Supporting Information

Novel nitrogen-rich Lanthanum nitrides induced by the ligand effect under pressure

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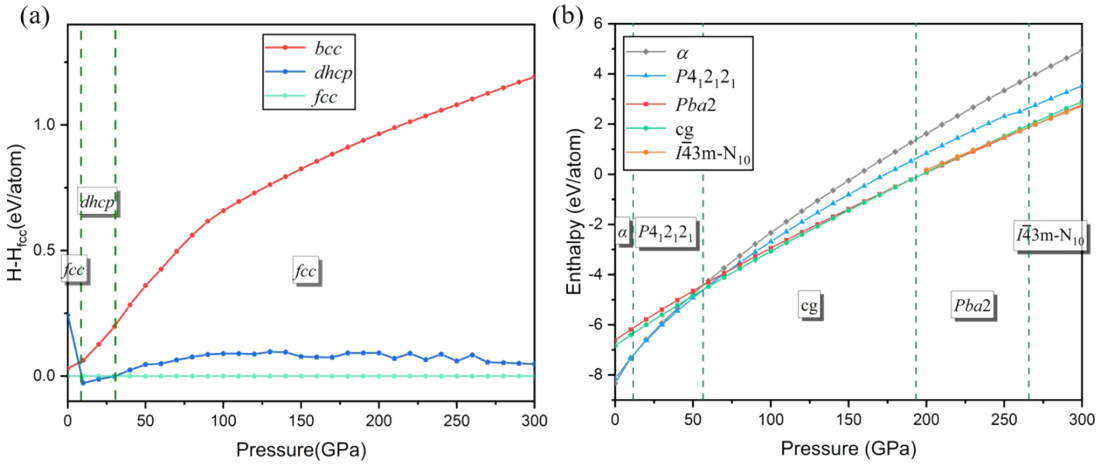

Figure S1. The enthalpy of (a) *fcc*, *bcc*, and *dhcp* phases of La, and (b) *α*, $P4_12_12_1$, *cg*-N, *Pba*2, and $\bar{I}43m$-N_{10} phases of N.

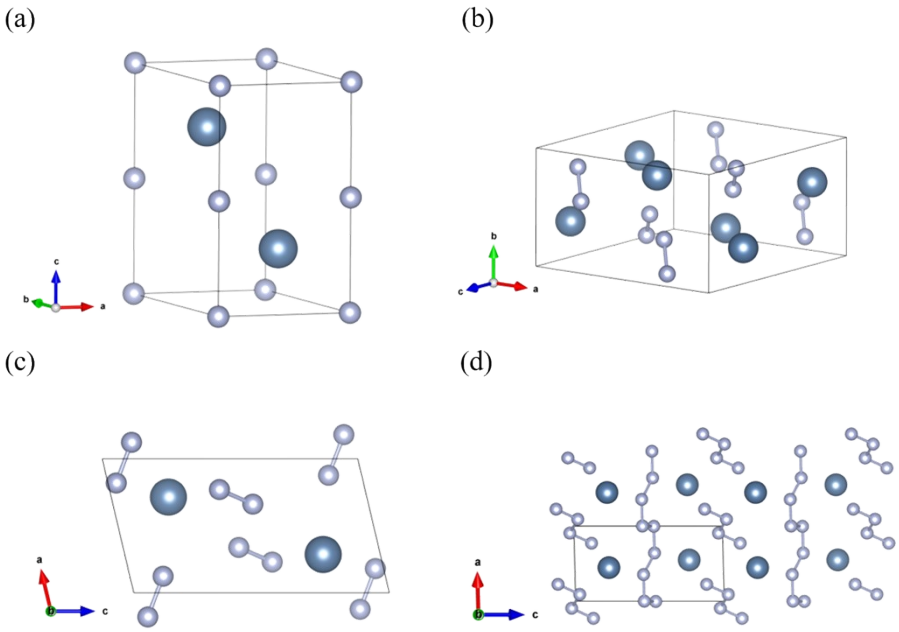

Figure S2. Crystal structures of predicted La-N compounds: (a) $P\bar{6}3mc$ LaN phase at 20GPa. (b) $C2/c$-LaN_2 phase at 100GPa. (c) $P\bar{1}$(I)-LaN_4 phase at 20GPa. (d) $P\bar{1}$(II)-LaN_4 phase at 50GPa. The large spheres are lanthanum atoms, and the small ones are nitrogen atoms.

