Additional information

Configuration	$E_{tot\text{-}relative}$ PBE [eV]	$E_{tot\text{-}relative}$ PBE +U [eV]
Ctype1Fluorite	0	0
Ctype1Pyro	0.10	0.31
Ctype1Rand3	0.27	0.35
Ctype1Rand1	0.28	0.39
Orand1Rand4	5.02	5.57
Orand4Rand1	5.33	5.84
Orand1Rand1	5.43	6.23

Table 1 GGA and GGA+U (U(Ce)=5 eV, U(Nd)=6.5 eV) minimized energies relative to the lowest energy one of $Nd_2Ce_2O_7$. $E_{tot\_relative} = E_{tot}(config) - E_{tot}(Ctype1Fluorite)$, and optimizations are carried out in an 88-ion supercell.

Configuration	$E_{tot\text{-}relative}$ PBE [eV]	$E_{tot\text{-}relative}$ PBE +U [eV]
Lowest energy config.	0	0
Ctype1Pyro	0.60	0.04
Ctype1Fluoritt	0.92	0.18
Ctype1Rand1	1.08	0.44
Ctype1Rand3	1.10	0.43
Pyrochlore	2.31	3. 50
Orand1Rand4	4.72	4.55
Orand1Rand1	5.13	5.12
Orand4Rand1	5.32	5.07

Table 2 GGA and GGA+U (U(Ce)=5 eV) minimized energies relative to the lowest energy one of $La_2Ce_2O_7$. $E_{tot\_relative} = E_{tot}(config) - E_{tot}(Lowest\ energy\ config)$, and optimizations are carried out in an 88-ion supercell.

