

# Supplementary Information

Chemical composition of lithiated  
nitrodonickelates  $\text{Li}_{3-xy}\text{Ni}_x\text{N}$ : evidence of the  
intermediate valence of nickel ions from ion beam  
analysis and *ab-initio* calculations.

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S.I. 1: schematic representation of the various LiNiN structural models evaluated in this work.

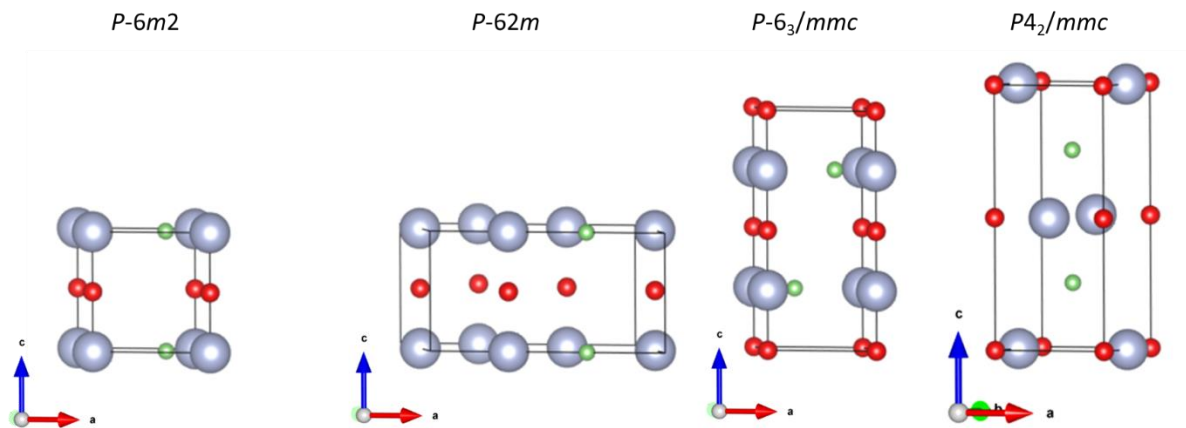


Figure S1 : schematic representation of the various LiNiN structural models evaluated in this work.

S.I. 2: Cell parameters and Enthalpy of formation for LiNiN calculated in several prototypes.

	Cell parameters (Å)		Enthalpy of formation (kJ.mol <sup>-1</sup> .at <sup>-1</sup> )
	<i>a</i>	<i>c</i>	
LiNiN ( <i>P-6m2</i> )	3.637	3.415	-7.50
LiNiN ( <i>P-62m</i> )	7.268 (3.634*2)	3.415	-7.49
LiNiN ( <i>P6<sub>3</sub>/mmc</i> )	3.632	6.828 (3.41*2)	-7.64
LiNiN ( <i>P4<sub>2</sub>/mmc</i> )	3.368	7.557	17.1

### S.I.3: Bond Valence Sum analysis of $\text{Li}_{3-x}\text{Ni}_x\text{N}$ solid solution phases.

The Bond Valence Sum analysis is an empirical method which linked the lengths of bonds formed by an ion to its oxidation state [1]. A fraction of valence is attributed to each bond according to:

$$v. b. = e^{\left(\frac{R_0 - R}{b}\right)} \quad (\text{S1})$$

Where  $v. b.$  is the valence bond fraction,  $R$  is the bond length, and  $R_0$  and  $b$  are tabulated values determined. The sum of all the  $v. b.$  attributed to each bond formed by the ion should be close to the expected valence. In this work, we used the tabulated values determined by Gagné recently for nitrides [2]. Thus,  $R_0$  and  $B$  are 1.611 Å and 0.457 for  $\text{Ni}^{2+}-\text{N}^{3-}$  bonds (parameters for lower nickel valence are not available) and for  $\text{Li}^+-\text{N}^{3-}$  bonds,  $R_0$  and  $B$  are 1.713 Å and 0.312 respectively. The next figure shows the bond valence evolution versus the bond length for  $\text{Ni}^{2+}-\text{N}^{3-}$  and  $\text{Li}^+-\text{N}^{3-}$  bonds (red curve and black curve respectively). In the 2-fold coordination of the 1b site, a Ni valence greater than 1 ( $v. b. > 0.5$  to 1) is expected to lead to shorter bond lengths than  $\text{Li}^+$ .