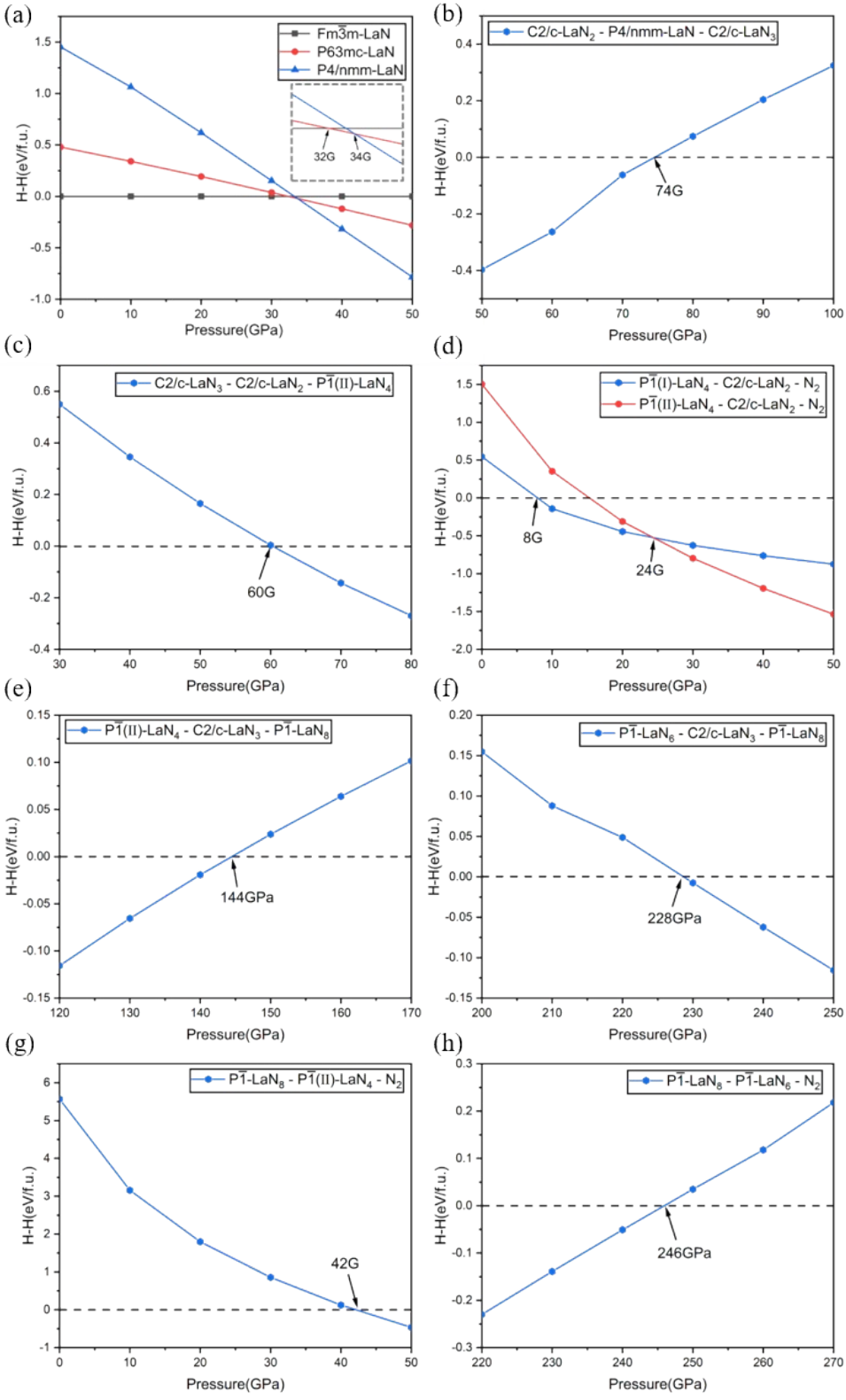

Figure S3. The enthalpy differences of (a) *P*63*mc* phase and *P*4/*nm*^{m} phase relative to *Fm*$\bar{3}$*m* LaN. (b) *C*2/*c*-LaN_2 relative to *P*4/*nmm*-LaN and *C*2/*c*-LaN_3, (c) *C*2/*c*-LaN_3