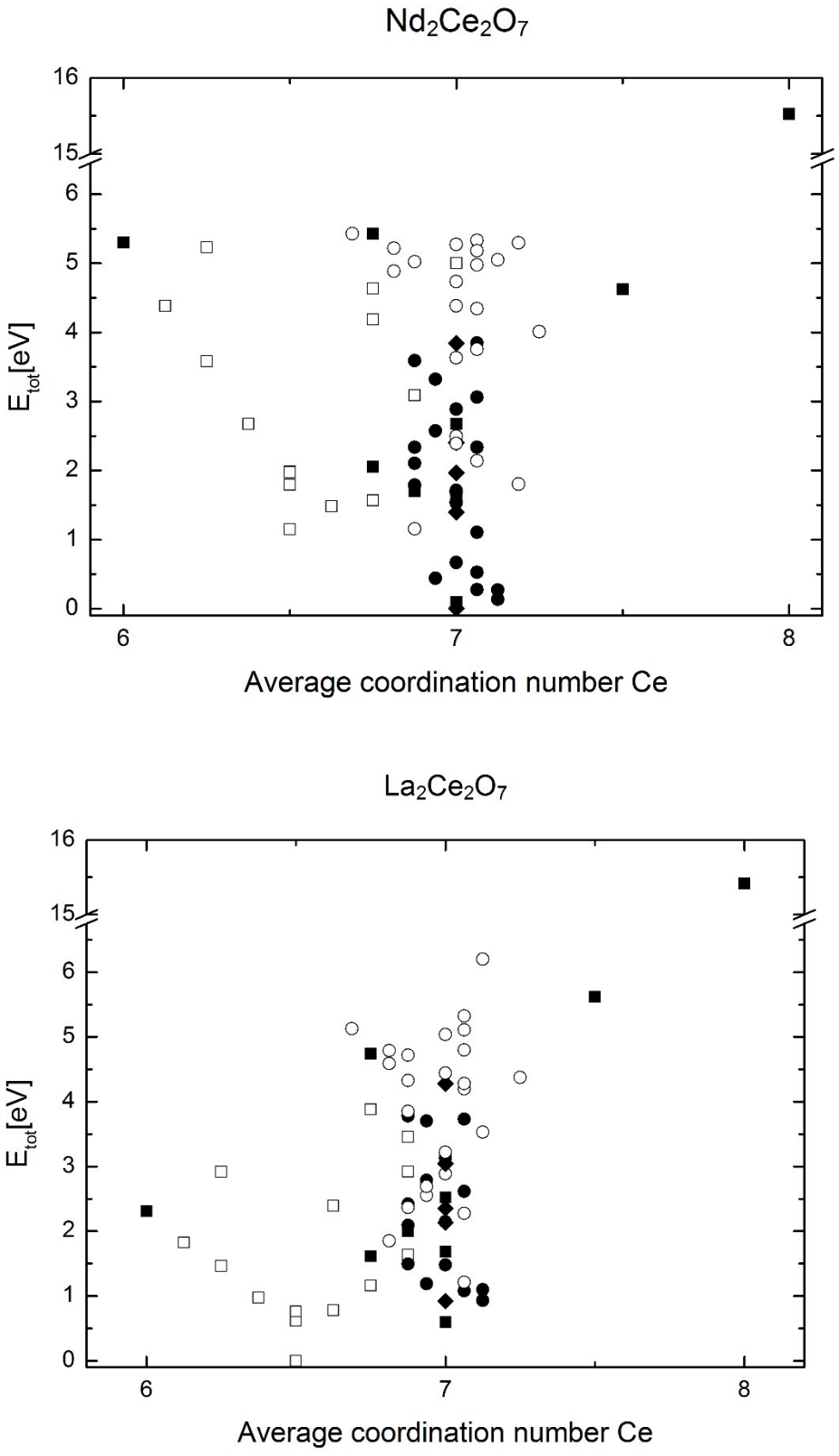

Fig. A Total energy relative to that with the lowest energy configuration of an 88 atom supercell of a) $Nd_2Ce_2O_7$ and b) $La_2Ce_2O_7$ versus the average number of oxygen around a Ce^{4+}. Squares marks a pyrochlore ordered cation sublattice, diamond marks a "fluorite"-ordered cation sublattice and circles represent a random cation sublattice. Filled symbols represent configurations that have a fully ordered oxygen ion sublattice and open symbols are those with "low" symmetry in the oxygen ion sublattice. The average coordination number for all cations in the sublattice is always 7, thus the coordination number for Nd or La, $CN_{Nd/La}$, is given as $CN_{Nd/La} = 14 - CN_{Ce}$