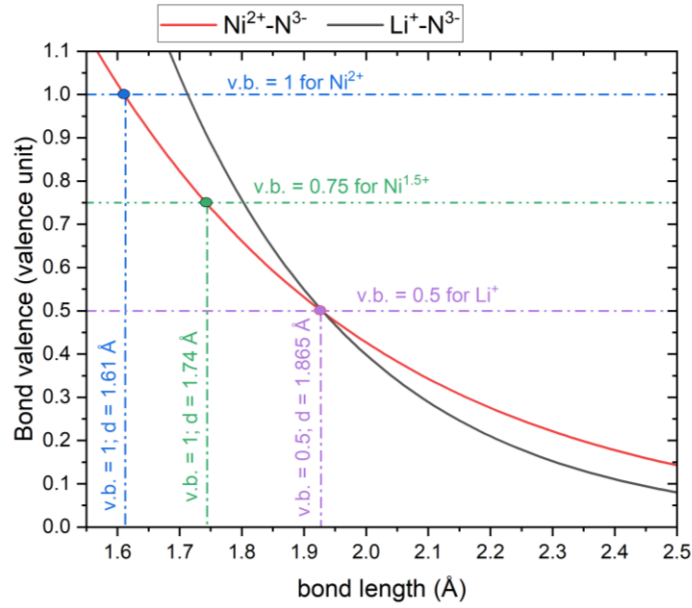


Figure S2: bond valence vs bond length for  $\text{Ni}^{2+}-\text{N}^{3-}$  (red curve) and  $\text{Li}^+-\text{N}^{3-}$  (black curve) bonds.

The  $c$  parameter is directly related to these bond lengths: increasing the Ni content leads to a contraction of the cell parameter. According to the BVS method, in 2-fold coordination, the  $v. b.$  should be 0.5 for  $\text{Li}^+$  and  $v. b.$  0.75 for  $\text{Ni}^{1.5+}$ . Thus, the  $c$  parameter evolution with Ni content might follow the expression:

$$c = 2[(1 - x_{\text{Ni}})(1.713 - 0.312 \ln 0.5) + x_{\text{Ni}}(1.611 - 0.457 \ln 0.75)] = 3.858 - 0.373x_{\text{Ni}} \quad (\text{S2})$$

Conversely, the  $a$  parameter increases with increasing Ni content is related to the three Li-N bonds into the P/6mmm  $\text{Li}_3\text{N}$  type structure. The fractional occupation by Li ions of the 2c site is  $(1-0.25x_{\text{Ni}})$  for a  $\text{Ni}^{1.5+}$  valence, i.e.,  $0.5x_{\text{Ni}}$  vacancies created in the site of multiplicity 2. According to the crystal structure, the  $a$  parameter might follow the expression:

$$a = 2 \cos\left(\frac{\pi}{6}\right) \times d_{Li-N} = 2 \cos\left(\frac{\pi}{6}\right) \times \left(1.713 - 0.312 \ln\left(\frac{1 - 0.25x_{Ni}}{3}\right)\right) \quad (S3)$$

These expected evolutions are plotted in the following figure. Using this empirical approximation, overall evolutions are respected. Main weakness of this reflection lies with the reliability of the tabulated parameters and to the assumption of localized bonds within the structure (i.e., ionic structure), which is completely the case here.

