Results from the DOS analysis for AlCoNi QC

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I. THE PROBLEM

The forces on TM atoms in decagonal QC were studied in a previous paper. The TM atoms were found to repel each other consistent with expectations but in contradiction to the prediction of GPT. We found that, in AlCoNi QC, similar TM atoms like to be adjacent to each other. The GPT pair potentials were corrected at short distance to comply with the VASP calculation. To get insight into the forces and to understand the root cause for such TM atoms behavior, the densities of states of the QC are studied. Band narrowing and peak shifts in local and total DOS are expected under moving the TM atoms away from each other.

II. SUMMARY

The total and band energy were calculated for four structures. The basic structure shown in Fig. 1 (d0c0s0) is our same structure we used for the pair potential correction. It is $Al_{34}Co_{10}Ni_6$ with CoNi pairs on the tile edges and two Co atoms surrounding the central Al atom. The unit cell is shown with the atoms numbered. Gray atoms are Co, black are

Ni and white are Al. Moving the pair 23 and 26 away from each other by Δr=0.2 au in the x-direction and similarly for the pair 3 and 49 (adjacent through cell repetition) produces the basic-displaced (d200c0s0) structure. Swapping atom 23(Ni) with atom 3(Co) produces the swapped (d0s2303) structure and performing the same displacement, as in d200c0s0 but this time on CoCo and NiNi pairs, results in the swapped-displaced (d200s2303) structure. In all, the displacement was performed on two CoNi pairs, one CoCo pair and one NiNi pair. The total and the atomic densities of states were calculated for all structures.

Table I shows the different parameters calculated by VASP for each structure. Note that the Fermi energies differ by less 0.02. In all coming graphs the differences between the Fermi energies will not be noticeable. Table II shows the differences in energies between the structures. As expected and calculated before, the swapping lowers the energy, reflecting the fact that TM atoms prefer to be close to similar species (slightly). Displacing the TM pairs away from each other lowers the energy in both the basic and the swapped structures. The band energy differences are always much larger than the total energy differences. The total energy cost of stretching two CoNi bonds almost equal to the cost of stretching CoCo and NiNi bonds. However, the band energy difference is higher when stretching the CoNi pairs. The fourth column in table II shows the forces estimated from the displacement energies. As discussed, four TM atoms are each displaced by Δr = 0.2 au in the direction of the forces shown in fig. 2. We define $\overline{F}$ as -ΔE$_{tot}$/4Δr. The calculated forces here agree with the directions of the forces in fig. 2. The magnitude of the forces calculated on the TM atoms, about 0.9 eV/Å, lies between the magnitude of the forces prior to displacement and after displacement, as expected.

Fig.[3-6] show the averaged total and elemental DOS for the four structures. The Al DOS is flat because it doesn't tend to have d-electrons. Co curve peaks are always higher than Ni in magnitude and position at higher energies (dE=1-2 eV). They are broader which might accounts for the different behavior of stretching CoNi pairs versus CoCo and NiNi pairs. All the DOS graphs were obtained from the VASP calculated DOS using a k-space grid of 3x6x10 and smoothed out (Gaussian with sigma=0.2) for clarity. Individual atom densities of states obtained from VASP by dividing the space into cells around the atoms. The cells can overlap and they are not necessarily covering the space. Missing and/or overcounting portions of the space happen as a result. This can be seen from these graphs where the sums of the elemental densities of states do not match the total because the total DOS is calculated accurately for the whole space.

Fig.[7-10] show the decomposition of the density of states into s, p and d-band contributions. The peaks in the total DOS are d-band peaks. In fig.10 (swapped displaced) there is a noticeable peak at about -2.7 eV. As the decomposition and fig 6 show, it is an Al, s-band peak and contributed mostly from Al atoms close to Co atoms.

In fig. 11, the total DOS for the basic and the basic-displaced structures were plotted on the same graph for comparison. Fig. 12 is for the swapped structures and fig. 13 is for basic and swapped structures. State migration from one side of the curve to another is an energy altering mechanism. States moving down lowers the band energy and states moving up raises the band energy.

The set of figures [14 - 16] are the differences between the structures plotted together in the previous set of figures. In fig 14, the energy lowering mechanism discussed earlier is apparent. States are moving from higher to lower energies. Fig. 15 shows the puzzling peak at -2.7 eV. The graph shows that the density of states are not accurate because the number of states is conserved. The difference plot shows that some states moved to lower energies but it is clear that there are more states after displacement. The difference between the swapped and the basic DOS (fig. 16) is oscillating. This is not surprising because the energy difference is very small between these two structures.

The next group of the figures [17-22] show the difference in atomic density of states between the displaced-basic and the basic structures for Co atoms(fig. 17) and for Ni atoms(fig. 18), the displaced-swapped and the swapped (Co fig 19 and Ni 20) and the swapped and the basic (Co fig 21 and Ni 22). The differences for Al atoms are not shown because they are negligible. Some of the local TM-atom DOS difference plots show a signature of w-shape. In simple cases the symmetric w-shape is a sign of band narrowing and asymmetric w-shape is an indicator of peak shift. All the TM atoms change their band structures after displacement or swapping but the magnitude of the change is much larger for atoms participated in the change.

TABLES

TABLE I. Parameters calculated from VASP for the different structures

Structure	Name	E_{tot}(eV)	E_{band}(eV)	E_{Fermi} (eV)
d0c0s0	basic	-281.90	677.85	5.7553
d200c0s0	basic displaced	-282.29	675.85	5.7589
d0s2303	swapped	-281.94	677.12	5.7768
d200s2303	swapped displaced	-282.33	675.38	5.7753

TABLE II. Energy differences between the structures. The column $\overline{F}$ is the estimated force.

Structure	Comments	ΔE_{tot} (eV)	$\overline{F}$ (eV/Å)	ΔE_{band} (eV)
d0s2303-d0c0s0	Swap energy	-.042	NAN	-.727
d200c0s0-d0c0s0	2 CoNi bonds stretched	-.392	.921	-2.002
d200s2303-d0s2303	(CoCo + NiNi) bonds stretched	-.385	.910	-1.737

FIGURES

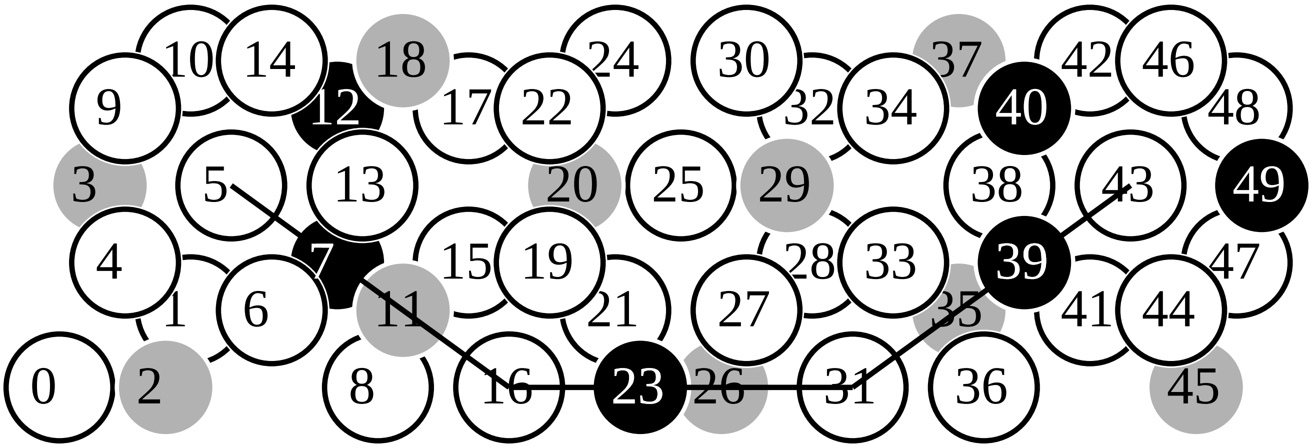

FIG. 1. The unit cell with the atoms numbered for clarity. Black atoms are Ni, gray are Co and white are Al.

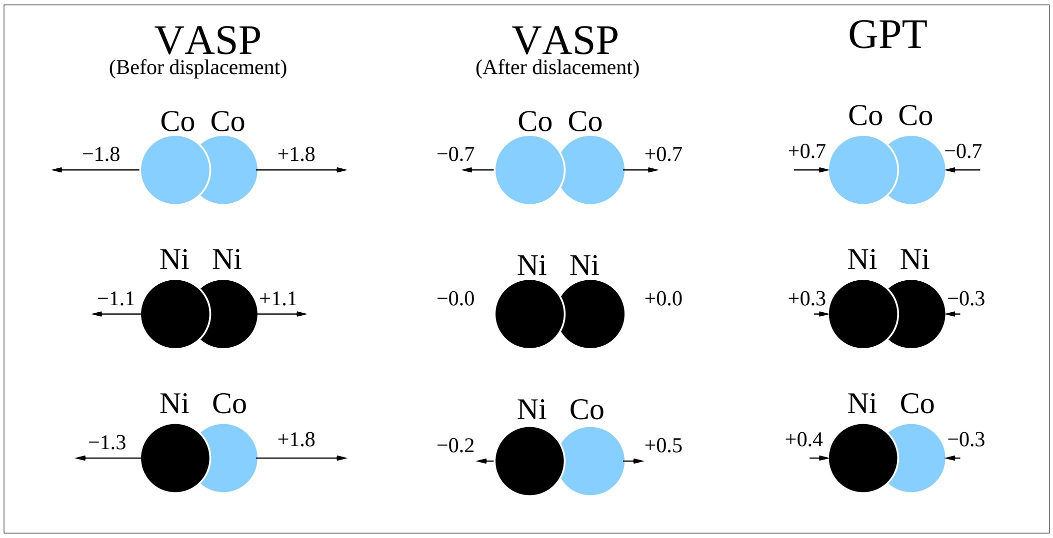

FIG. 2. The forces calculated by VASP and GPT. Columns from left to right correspond to undisplaced pairs, displaced pairs and GPT.