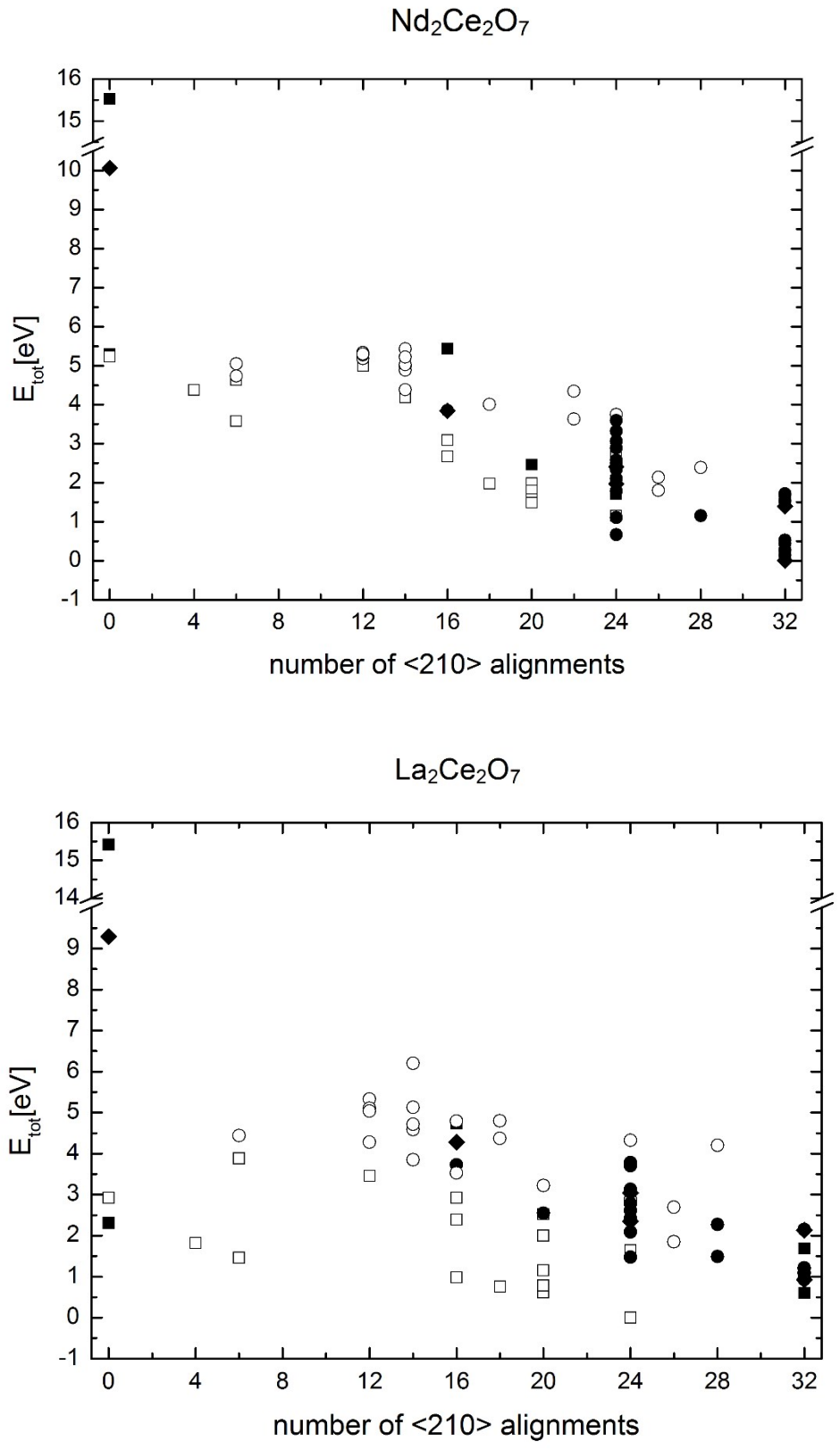

Fig. B Total energy relative to that with the lowest energy configuration of an 88 atom supercell of a) $Nd_2Ce_2O_7$ and b) $La_2Ce_2O_7$ versus the counted number of <210> vac-vac pairs. Squares marks a pyrochlore ordered cation sublattice, diamond marks a "fluorite"-ordered cation sublattice and circles represent a random cation sublattice. Filled symbols represent configurations that have a fully ordered oxygen ion sublattice and open symbols are those with "low" symmetry in the oxygen ion sublattice..

