Electronic Supplementary Information (ESI) : Antisite-disorder engineering in La-based oxide heterostructures via oxygen vacancy control

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Using Eq. (1) and Eq. (2) defined in the main text, we have calculated the antisite defect formation energy $\Delta E_{antisite}$ both in absence and in presence of OV. In ESI Table 1, we have listed the lowest energy configurations and the transport properties of the 21 heterostructures obtained by taking all the possible combinations of A and A', where, A and A' are the first row transition metals (A, A' : Ti, V, Cr, Mn, Fe, Ni, Co). In each case, the ground state energies are calculated for four different magnetic configurations, namely (1) A-AFM : A-type antiferromagnetic, (2) C-AFM : C-type antiferromagnetic, (3) G-AFM : G-type antiferromagnetic, (1) FM: ferromagnetic (ESI Fig. 1) and with and without OV.

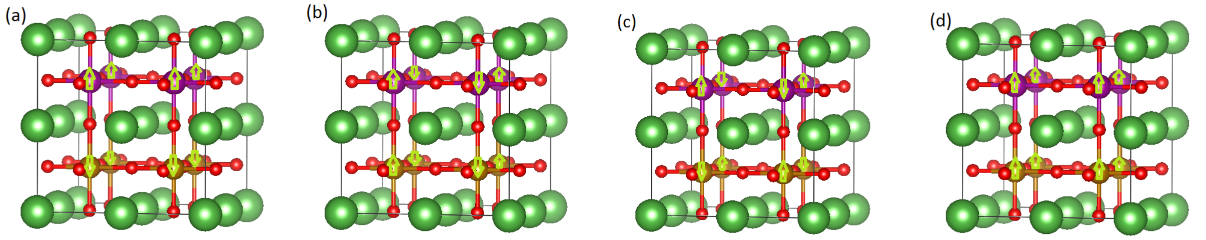


Figure 1: Different types of spin orderings (a) A-type antiferromagnetic, (b) C-type antiferromagnetic, (c) G-type antiferromagnetic and (d) Ferromagnetic.

In the ordered structure, all the interfacial oxygen sites are equivalent and hence there is only one way to put the OV at the interfacial LaO layer. However, for a disordered structure containing one antisite defect, there are four possible ways in which the OV can be introduced at the interface for a given position of the antisite defect. In our work, we keep the position of the defect fixed and place an OV at the four possible sites as shown in ESI Fig. 2.

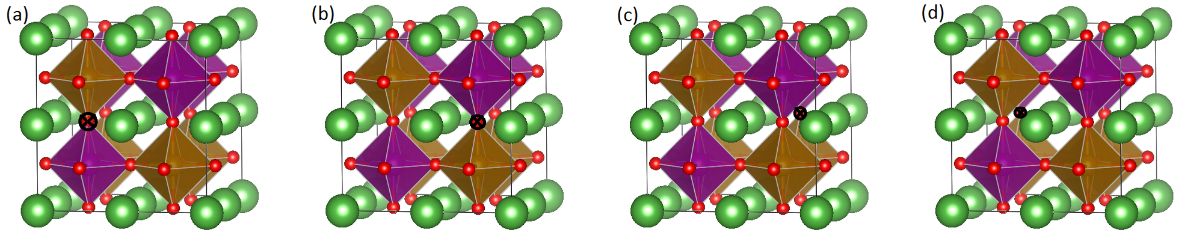


Figure 2: Disordered structure with an OV at the four different positions : (a) Position-1 (b) Position-2 (c) Position-3 (d) Position-4.

In ESI Table 1, we have shown the most favorable magnetic configurations calculated both in absence and in presence of OV. The text in green (red) indicates the ground states of those combinations that favor the ordered structure (disordered structure). The energies (relative to the energy of the ordered FM state) of all the configurations considered for the 21 heterostructures are shown in ESI Fig. 3 using bar diagrams. The first, second, third and forth columns of ESI Fig. 3 correspond to the ordered (without OV), disordered (without OV), ordered (with OV) and disordered (with OV) structures respectively. The red, blue, green and violet bars are the energies for the A-AFM, C-AFM, G-AFM and FM spin configurations relative to the energy of the ordered FM state. For the disordered cases with OV, ground state energies are calculated for the four positions of the O-vacancy with four different magnetic states. In the forth column of ESI Fig. 3, (a), (b), (c), (d) correspond to the four positions of the OV as shown in ESI Fig. 2.