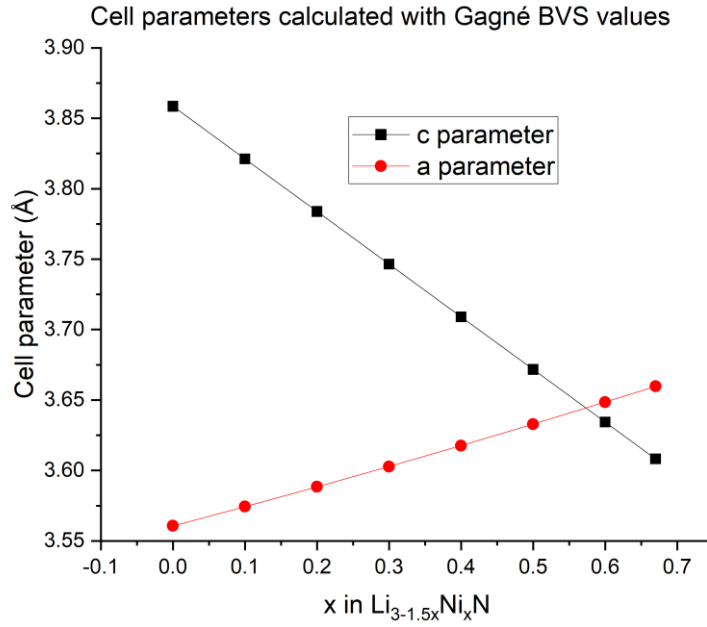


Figure S3: cell parameters evolution expected using Bond Valence approach with Gagné parameters [2].

S.I.4: Phonon dispersion curves for LiNiN within the 4 structures evaluated.