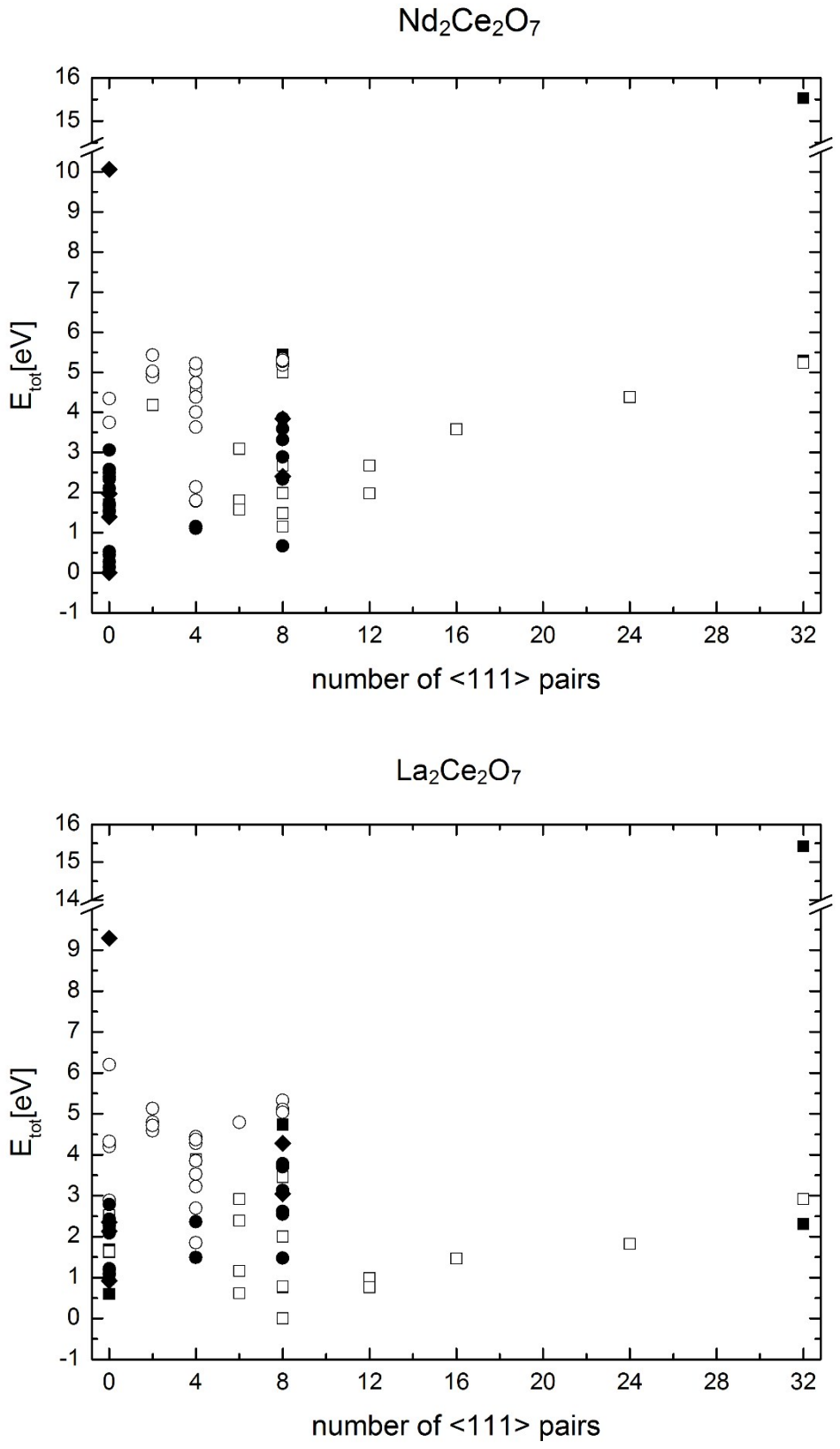

Fig. C Total energy relative to that with the lowest energy configuration of an 88 atom supercell of a) $Nd_2Ce_2O_7$ and b) $La_2Ce_2O_7$ versus the counted number of <111> vac-vac pairs. Squares marks a pyrochlore ordered cation sublattice, diamond marks a "fluorite"-ordered cation sublattice and circles represent a random cation sublattice. Filled symbols represent configurations that have a fully ordered oxygen ion sublattice and open symbols are those with "low" symmetry in the oxygen ion sublattice.