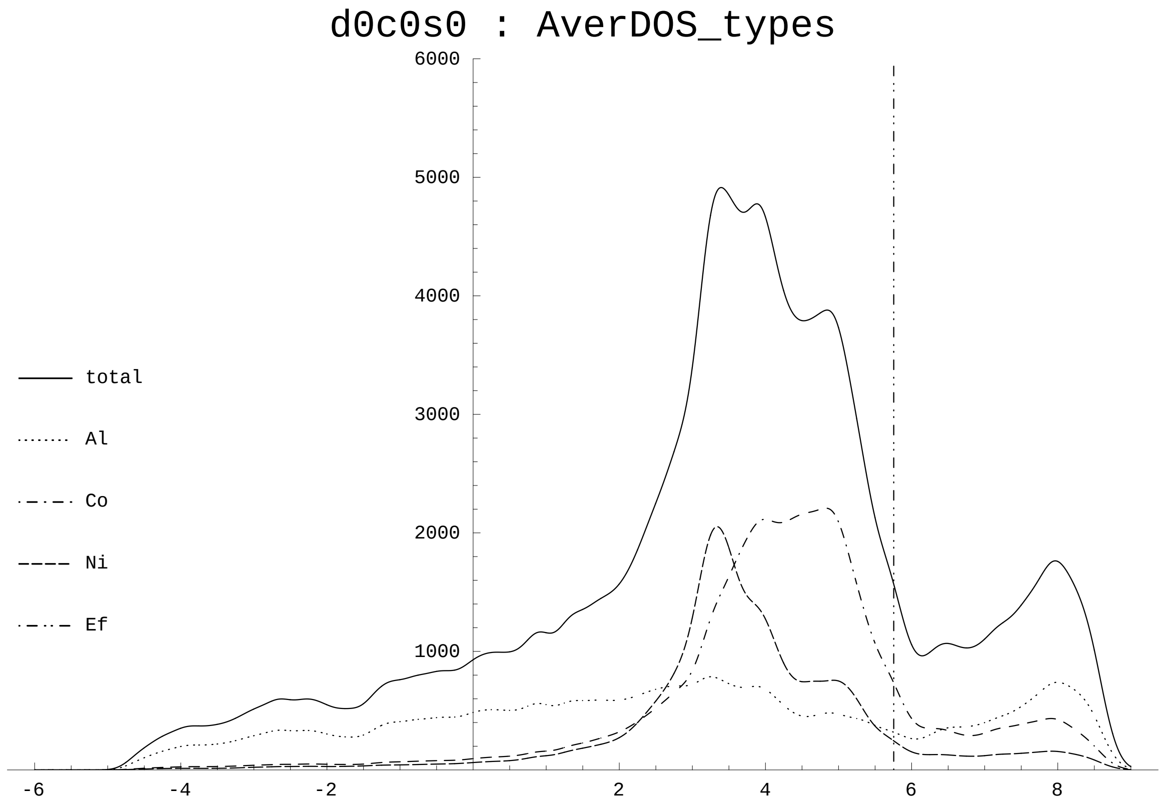

FIG. 3. The total and elemental density of states for the basic structure. The Co peak is broader than the Ni peak. That is because the ten Co atoms are divided into three groups. Each group has their peaks very close to each other but the different group peaks are spread along the range shown in the graph . Ni peaks are close to ech other.

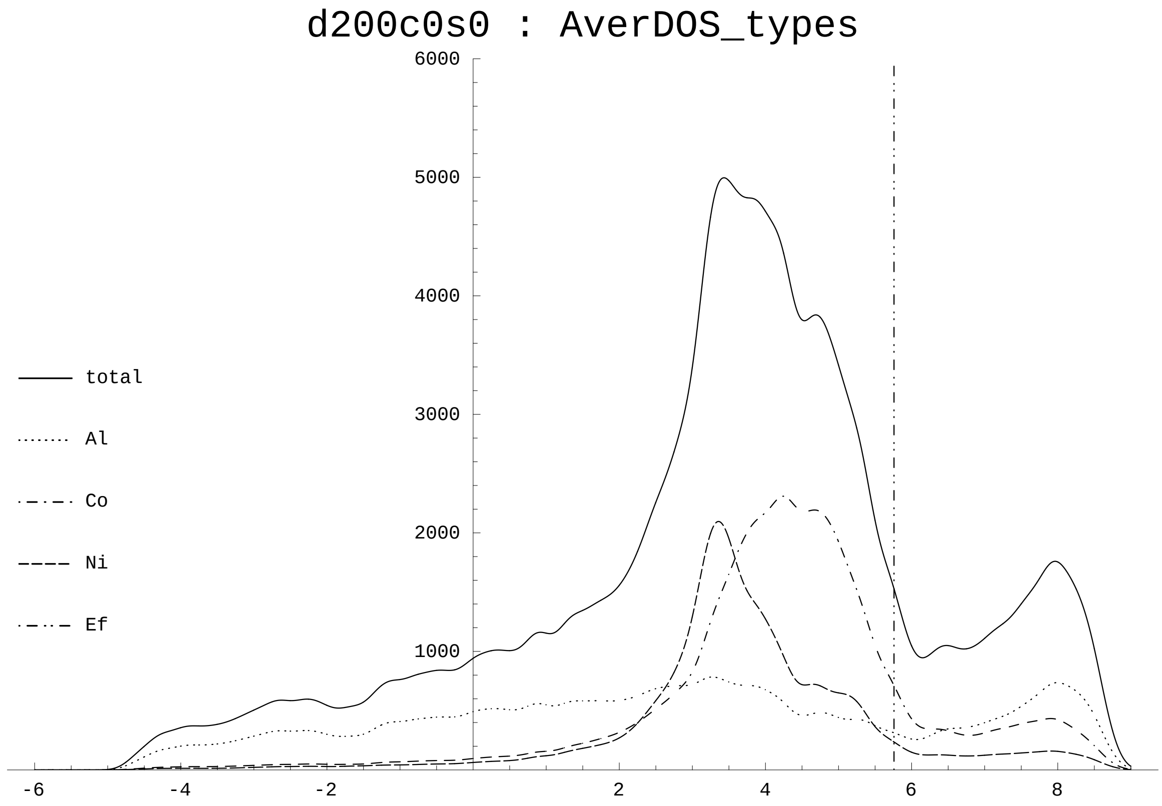

FIG. 4. The total and elemental density for states for the basic-displaced structure.

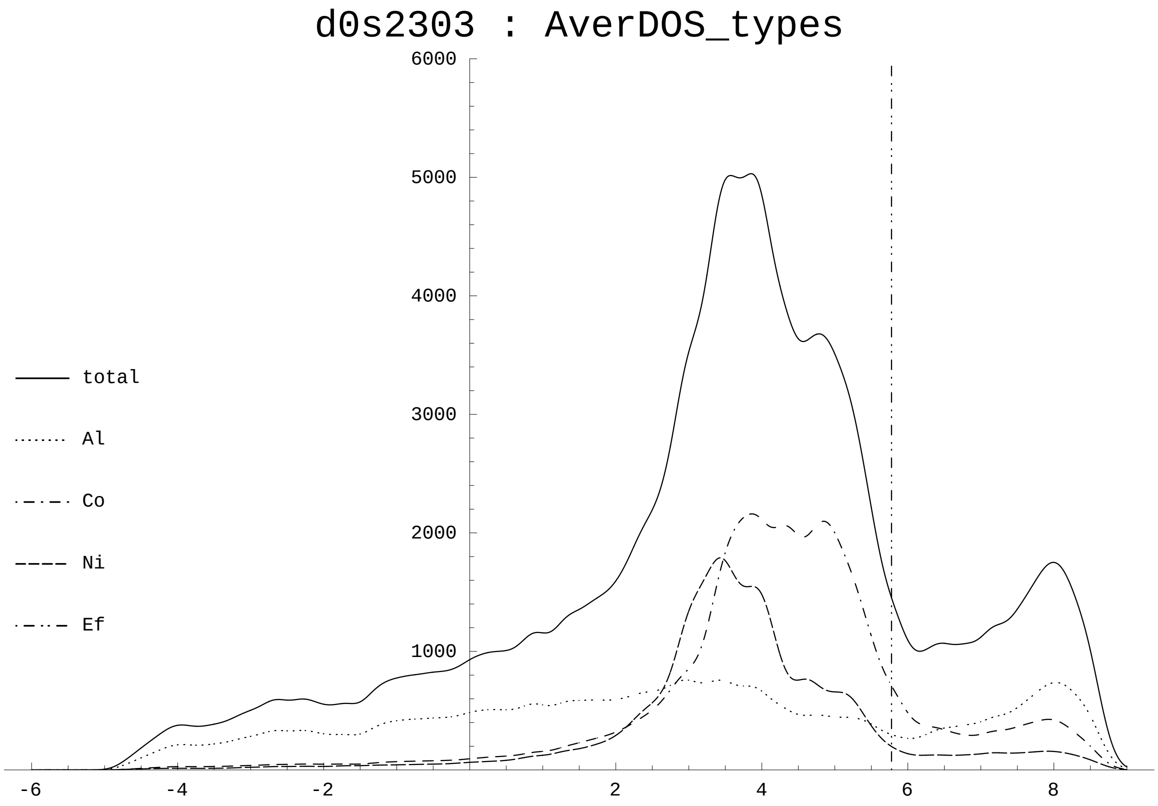

FIG. 5. The total and elemental density for states for the swapped structure.