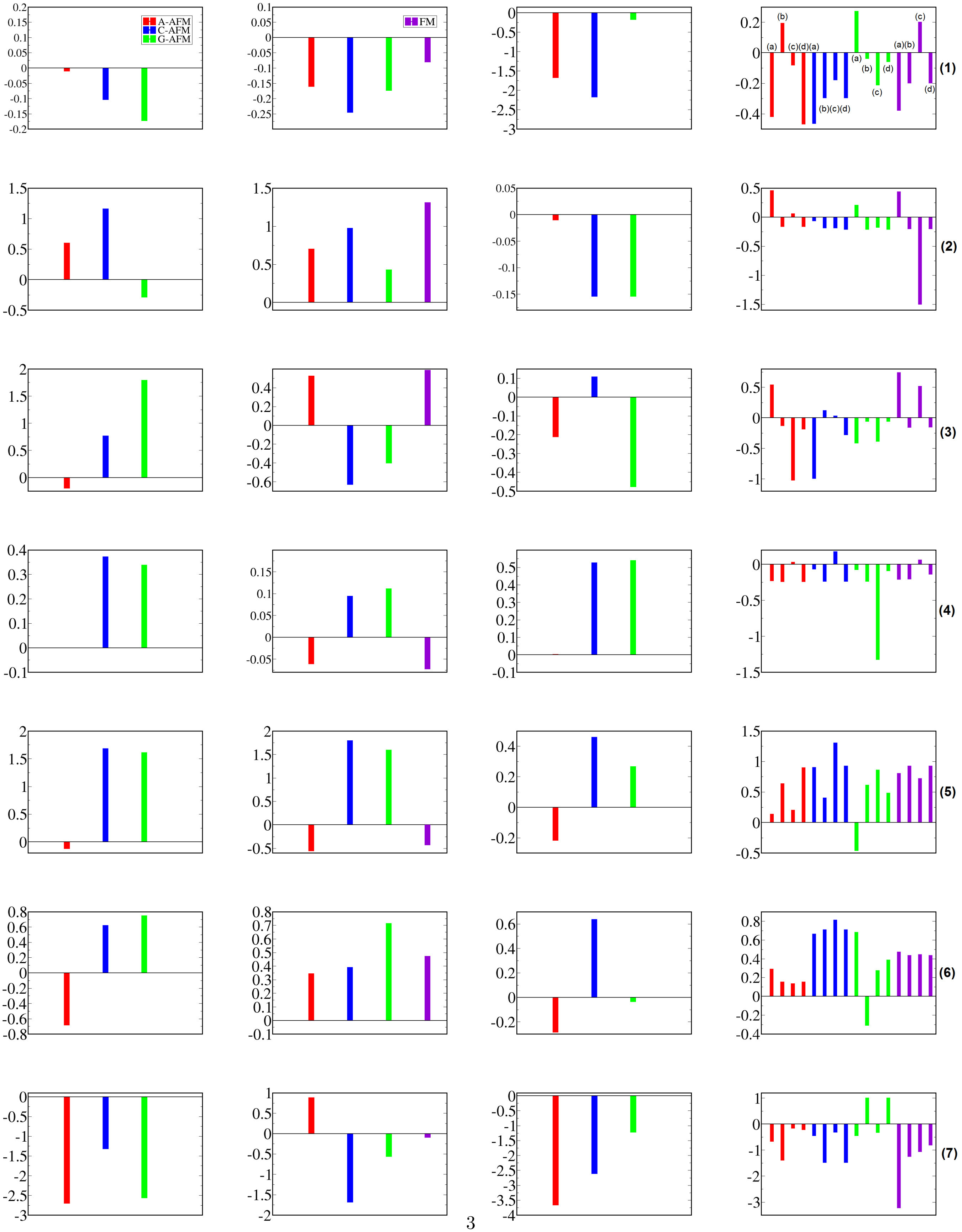
Table 1: The lowest energy magnetic configurations, transport properties and defect formation energies ($\Delta E_{antisite}$ in eV) of the 21 LaAO$_3$/LaA'O$_3$ heterostructures, where A, A' : Ti, V, Cr, Mn, Fe, Ni, Co. The text in green (red) indicates the ground states of those combinations that favor the ordered structure (disordered structure). Here, A-AFM, C-AFM, G-AFM and FM denote A type, C-type, G-type antiferromagnetic orderings and ferromagnetic ordering respectively. M and I stand for metallic and insulating states.