relative to $C2/c$-LaN_2 and $P\bar{1}$(II)-LaN_4, (d) $P\bar{1}$(I) phase and $P\bar{1}$(II) phase LaN_4 relative to $C2/c$-LaN_2 and nitrogen, (e) $P\bar{1}$(II)-LaN_4 relative to $C2/c$-LaN_3 and $P\bar{1}$-LaN_8, (f) $P\bar{1}$-LaN_6 relative to $C2/c$-LaN_3 and $P\bar{1}$-LaN_8, (g) $P\bar{1}$-LaN_8 relative to $P\bar{1}$(II)-LaN_4 and nitrogen, (h) $P\bar{1}$-LaN_8 relative to $P\bar{1}$-LaN_6 and nitrogen.

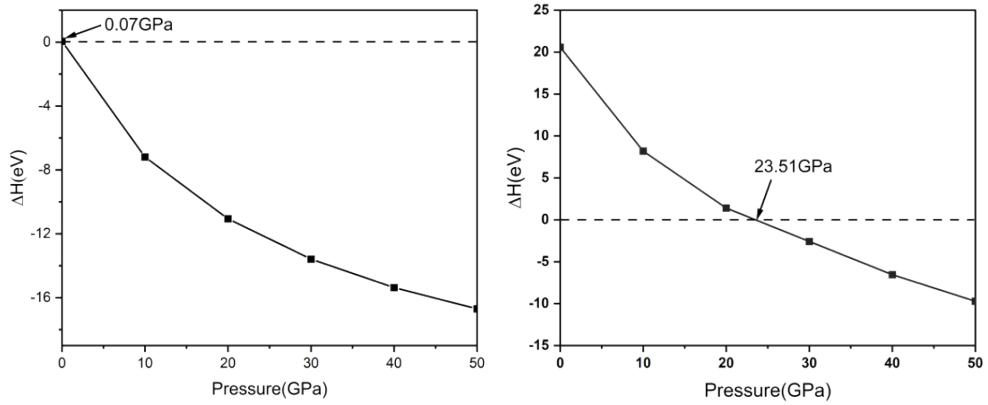

Figure S4. The enthalpy differences of (a) $Pm\bar{3}m-LaN_6$ and (b) $Imm2$-LaN_{10} relative to pure La and pure N.