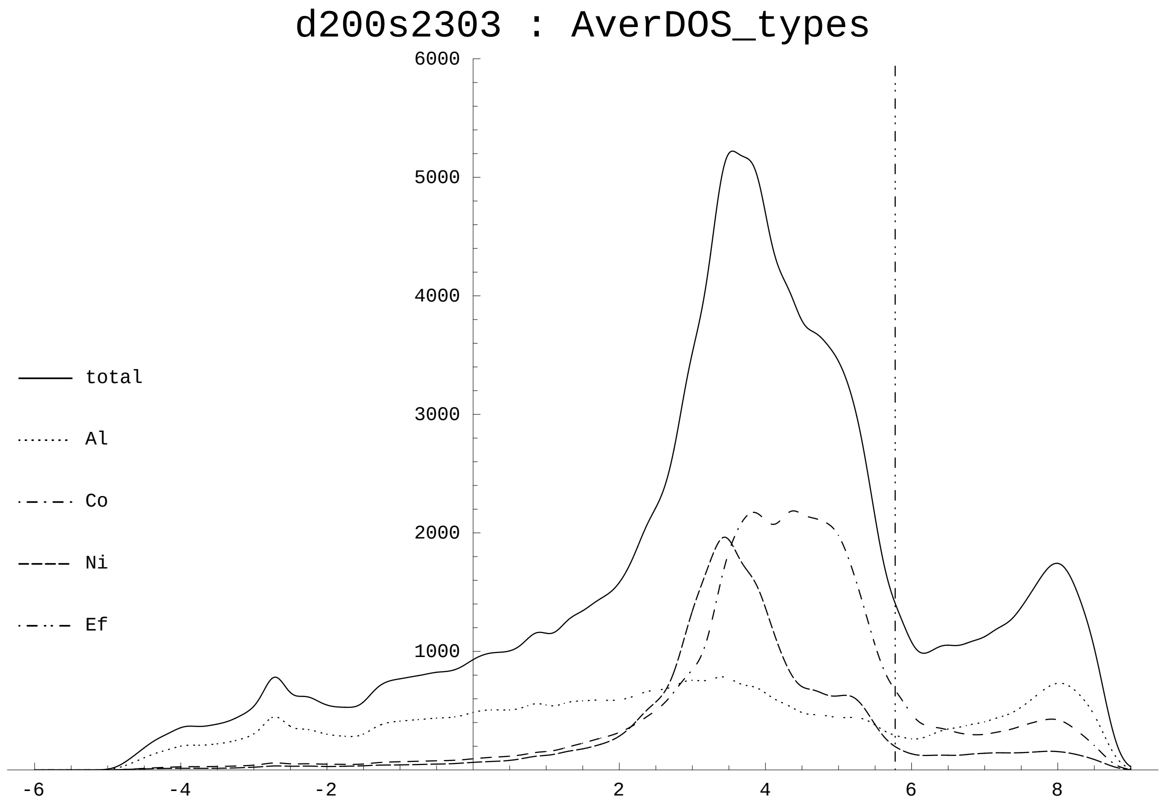

FIG. 6. The total and elemental density for states for the swapped-displaced structure.

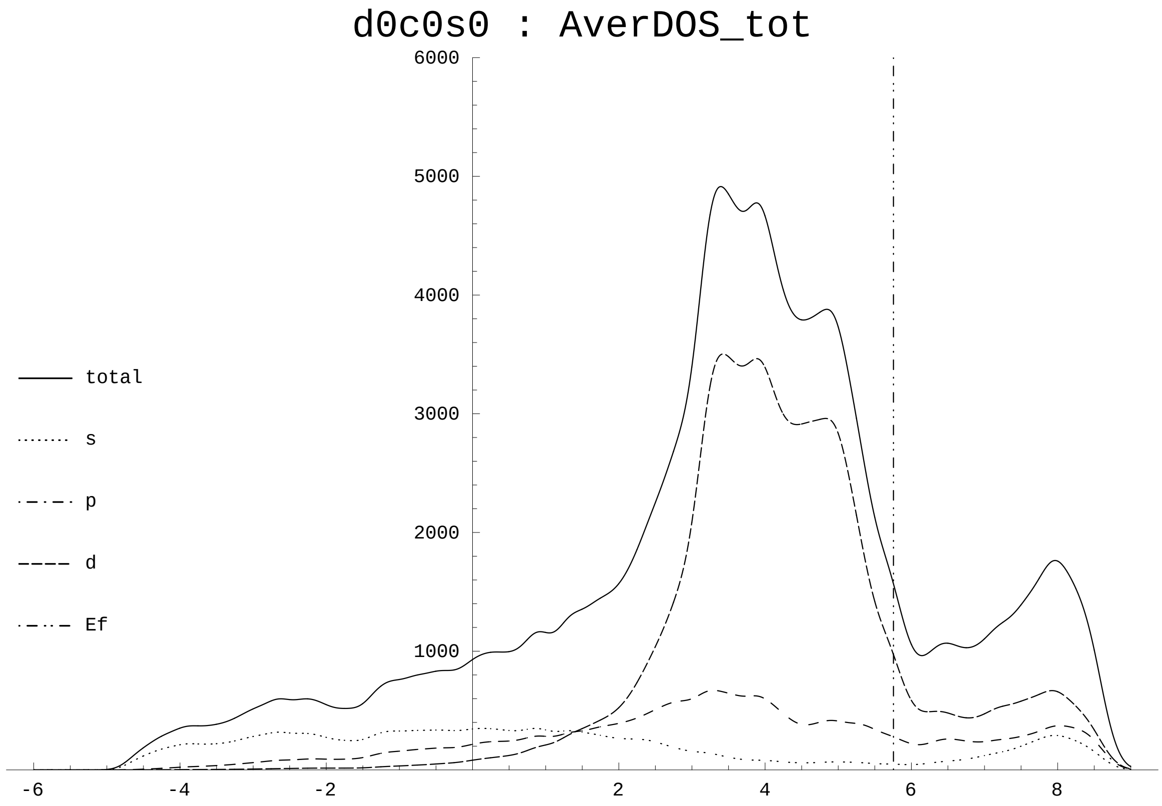

FIG. 7. Total and spd-decomposed density of states for the basic structure. The peak in the total DOS is almost all from the d-band.

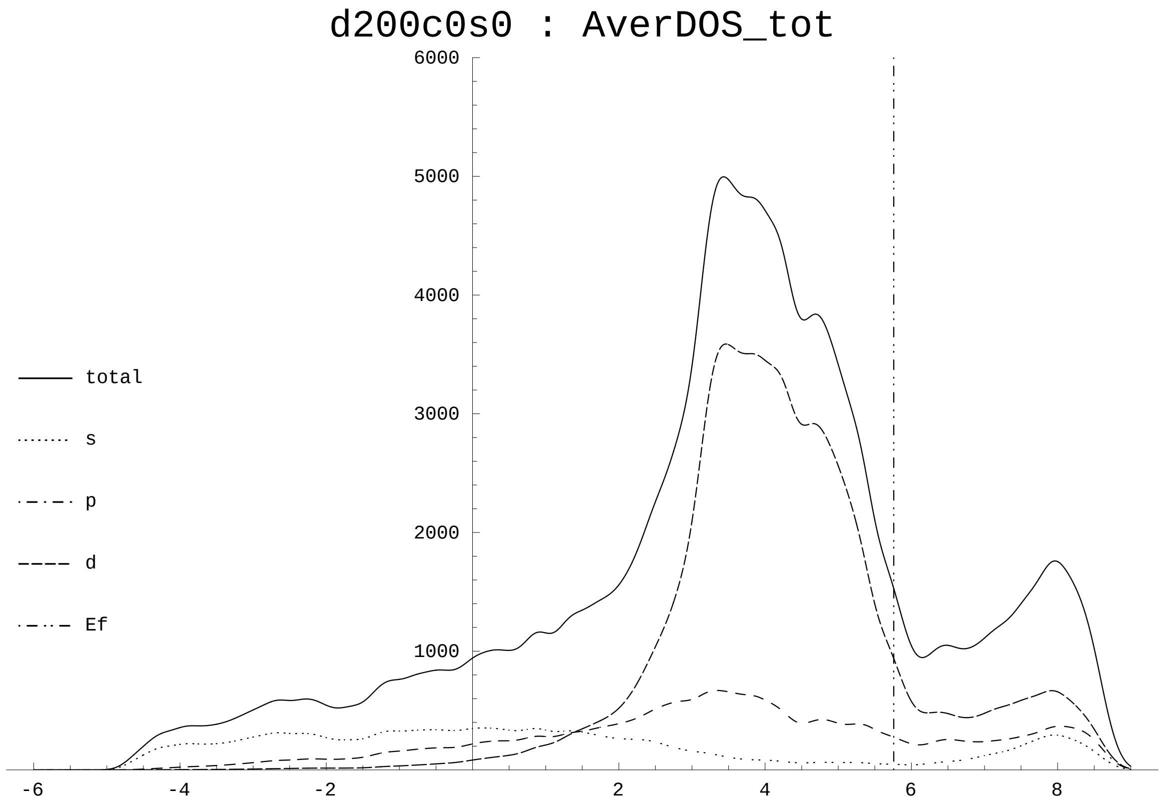

FIG. 8. Total and spd-decomposed density for states for the basic-displaced structure.

