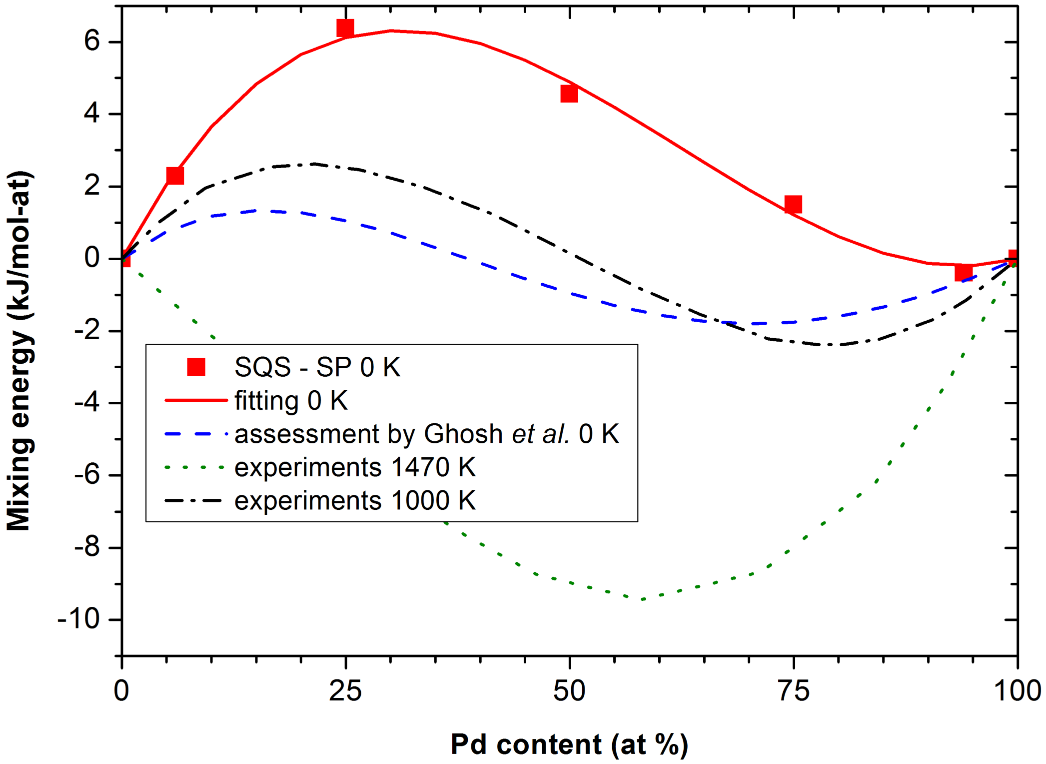
2 steps have been considered : `vol` for an unique volume relaxation, and `full` for a full relaxation (*i.e.* volume and internal position), all with spin-polarization.



In page 9, the mixing energy without spin polarization shows a strong repulsion interaction between Co and Pd in *fcc* phase. With spin polarization (upper graph), the mixing energies values still positive but are lower. The $x_{\mathrm{Co}} = \frac{1}{16}$ composition even shows a negative value for the `full` relaxation. This results may being surprising since the Co–Pd phase diagram is characterized by a complete miscibility in the *fcc* phase[11]. However, the miscibility exists only at a temperature different of 0 K (Co is *hcp* at RT), and the existing thermodynamic assessment[12] agrees with an inversion of Gibbs energy sign with x_{Co}. To overcomes the positive mixing energy, Ghosh *et al.* suggests an temperature dependence of the interaction parameters in the thermodynamic modeling. The assessment values are given in following table (in Joule/mole).

L^{ν}	Ghosh *et al.*		SQS-fit
$L^{0,fcc}_{\mathrm{Co,Pd}}$	-3823	-11 T	+19566
$L^{1,fcc}_{\mathrm{Co,Pd}}$	+14981	+5 T	-26234
$L^{2,fcc}_{\mathrm{Co,Pd}}$	+7751	-11 T	–

A comparison of the Gibbs energies at 0 K is given in the graph on the next page. Some experiments at 1000 K [13] and 1470 K [14] are also given for comparison.



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