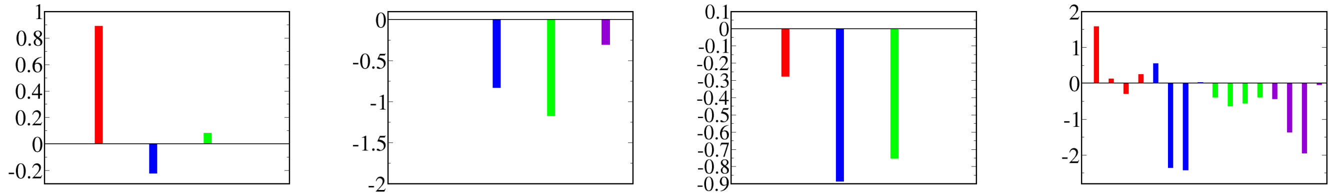
	A	A'	Without OV			With OV		
			ordered	disordered	$\Delta E_{antisite}$	ordered	disordered	$\Delta E_{antisite}$
1	V	Ti	G-AFM	C-AFM	-0.07292	C-AFM	A-AFM (Position-4)	1.70884
2	Cr	Ti	G-AFM	G-AFM	0.72168	G-AFM	FM (Position-3)	-1.34554
3	Cr	V	A-AFM	C-AFM	-0.42961	G-AFM	A-AFM (Position-3)	-0.54566
4	Mn	Ti	FM	FM	-0.07265	FM	G-AFM (Position-3)	-1.32485
5	Mn	V	A-AFM	FM	-0.31137	A-AFM	G-AFM (Position-1)	-0.24608
6	Mn	Cr	A-AFM	A-AFM	1.03069	A-AFM	G-AFM (Position-2)	-0.02194
7	Fe	Ti	A-AFM	C-AFM	1.01954	A-AFM	FM (Position-1)	0.44403
8	Fe	V	C-AFM	G-AFM	-0.94853	C-AFM	C-AFM (Position-3)	-1.53395
9	Fe	Cr	C-AFM	C-AFM	0.15660	C-AFM	G-AFM (Position-4)	-0.32022
10	Fe	Mn	G-AFM	C-AFM	-0.17020	G-AFM	G-AFM (Position-4)	0.05659
11	Co	Ti	G-AFM	A-AFM	0.76040	C-AFM	FM (Position-4)	-3.21332
12	Co	V	C-AFM	FM	0.11117	C-AFM	A-AFM (Position-4)	-1.40351
13	Co	Cr	G-AFM	C-AFM	0.47923	A-AFM	FM (Position-4)	-1.50503
14	Co	Mn	FM	FM	0.33165	FM	FM (Position-2)	-0.85893
15	Co	Fe	C-AFM	G-AFM	-0.07086	C-AFM	G-AFM (Position-2)	-0.42689
16	Ni	Ti	C-AFM	G-AFM	0.21778	C-AFM	G-AFM (Position-4)	0.19104
17	Ni	V	C-AFM	A-AFM	0.06112	C-AFM	G-AFM (Position-4)	-0.09975
18	Ni	Cr	C-AFM	FM	0.84372	FM	FM (Position-3)	0.23725
19	Ni	Mn	FM	FM	-0.63623	C-AFM	FM (Position-4)	-0.52059
20	Ni	Fe	G-AFM	FM	0.33788	G-AFM	G-AFM (Position-4)	0.21421
21	Ni	Co	FM	A-AFM	0.10196	FM	FM (Position-3)	-0.21706

Effect of covalency

Apart from the octahedral volume differences and the distortion of the octahedra (discussed in the main text), covelency also acts as an important factor in determining the stability of the ordered/disordered structures. In order to see the effect of covalency we calculate the charge density of the minimum energy ordered configuration and minimum energy disordered configuration for LaCoO$_3$/LaCrO$_3$, LaCoO$_3$/LaMnO$_3$ and LaNiO$_3$/LaCoO$_3$. As seen from ESI Fig. 4, covalency is enhanced when one of the atoms is exchanged across the interface in presence of oxygen vacancy. Therefore covalency works hand-in-hand with distortions in the octahedra to make the antisite disordered state stable in these systems. Although covalency plays some role in stabilizing the disordered structures, the difference in the charge densities between the ordered and disordered structures is found to be very small as is clear from the charge density plots.