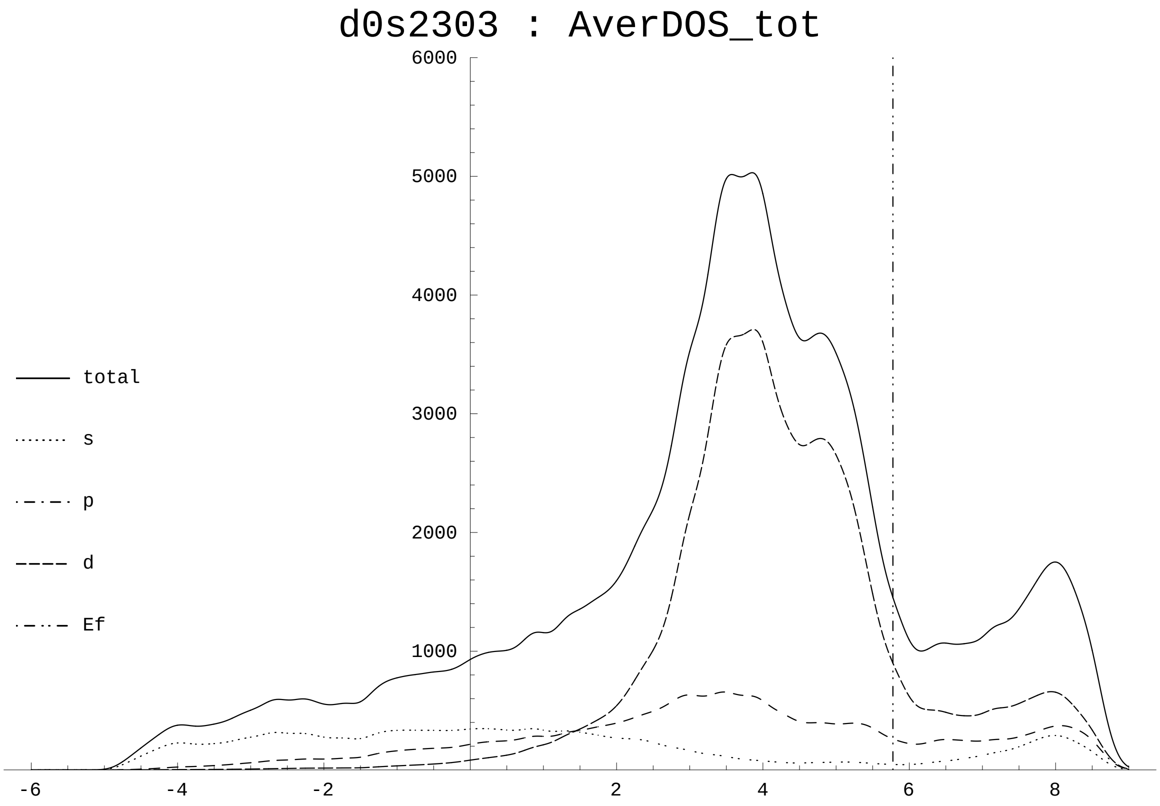

FIG. 9. Total and spd-decomposed density for states for the swapped structure.

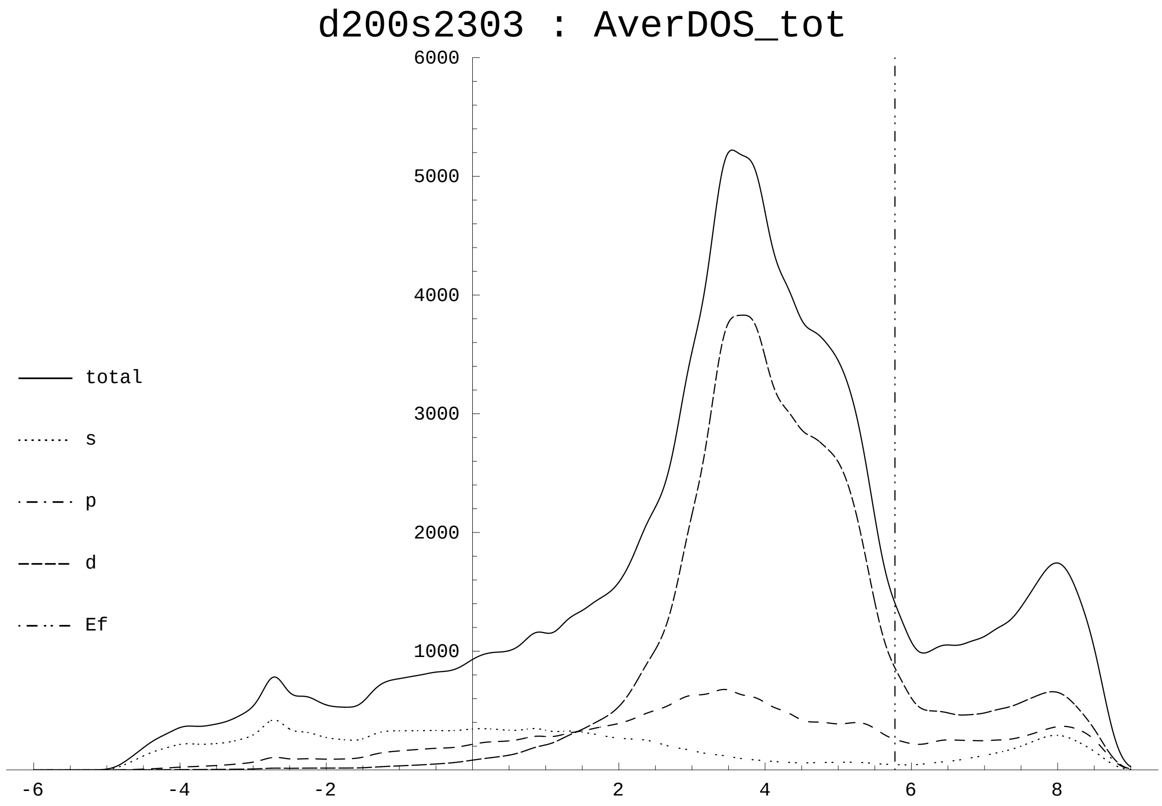

FIG. 10. Total and spd-decomposed density for states for the swapped-displaced structure.

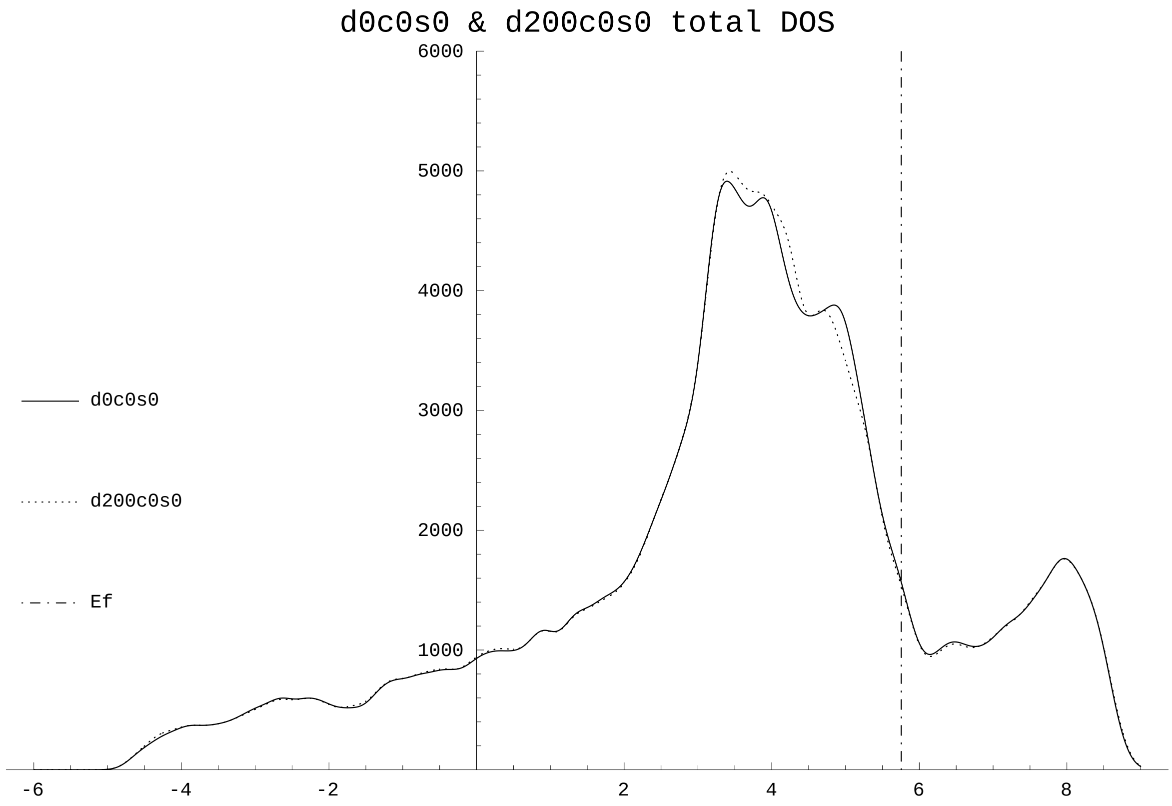

FIG. 11. The total density of states for both basic and basic-displaced structures. Some states with energies right below the Fermi energy moved to lower energies after displacement. The first peak from right is smoothed out a little.