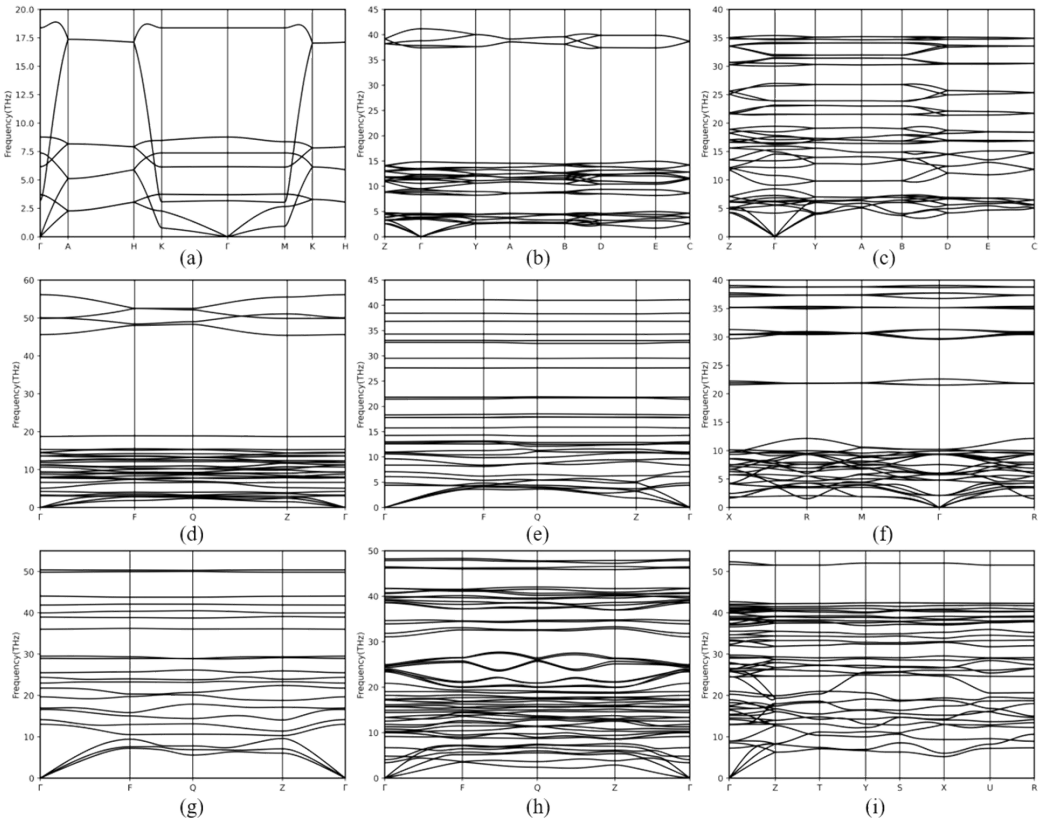

Figure S5. Phonon dispersion curves of nine predicted phases: (a) $P63mc$ – LaN phase at 20GPa. (b) $C2/c$-LaN_2 phase at 0GPa. (c) $C2/c$-LaN_3 phase at 100GPa. (d) $P\bar{1}$(I)-LaN_4 phase at 20GPa. (e) $P\bar{1}$(II)-LaN_4 phase at 50GPa. (f) $Pm\bar{3}m$ – LaN_6 phase at 20GPa. (g) $P\bar{1}$-LaN_6 phase at 300GPa. (h) $P\bar{1}$ – LaN_8 phase at 100GPa. (i) $Imm2$-LaN_{10} phase at 300GPa.