Figure 3: The relative energies of all the magnetic configurations of the LaAO_3/La$A'O_3$ heterostructures both in absence and in presence of OV, where A, A' : Ti, V, Cr, Mn, Fe, Ni, Co. The figures are arranged according to the serial orders of the heterostructures in ESI Table 2. The first, second, third and forth columns correspond to the ordered (without OV), disordered (without OV), ordered (with OV) and disordered (with OV) structures respectively. The red, blue, green and violet bars are the energies for the A-AFM, C-AFM, G-AFM and FM spin configurations relative to the energy of the ordered FM state. For the disordered cases with OV, ground state energies are calculated for the four positions of the O-vacancy with four different magnetic states. In the forth column, (a), (b), (c), (d) correspond to the four positions of the OV as shown in ESI Fig. 2.





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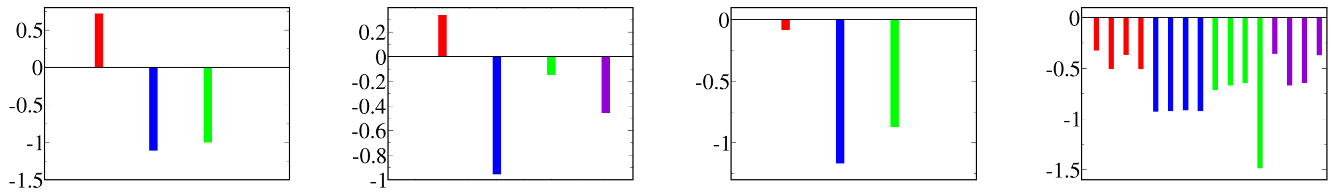

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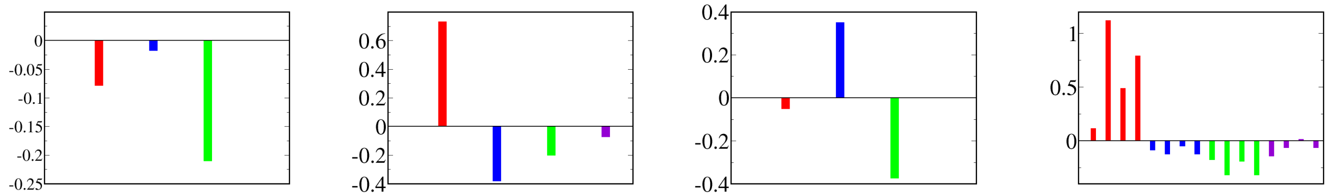

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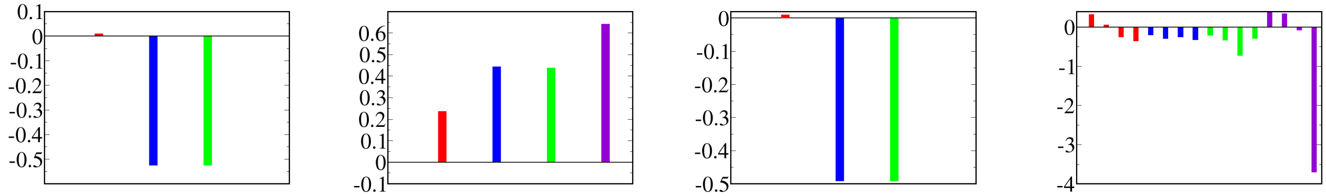