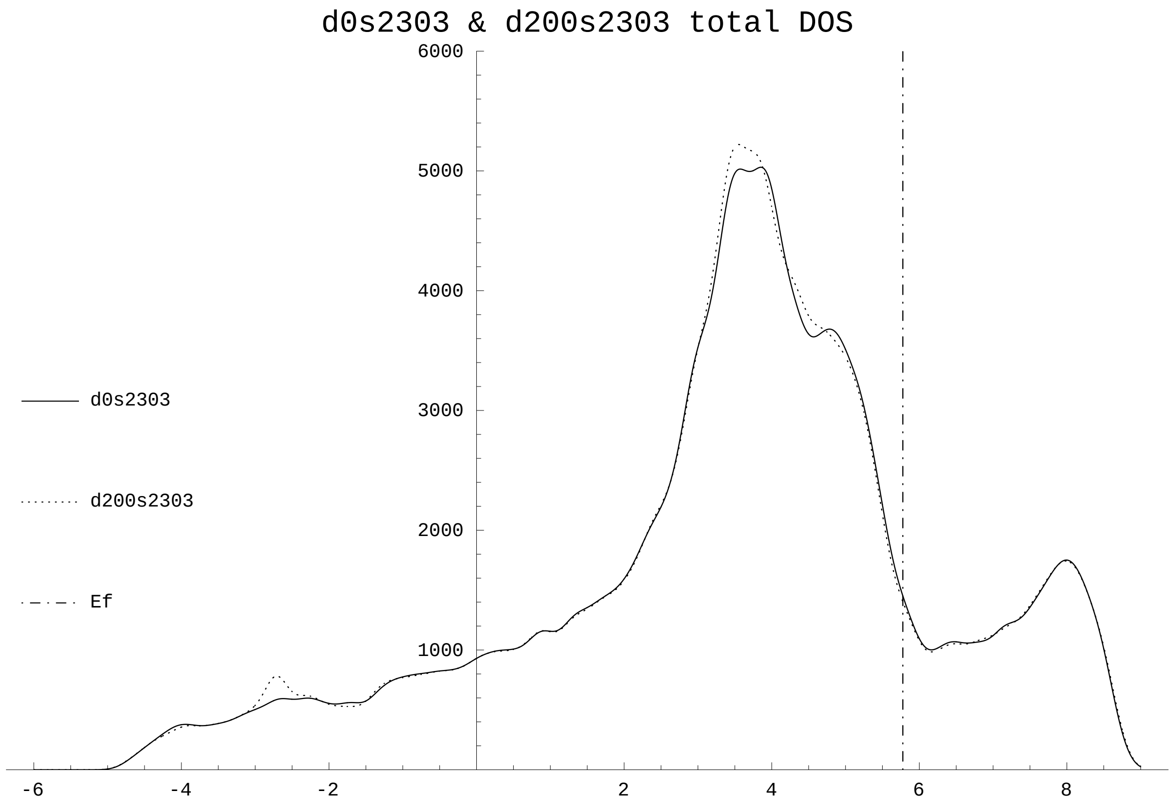

FIG. 12. The total density of states for both swapped and swapped-displaced structures.

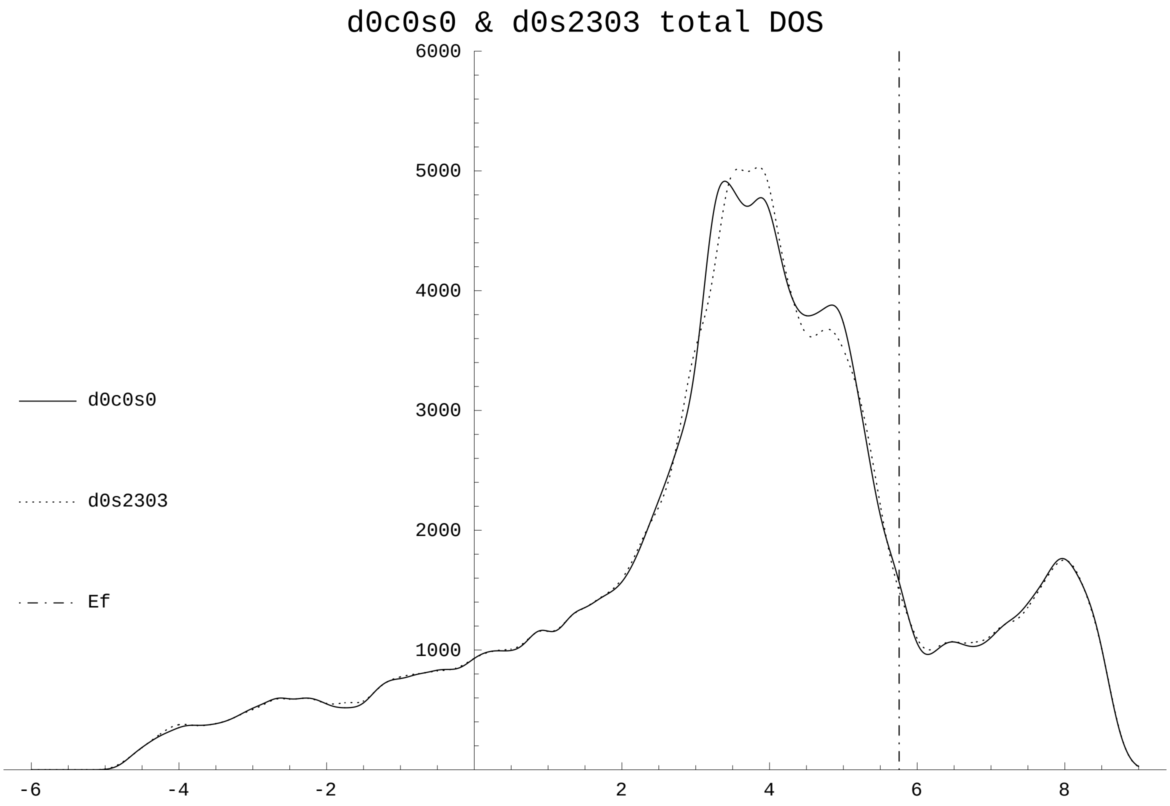

FIG. 13. The total density of states for both swapped and the basic structures

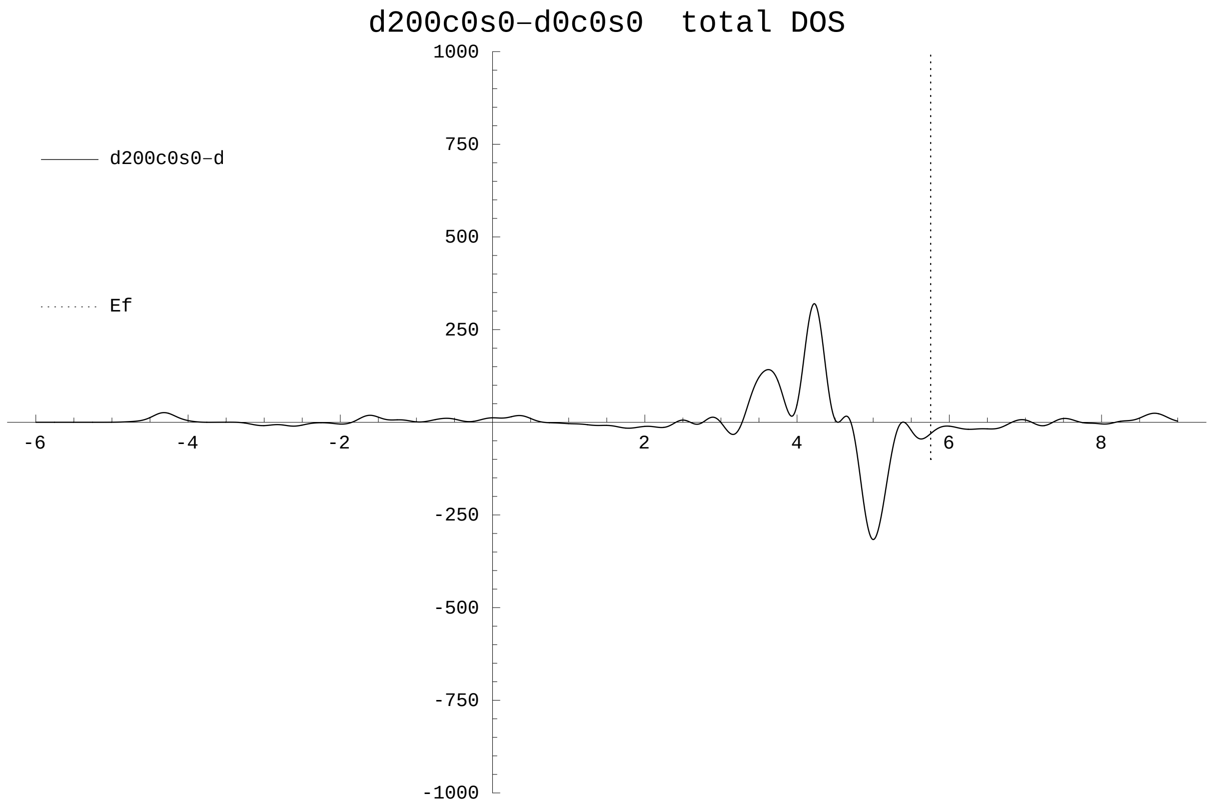

FIG. 14. The difference between the density of states for the basic-displaced and the basic structures. This figure shows the energy-lowering mechanism discussed in fig 11 and the text. States are moving from the right of the band to the left.