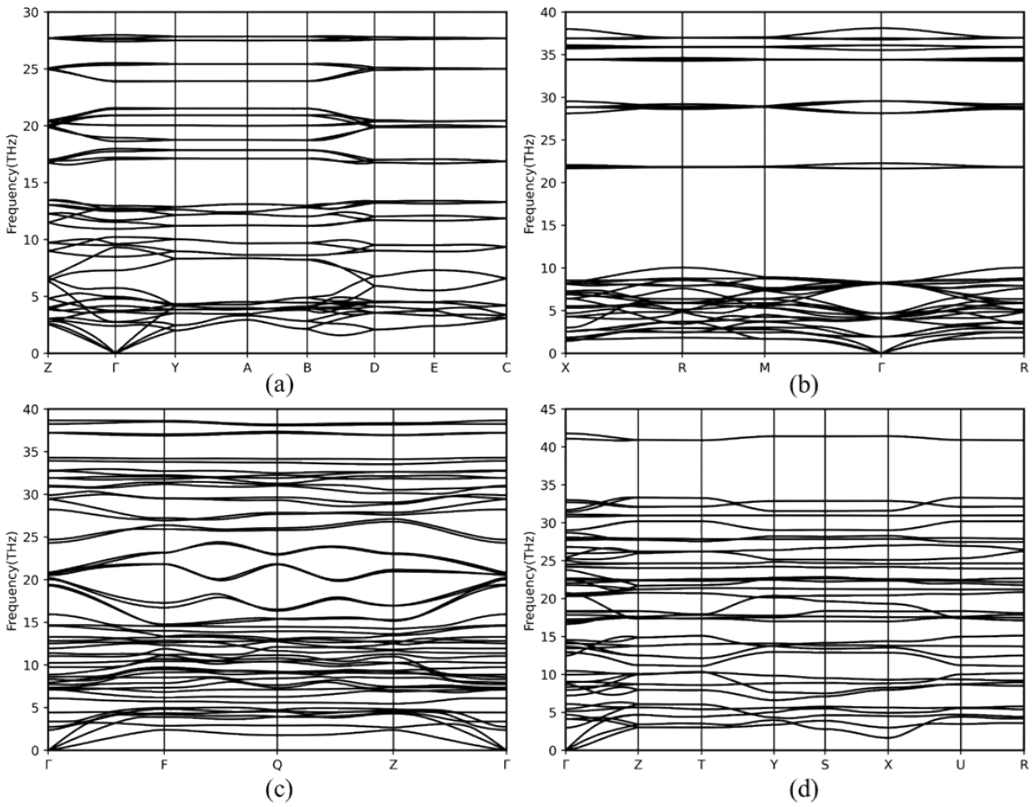

Figure S6. Phonon dispersion curves for (a) *C*2/*c*-^{LaN_3} phase at 0GPa. (b) *Pm* $\bar{3}m$ − LaN_6 phase at 0GPa. (c) $P\bar{1}$-^{LaN_8} phase at 0GPa. (d) *Imm*2-$^{LaN_{10}}$ phase at 25GPa.

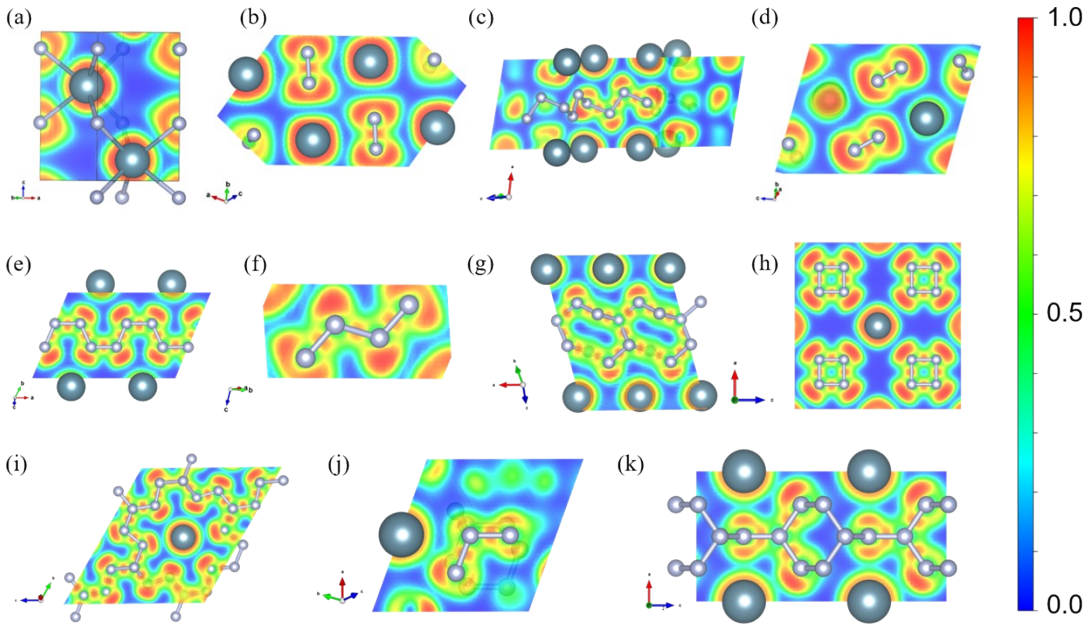

Figure S7. ELF of (a) *P*63*mc* – LaN phase at 20GPa. (b) *C*2/*c*-LaN_2 phase at 0GPa. (c) *C*2/*c*-LaN_3 at 100 GPa, (d) $P\bar{1}$(I)-LaN_4 phase at 20GPa. (e) and (f) $P\bar{1}$(II)-LaN_4 phase at 50GPa, (g) $P\bar{1}$ – LaN_6 at 300 GPa, (h) $Pm\bar{3}m$-LaN_6 at 20 GPa, (i) $P\bar{1}$-LaN_8 at 100 GPa, (j) and (k) *Imm*2-LaN_{10} at 300 GPa.

Table S1. Structural parameters of predicted La-N compounds.