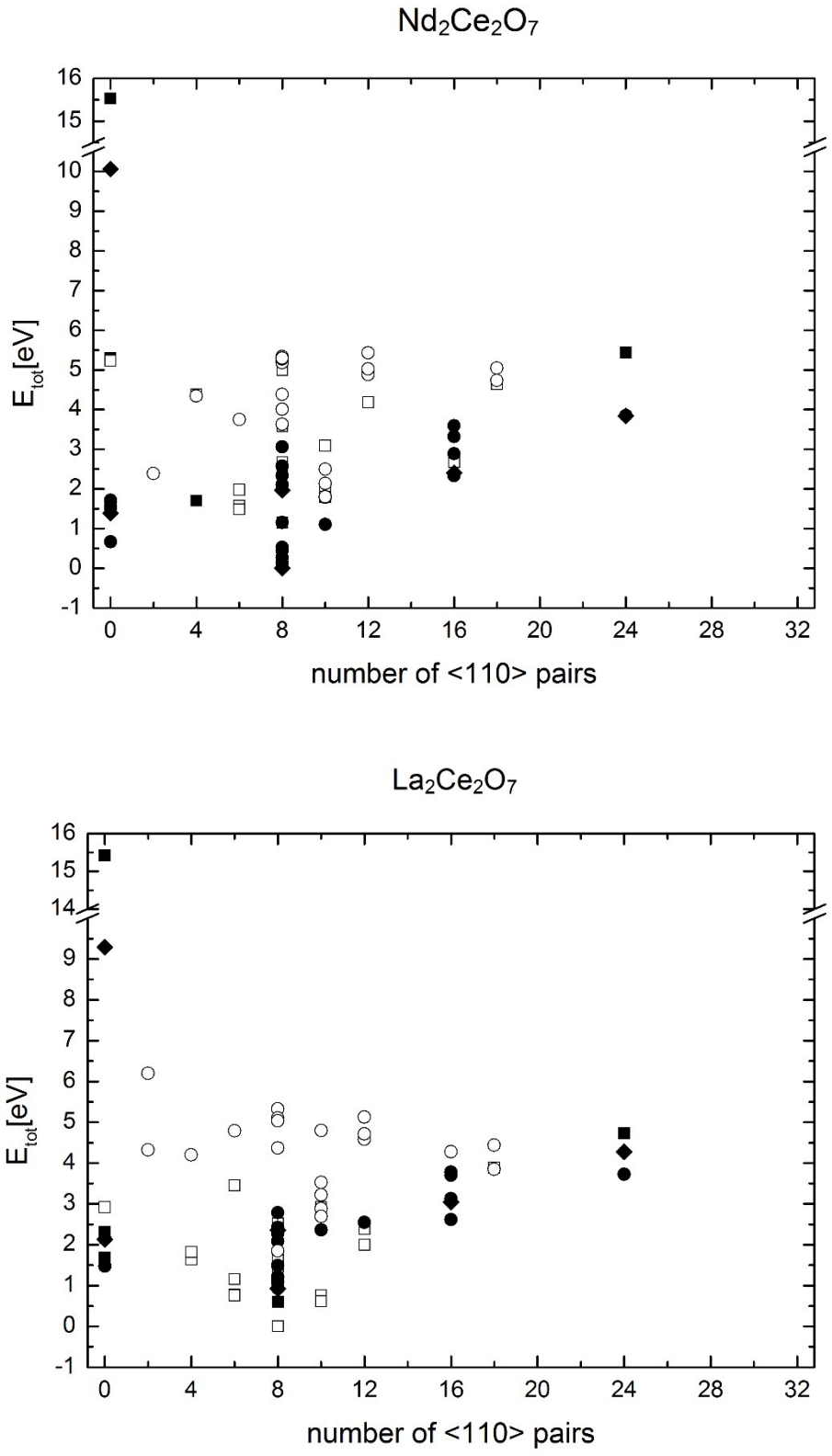

Fig. D Total energy relative to that with the lowest energy configuration of an 88 atom supercell of a) $Nd_2Ce_2O_7$ and b) $La_2Ce_2O_7$ versus the counted number of <110> vac-vac pairs. Squares marks a pyrochlore ordered cation sublattice, diamond marks a "fluorite"-ordered cation sublattice and circles represent a random cation sublattice. Filled symbols represent configurations that have a fully ordered oxygen ion sublattice and open symbols are those with "low" symmetry in the oxygen ion sublattice.