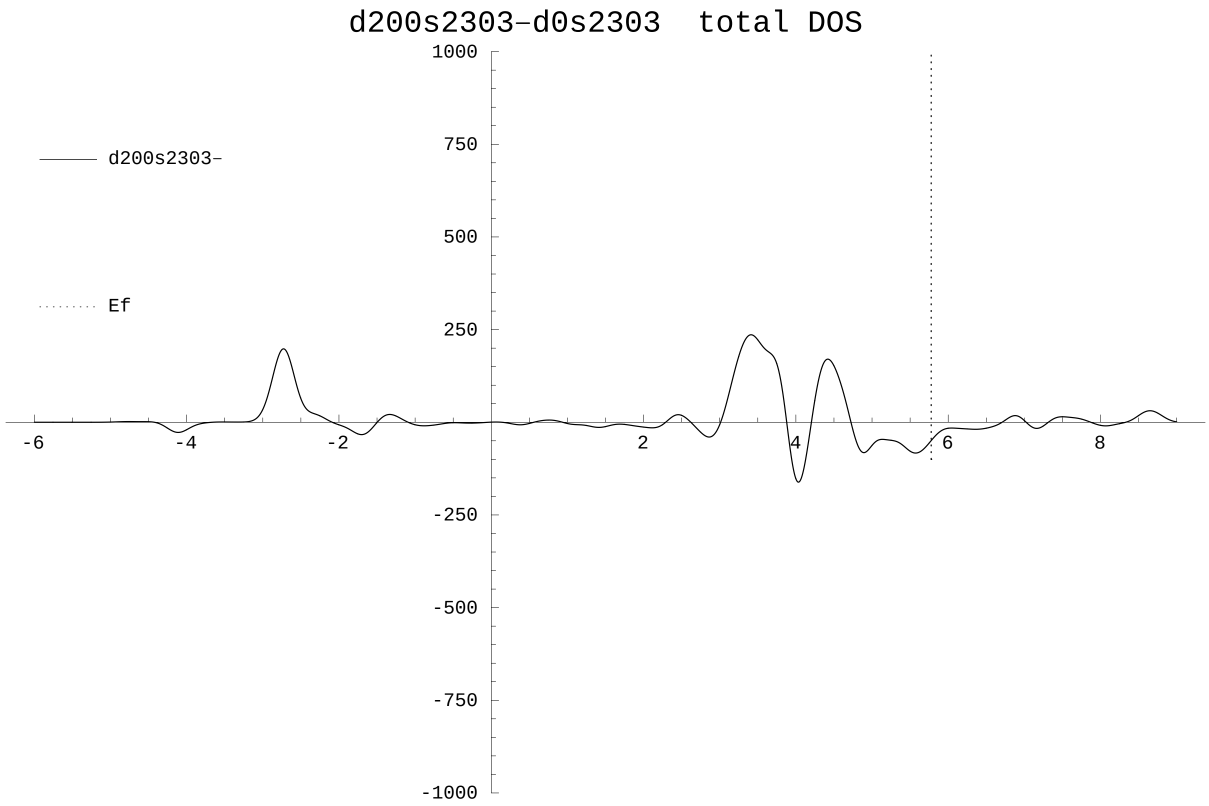

FIG. 15. The difference between the density of states for the swapped-displaced and the swapped structures. The number of states increased after displacement and the peak at -2.7 eV is clearly shown.

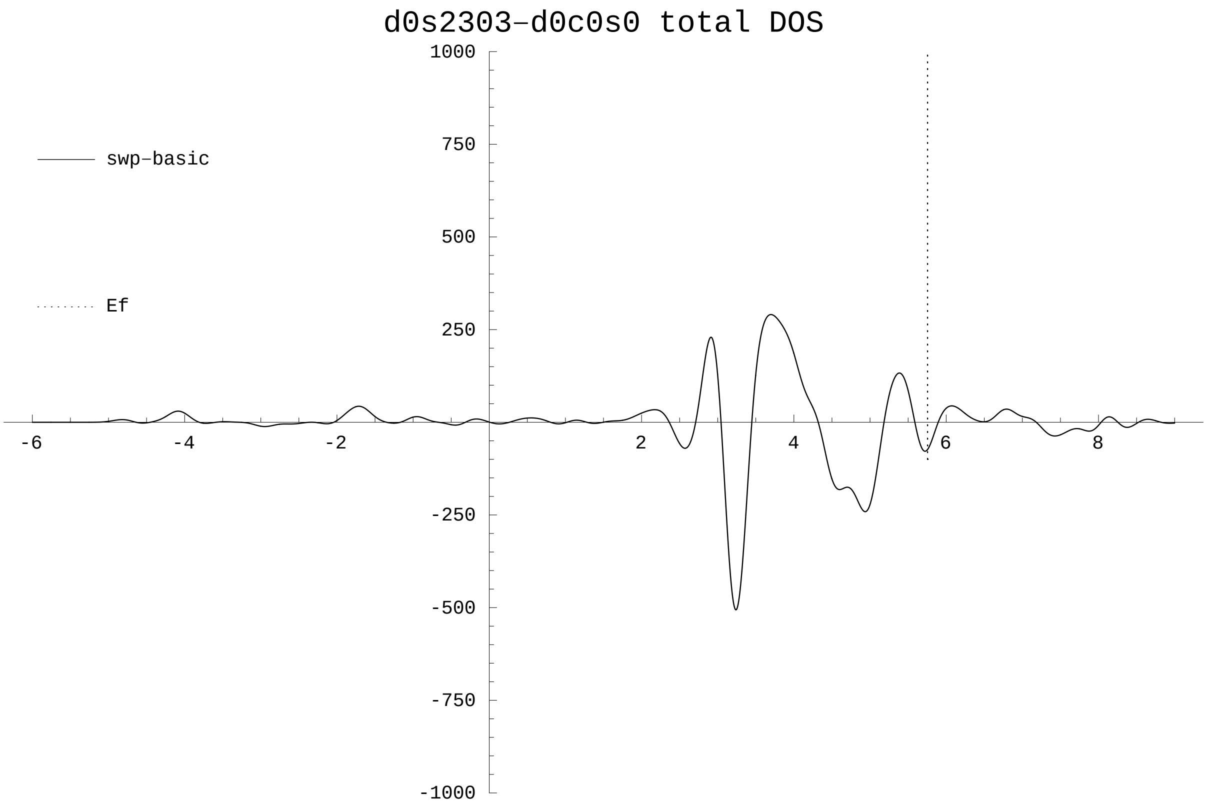

FIG. 16. The difference between the density of states for the swapped and the basic structures. The graph shows the asymmetric w-shape. As discussed in the text the w-shape is a signature of band narrowing and the asymmetry is an indication of a peak shift. The difference in band energy is small as shown in table table II. It is not as clear as in figures 14 and 5 that the energy-lowering mechanism is winning. The curve oscillates more than the others supporting the fact that the difference in band and total energies between the two structures is small.

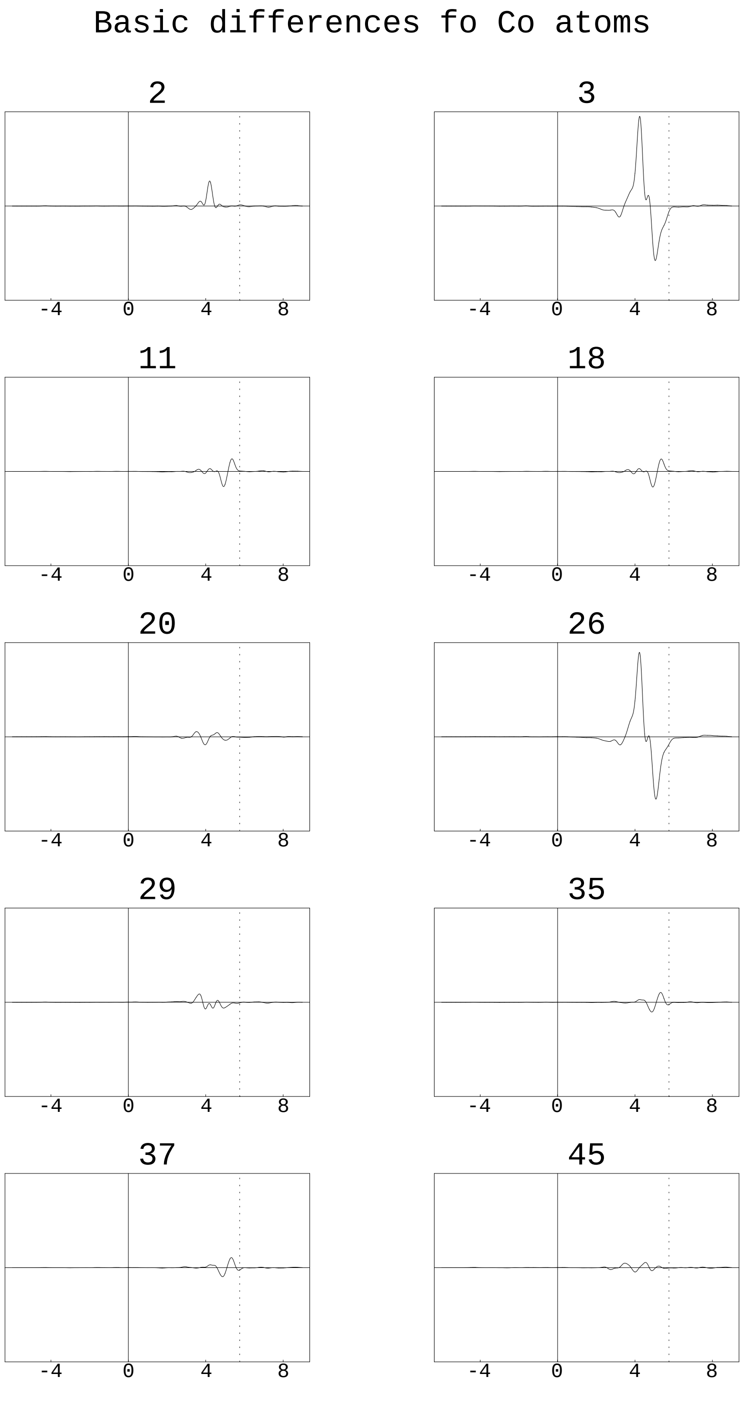

FIG. 17. The local density of states differences between the displaced-basic and the basic structures for Co atoms. All atoms are drown to the same scale. Atoms moved were pairs 3(Co),49(Ni) and 23(Ni),26(Co). For the atom numbers see fig. 1.The Al atoms are not plotted because the differences are very small. The differences are bigger for the atoms that moved and noticeable for the other Co atoms. This might be an evidence of d-band extension over the unit cell.