Phases	Pressure	Lattice Parameters (Å)	Wyckoff Positions			
			Atoms	x	y	z
***P*63*mc* – LaN**	20GPa	a = 3.5294 b = 3.5294 c = 6.2466 α = 90 β = 90 γ = 120	La1(2d) N1(2a)	0.3333 0.0000	0.6667 0.0000	0.7500 0.5000
***C*2/*c*-LaN_2**	1atm	a = 6.8040 b = 4.1854 c = 6.7624 α = 90 β = 104.1053 γ = 90	La1(4e) N1(8f)	0.5000 0.6989	0.1993 0.3675	0.2500 0.9473
***C*2/*c*-LaN_3**	100GPa	a = 4.9259 b = 5.5858 c = 5.0342 α = 90 β = 99.2436 γ = 90	La1(4e) N1(4e) N2(8f)	0.0000 0.5000 0.3843	0.3460 0.2963 0.4524	0.2500 0.2500 0.0453
***P*$\bar{1}$(I)-LaN_4**	20GPa	a = 3.9262 b = 4.3309 c = 7.1668 α = 94.8466 β = 103.9189 γ = 78.3645	La1(2i) N1(2i) N2(2i) N3(2i) N4(2i)	0.7140 0.1231 0.6613 0.1805 0.2295	0.2977 0.7214 0.7155 0.2293 0.1809	0.2238 0.1297 0.5475 0.9675 0.5701
***P*$\bar{1}$(II)-LaN_4**	50GPa	a = 3.7431 b = 4.0440 c = 6.9085 α = 102.4135 β = 96.3620	La1(2i) N1(2i) N2(2i) N3(2i) N4(2i)	0.4489 0.0921 0.6432 0.2263 0.0019	0.9837 0.6186 0.3624 0.6923 0.6371	0.2293 0.0280 0.5387 0.8836 0.4615

		γ = 65.7927				
$P\bar{1}$ – LaN_6	300GPa	a = 2.9699 b = 3.2655 c = 4.4789 α = 111.1590 β = 96.1780 γ = 72.9577	La1(1g) N1(2i) N2(2i) N3(2i)	0.0000 0.6277 0.6284 0.9828	0.5000 0.9759 0.2886 0.8229	0.5000 0.2349 0.8078 0.0393
Pm $\bar{3}m$ – LaN_6	20GPa	a = 5.1815 b = 5.1815 c = 5.1815 α = 90 β = 90 γ = 90	La1(1a) La2(1b) N1(12j)	0.0000 0.5000 0.5000	0.0000 0.5000 0.1322	0.0000 0.5000 0.1322
$P\bar{1}$-LaN_8	100GPa	a = 4.7182 b = 5.6176 c = 5.6641 α = 119.6460 β = 89.3950 γ = 76.2834	La1(2i) N1(2i) N2(2i) N3(2i) N4(2i) N5(2i) N6(2i) N7(2i) N8(2i)	0.2211 0.2583 0.3330 0.2407 0.2449 0.2536 0.2223 0.2534 0.2691	0.0968 0.4208 0.7285 0.6304 0.1740 0.4601 0.5569 0.9995 0.7193	0.7848 0.4484 0.0938 0.6923 0.4114 0.2425 0.8756 0.1416 0.3216
Imm2-LaN_{10}	300GPa	a = 4.3632 b = 5.6826 c = 4.2244 α = 90 β = 90 γ = 90	La1(2b) N1(2a) N2(2a) N3(4c) N4(4d) N5(8e)	0.0000 0.0000 0.0000 0.7463 0.0000 0.2474	0.5000 0.0000 0.0000 0.5000 0.8193 0.1851	0.3812 0.8765 0.1676 0.8374 0.6888 0.5160

Table S2. Bader calculation of predicted La-N compounds.

Structure (Pressure)	*P*63*mc* - LaN (20G)	*C*2/*c*-LaN_2 (0G)	$P\bar{1}$(I)-LaN_4 (20G)	$P\bar{1}$(II)-LaN_4 (50G)
Lost electrons of La	1.84	1.93	2.06	2.03

C2/c-LaN_3 (100G)	$P\bar{1}$ - LaN_6 (300G)	*Pm*$\bar{3}$*m* - LaN_6 (20G)	$P\bar{1}$-LaN_8 (50G)	*Imm2*-LaN_{10} (300G)
1.95	1.89	2.10	2.04	1.89