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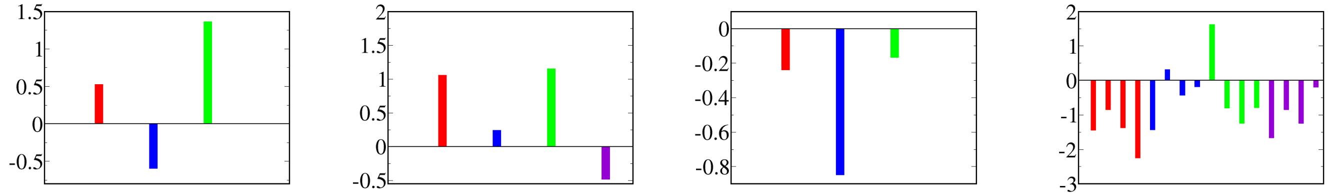

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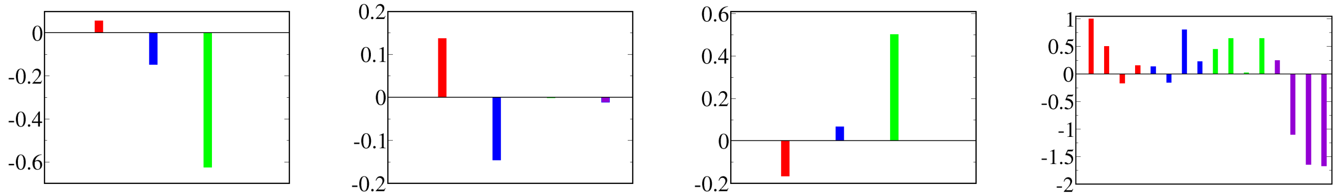

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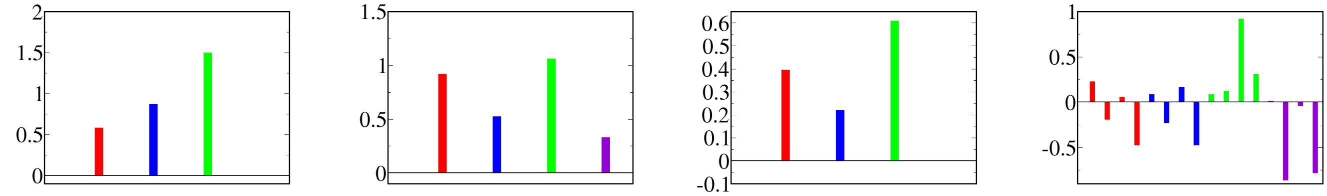

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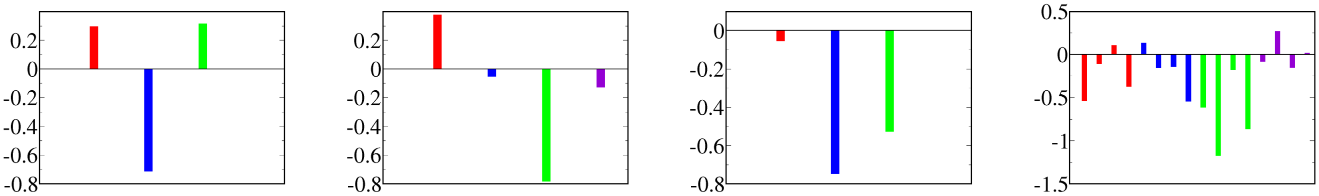

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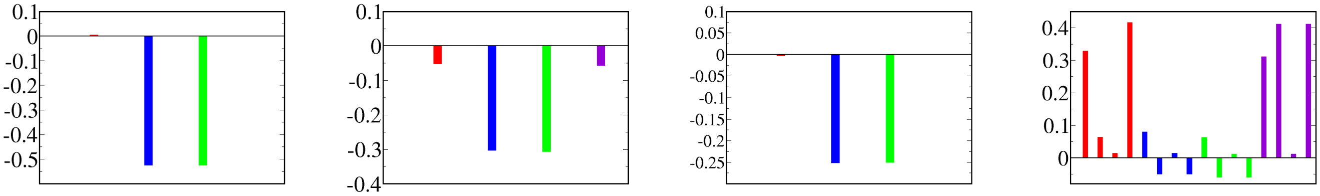