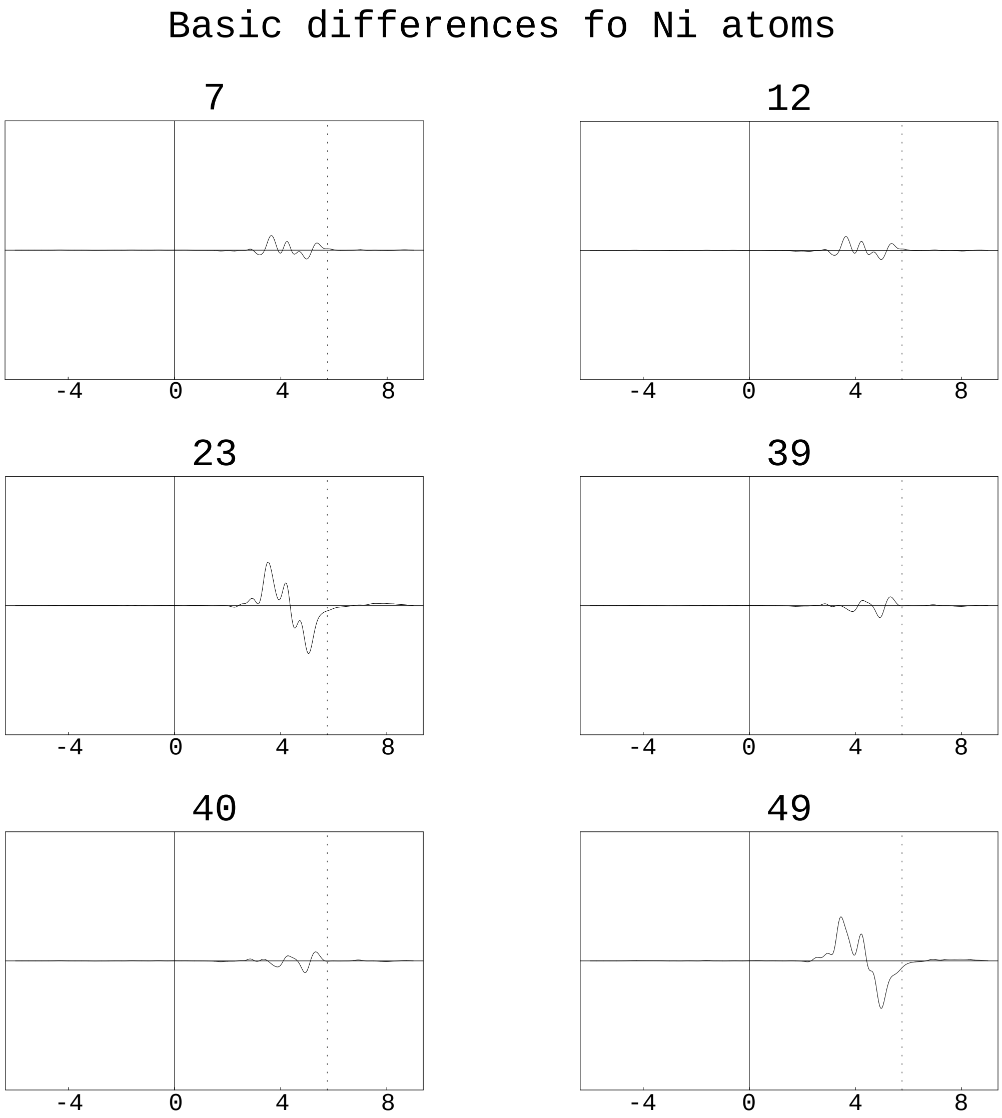

FIG. 18. Local DOS basic-displaced - basic for Ni atoms. As for the Co atoms, the differences are noticeable for all Ni atoms and bigger for the atoms moved.

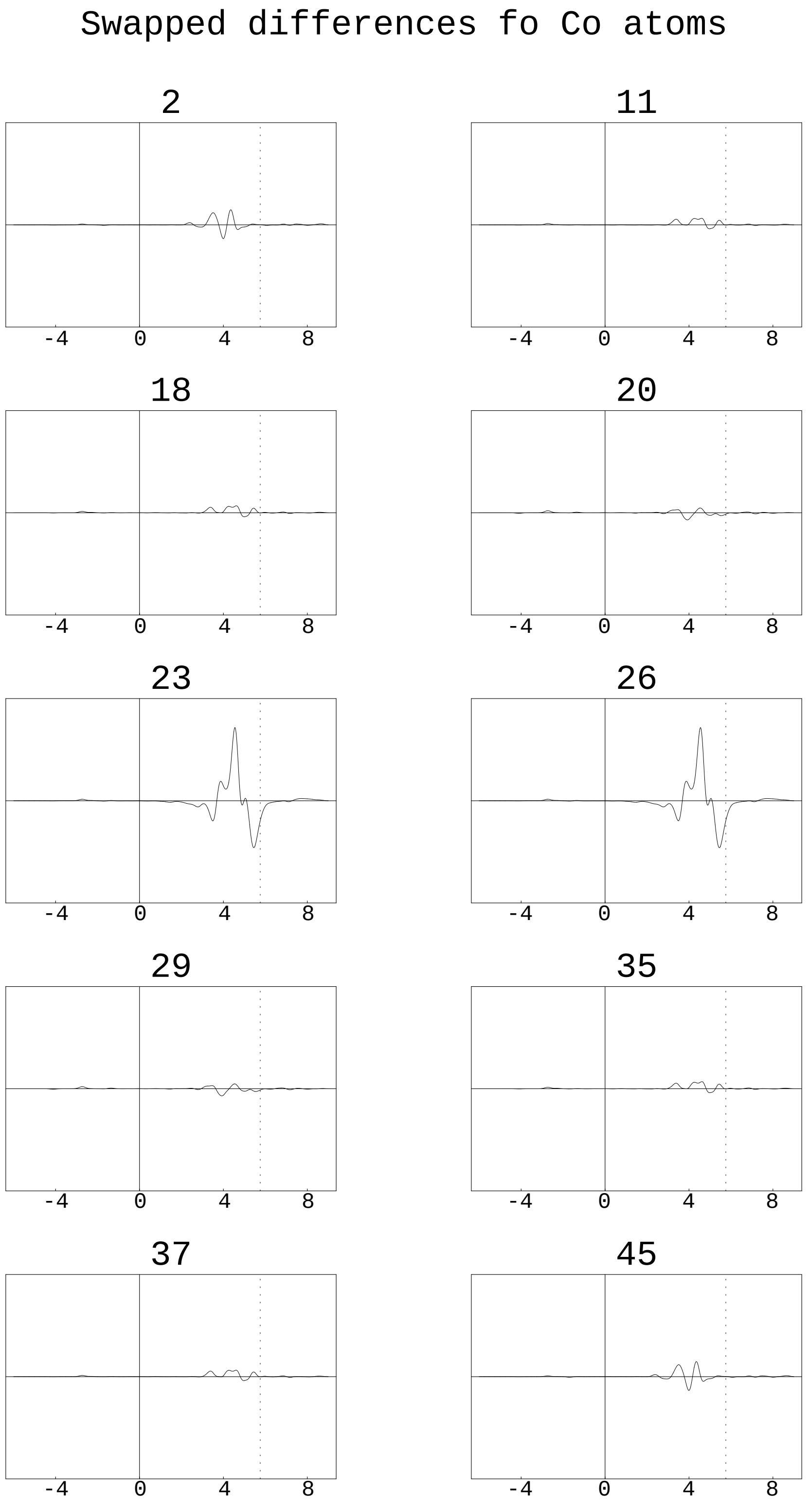

FIG. 19. local DOS swapped-displaced - swapped for Co atoms. The atoms moved are atoms 23 and 26.

