# Charge analysis based on number of electrons on P- and N- doped LaMnO3

- LaMnO3 => $La^{3+}$; $Mn^{3+}$; $O_3{}^{2-}$ - charge distribution.
- La3+ has 8 valence electrons; Mn3+ has 4 valence electrons; and O2- has 8 valence electrons. (=>$O_3^{2-}$ has 24 valence electrons); thus **one unit** of LaMnO3 has **36 valence electrons.**
- In the present case, the simulations are done on a 4x4x4 supercell; thus implying a total of (36*64) = 2304 valence electrons.(shown rightly in Bader charge analysis).
- Precisely, La = 64*8 = 512; Mn = 64*4 = 256; O = 64*3*8 = 1536 valence electrons.

## P-Doping

- P is substituted on the Mn site in systematically small amounts; starting from P=1 to P=7.
- Considering the case P=1: one P atom substitutes on the Mn site.
- P has 5 valence electrons; substituting 1 P to replace one Mn atom reduces the total valence electron number on Mn by 2. (**This is seen in 'mag' in VASP output**); thus indicating that P assumes 3+ state (2 valence electrons) thus replacing one Mn (4 valence electrons) (-4+2 = -2) => number of Mn valence electrons to 254. (hence the total valence electrons to 2302)
- Similarly, with more P concentration, the Mn valence electrons (and hence charge) reduces @2 per P atom.
- The net magnetisation on Mn stays app. 4 indicating a d4 spin state.

## N-Doping

- N is substituted on the O site, again in very small amounts; starting from N=1 to N =11.
- Considering N=1; one N atom substitutes on O site.
- N has 5 valence electrons; therefore, N2- has 7 valence electrons; O2- has 8 valence electrons.
- This means that for each N substitution on the O-site; the total electrons should reduce by 1. (-8+7).
- This is again observed from 'mag' in VASP output, that for each N substitution, the 'mag' value reduces by 1.
- The net magnetisation on Mn still remains 4 i.e. a d4 state.

## Proposition

- It is thus seen that for both P and N substitution, the effect of charge compensation is seen on the Mn atom.
- However, the net valency on Mn still remains 3+ for both P and N substitutions.
- This contradicts the initial presumption that P and N doping should have counter-effects on Mn valency, thus cancelling the net magnetisation.
- Question: Should P and N be continued for site substitutions or other elements that have higher number of valence electrons in the respective oxidation states should replace?
- This does not really refrain from studying the surface catalytic properties using P and N, specially given that experimental results are promising. (?)

- These then decide the next steps in this context.

*P.S: The charge density plots of course do not coincide with this theory yet, but I think that's because there is some problem with the plotting itself and not with data. I will look into it.

| Number of P-atoms on Mn site | mag |
|---|---|
| 1 | 254 |
| 2 | 252 |
| 3 | 250 |
| 4 | 248 |
| 5 | 246 |
| 6 | 244 |
| 7 | 242 |

| Number of N-atoms on O site | mag |
|---|---|
| 1 | 255 |
| 2 | 254 |
| 3 | 253 |
| 4 | 252 |
| 5 | 251 |
| 6 | 250 |
| 7 | 249 |
| 8 | 248 |
| 9 | 247 |
| 10 | 246 |
| 11 | 245 |