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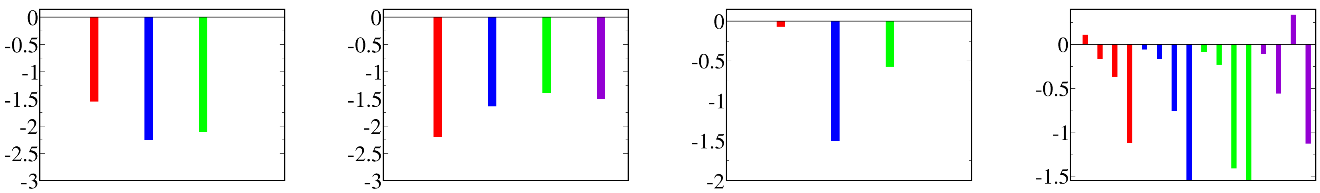

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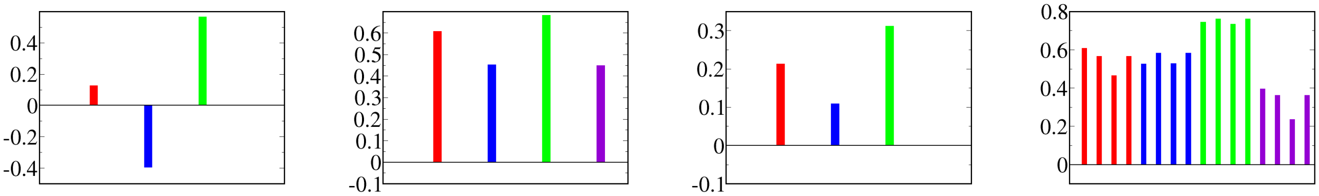

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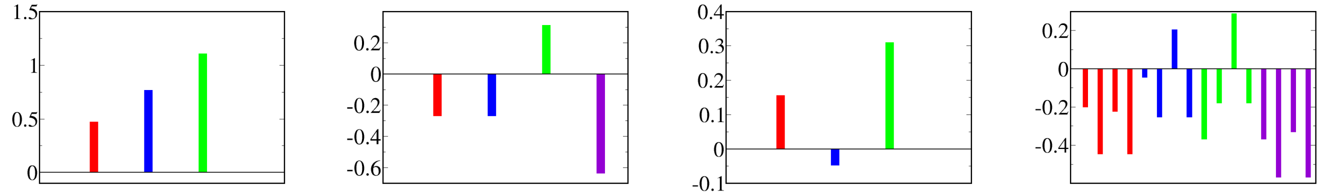

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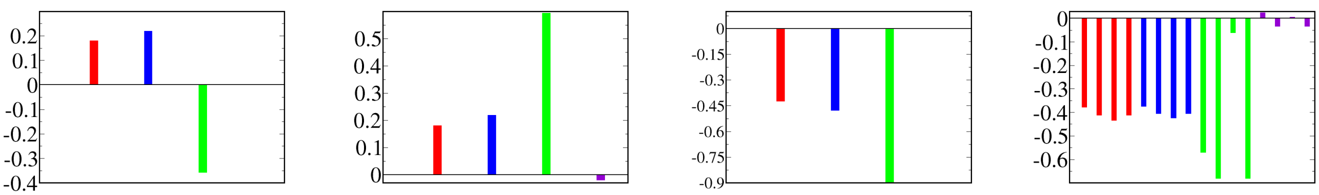

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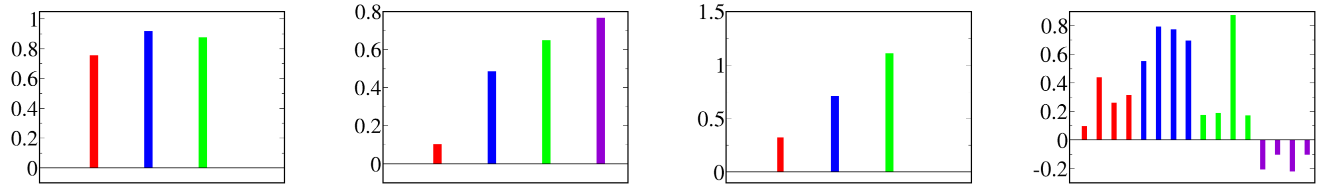