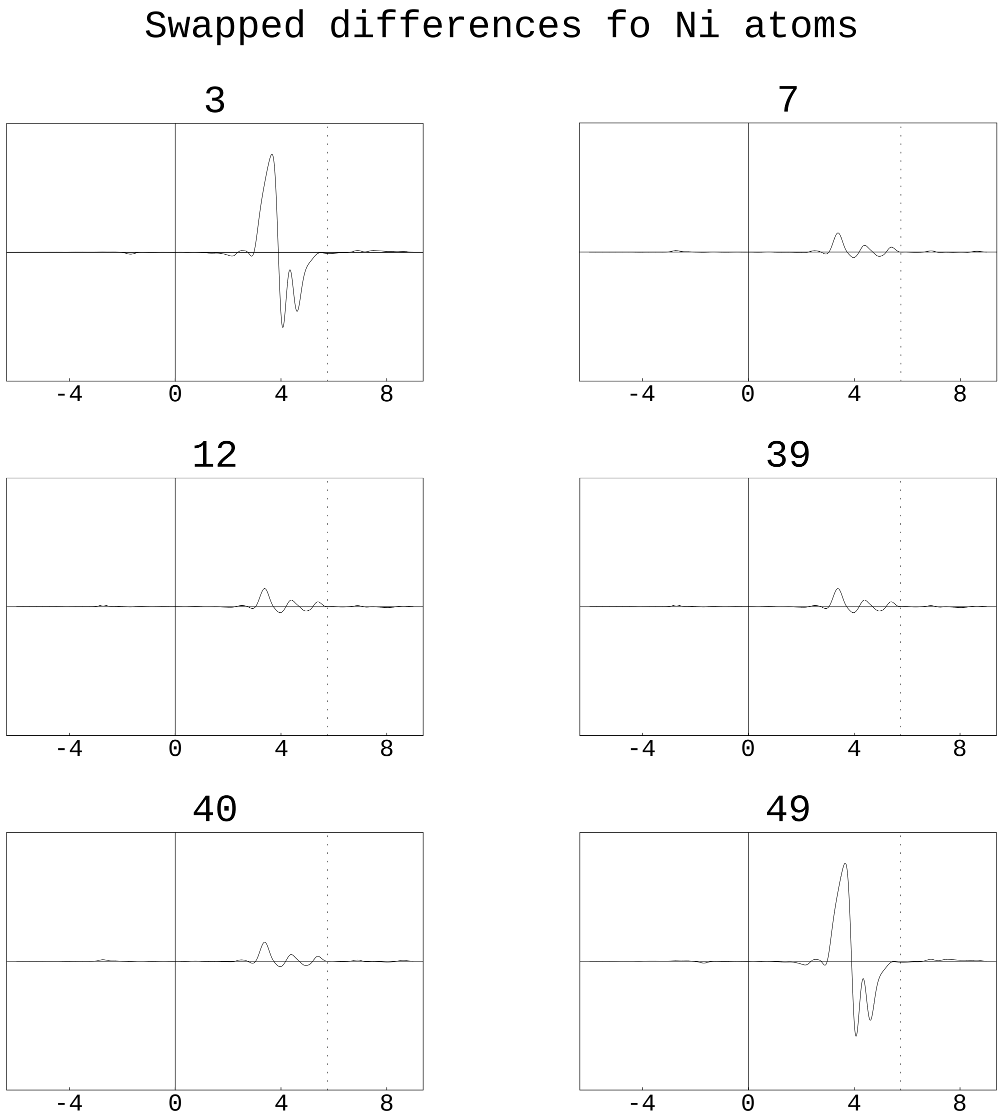

FIG. 20. local DOS swapped-displaced - swapped for Ni atoms. The atoms moved are atoms 3 and 49.

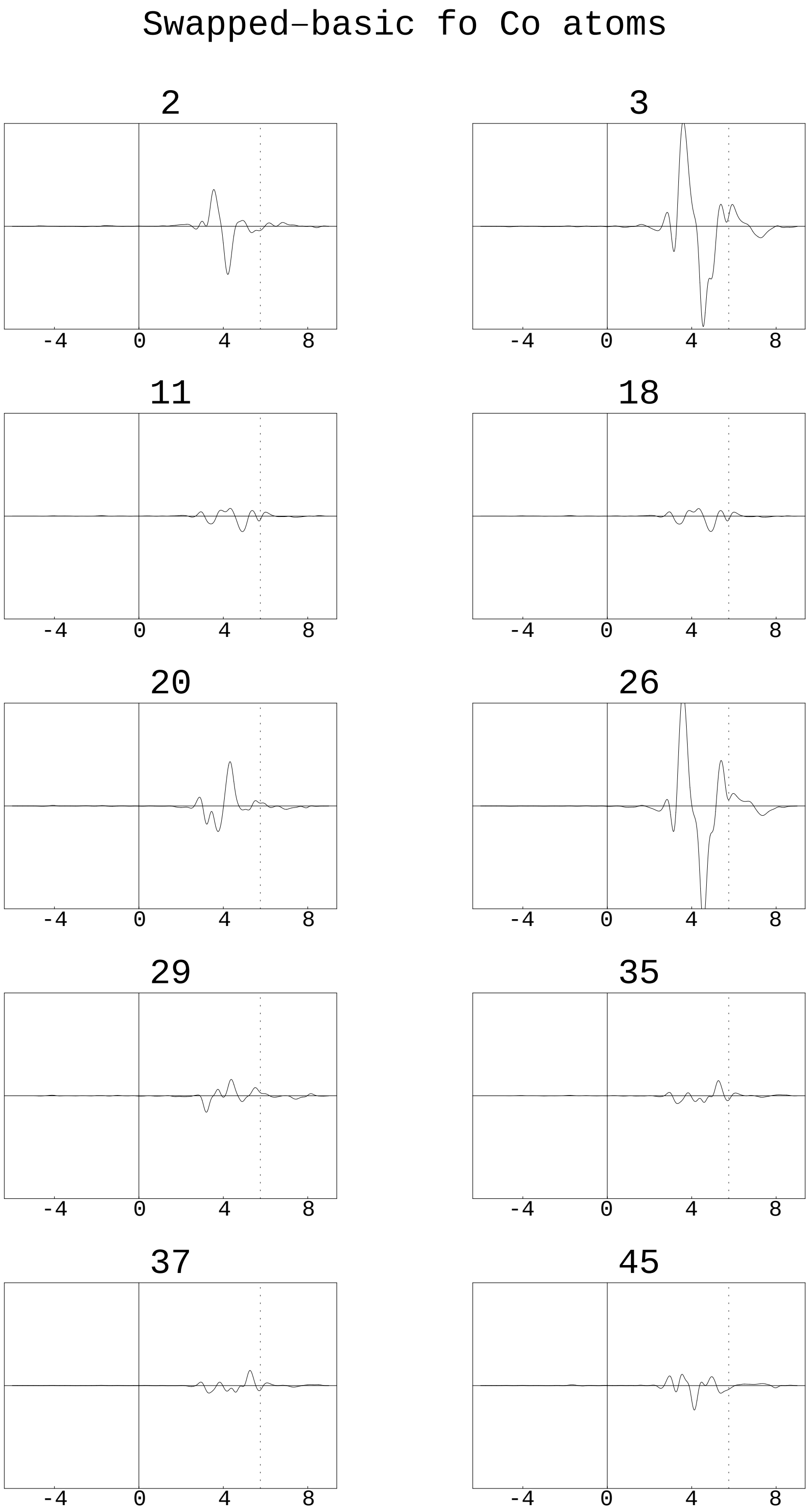

FIG. 21. Local DOS swapped - basic for Co atoms. The swapped atoms 3 and 23 in the swapped were compared with atoms 23 and 3 in the basic. Atoms 3 and 23 here correspond to the atoms in the basic structure.

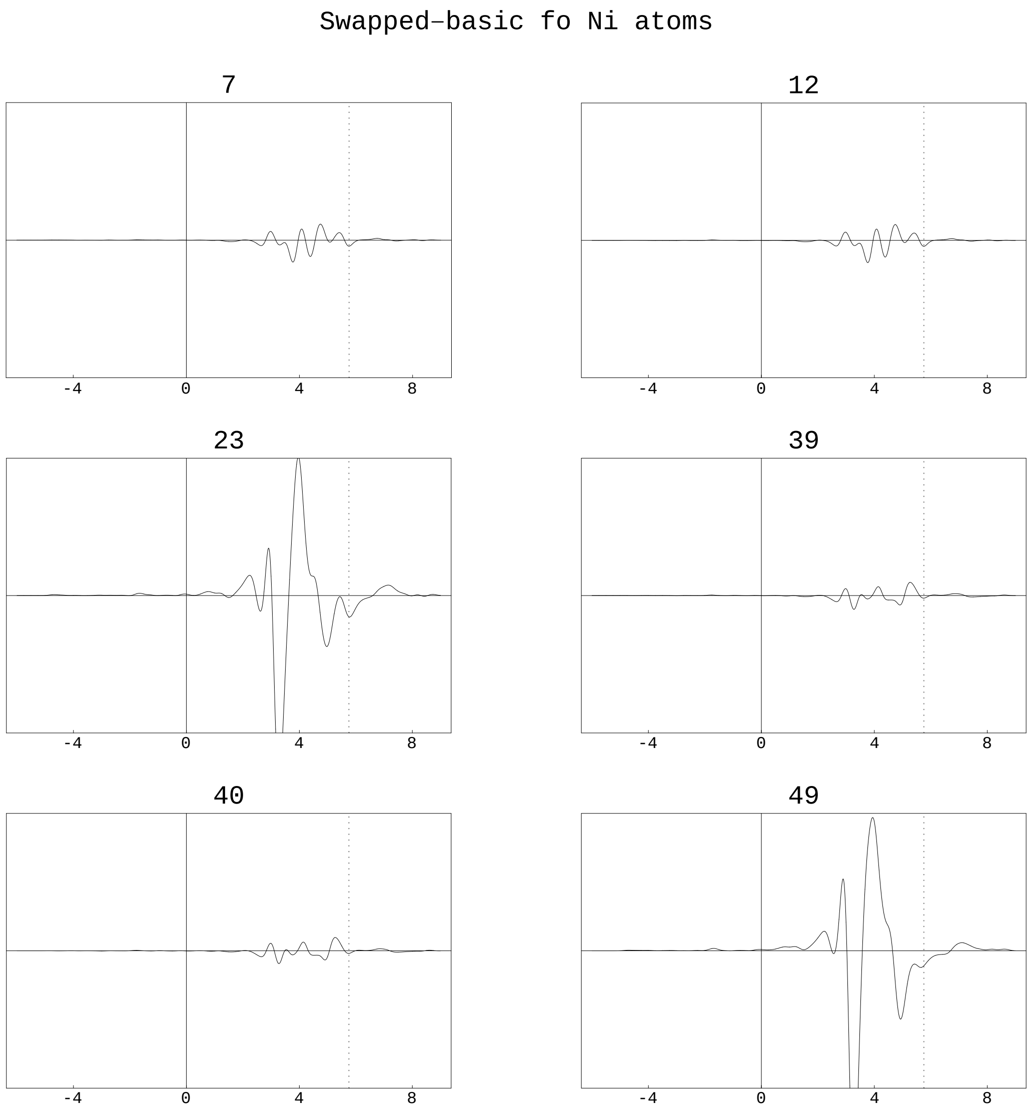

FIG. 22. Local DOS swapped - basic for Ni atoms.