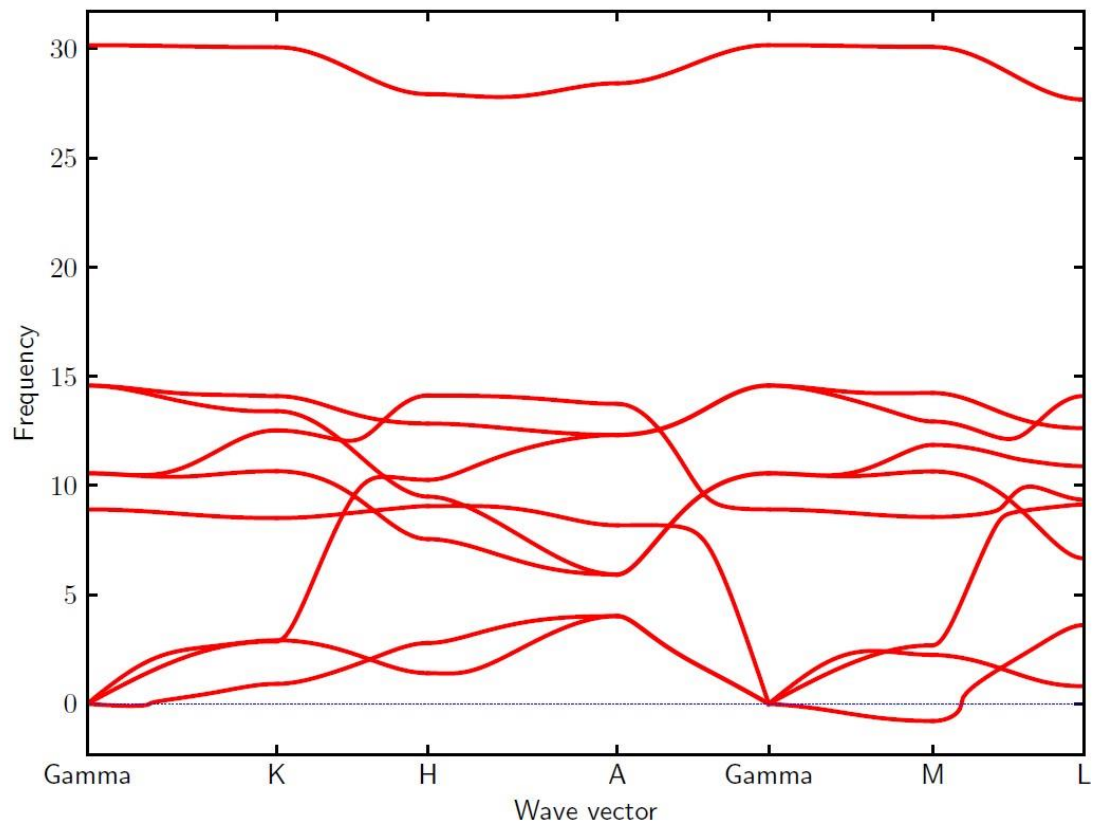


Figure S4: Phonon diagram for LiNiN in the P-6m2 prototype

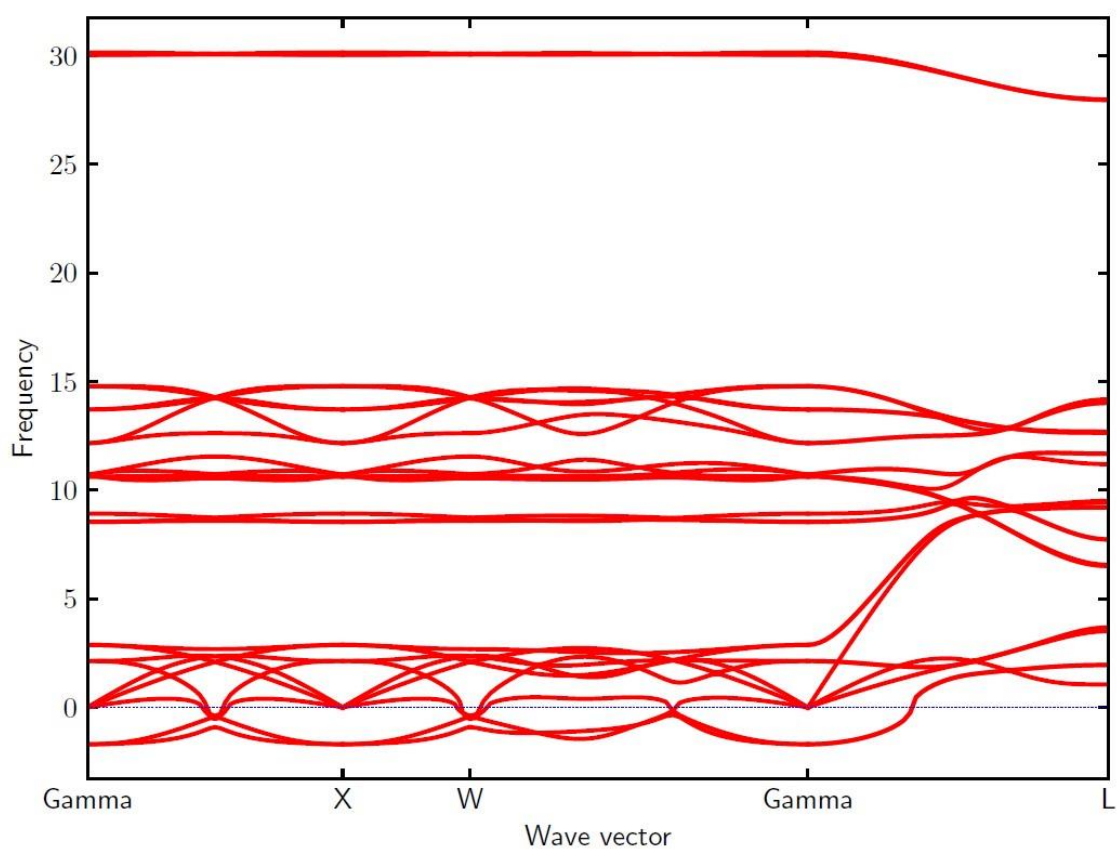


Figure S5: Phonon diagram for