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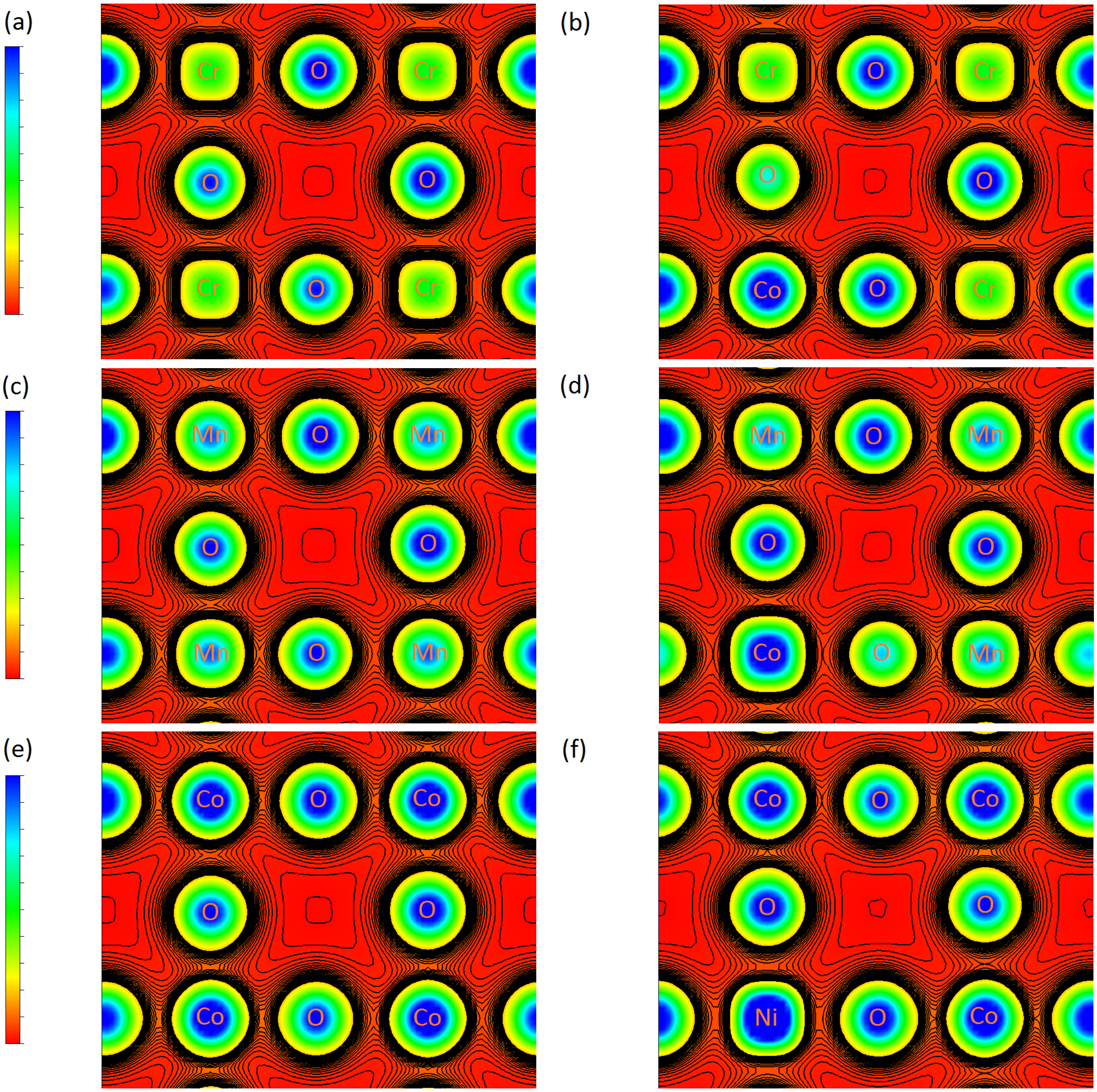

Figure 4: 2D charge density plots in presence of OV for (i) $LaCoO_3/LaCrO_3$ projected onto CrO_2 plane as shown in the upper panel. (ii) $LaCoO_3/LaMnO_3$ projected onto MnO_2 plane as shown in the middle panel. (iii) $LaNiO_3/LaCoO_3$ projected onto CoO_2 plane as shown in the lower panel. (a),(c),(e) are for the ordered structures and (b),(d),(f) are the charge densities for the disordered structures. Contour values are $\rho_n = \delta \times n \times e^-/\mathring{A}^3$, where $\delta = 0.008$ and n labels the contours.