LiNiN in the P-62m prototype

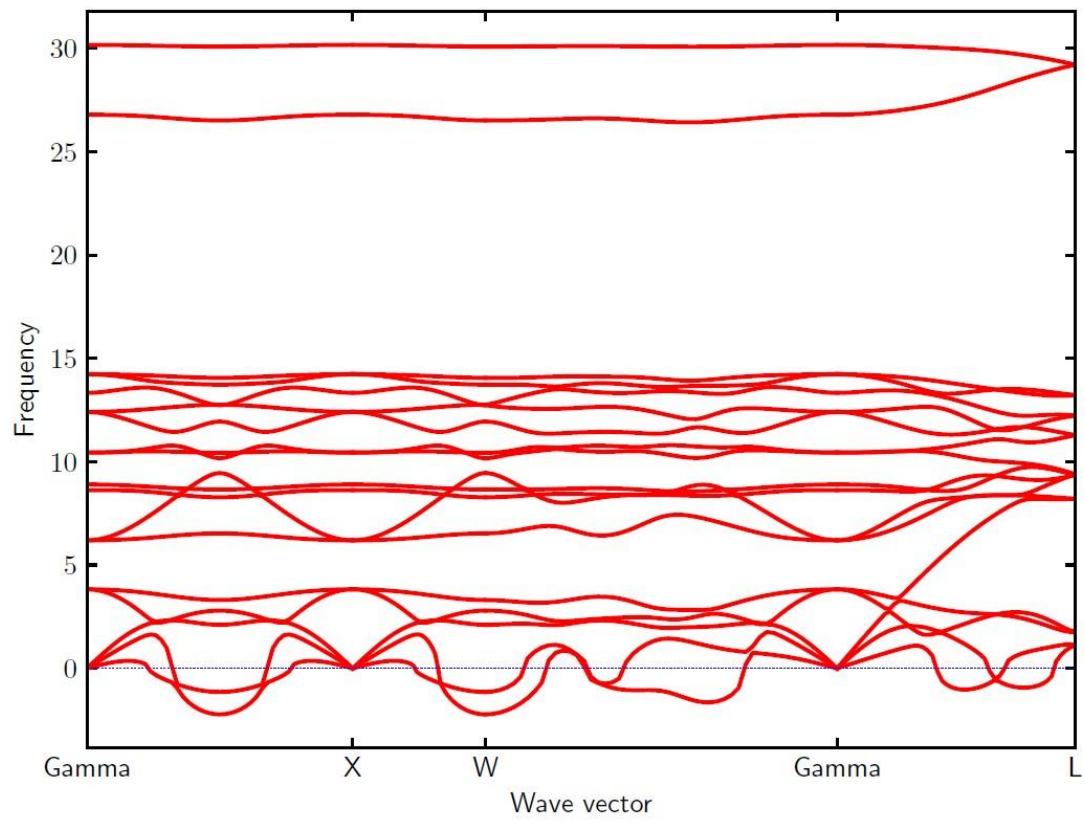


Figure S6: Phonon diagram for LiNiN in the P6<sub>3</sub>/mmc prototype



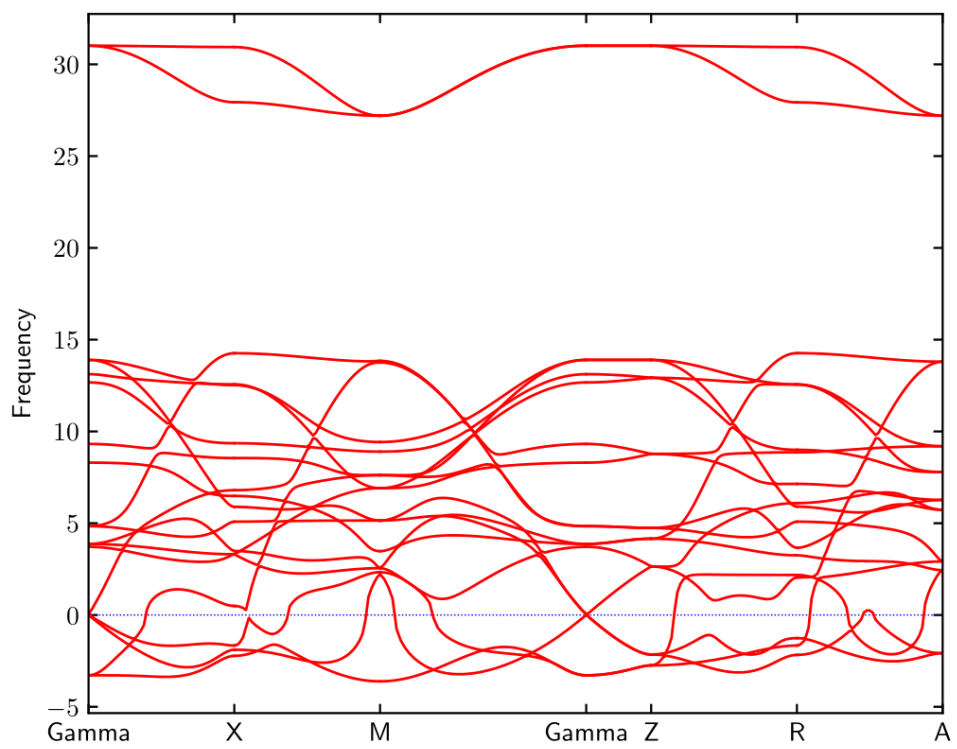


Figure S7: Phonon diagram for LiNiN in the  $P4_2/mmc$  prototype

S.I.5. Electronic density of states of  $\text{Li}_{3-x}\text{Ni}_x\text{N}$  solid solution phases.

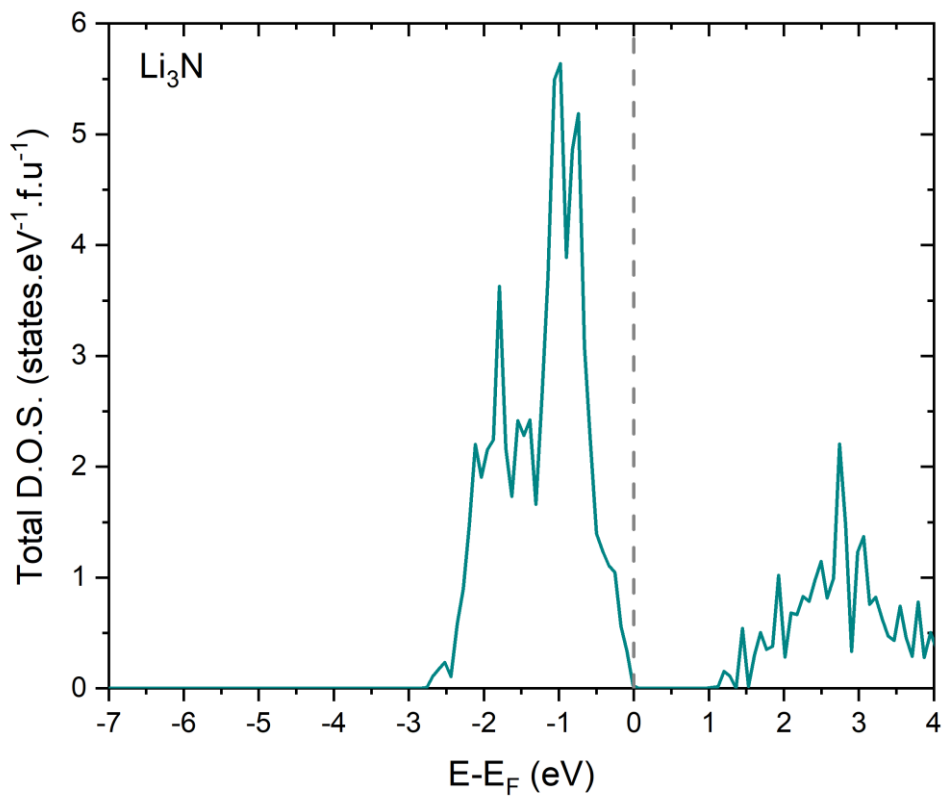


Figure S8: electronic density of states of  $\text{Li}_3\text{N}$

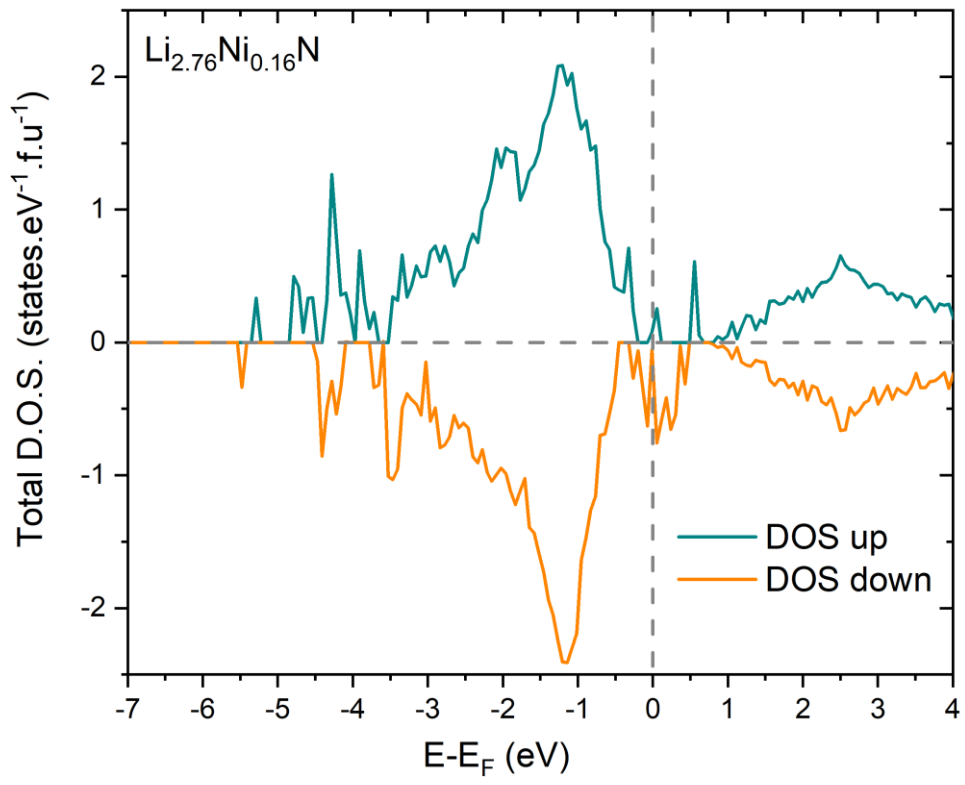


Figure S9: electronic density of states of  $\text{Li}_{2.76}\text{Ni}_{0.16}\text{N}$

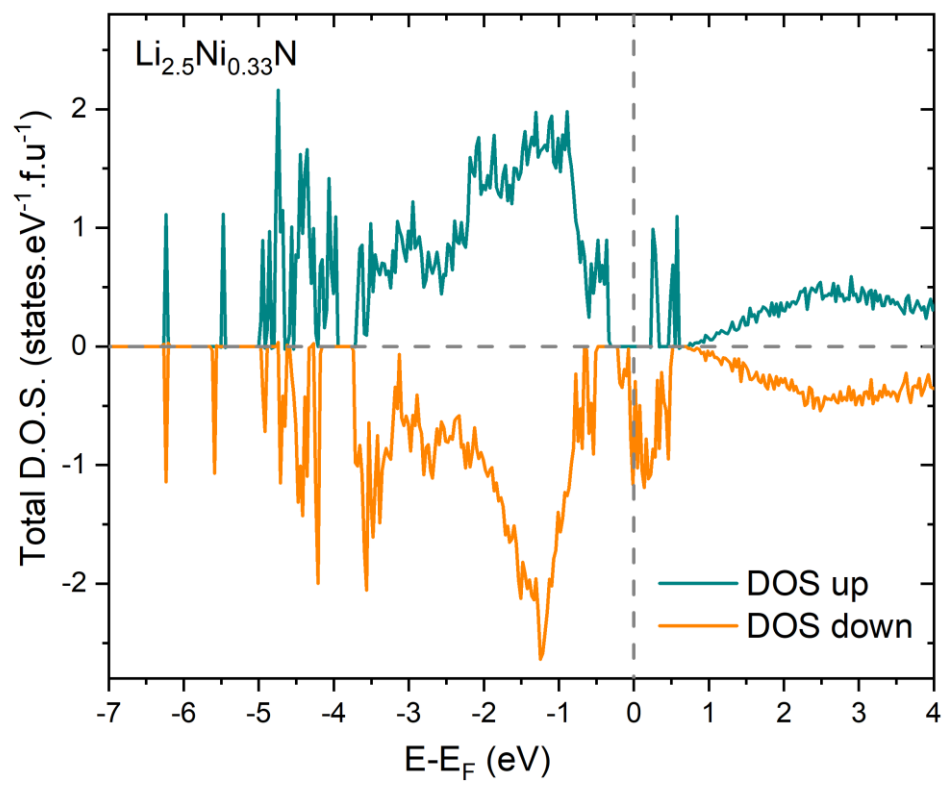


Figure S10: electronic density of states of  $\text{Li}_{2.5}\text{Ni}_{0.33}\text{N}$

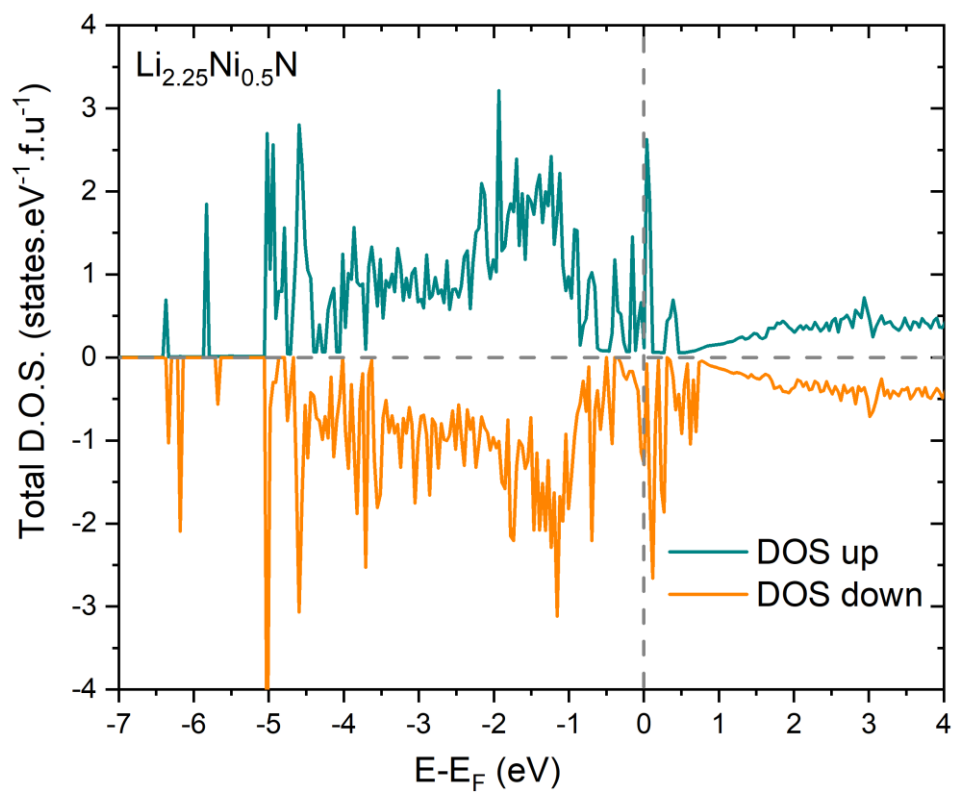


Figure S11: electronic density of states of  $\text{Li}_{2.25}\text{Ni}_{0.5}\text{N}$

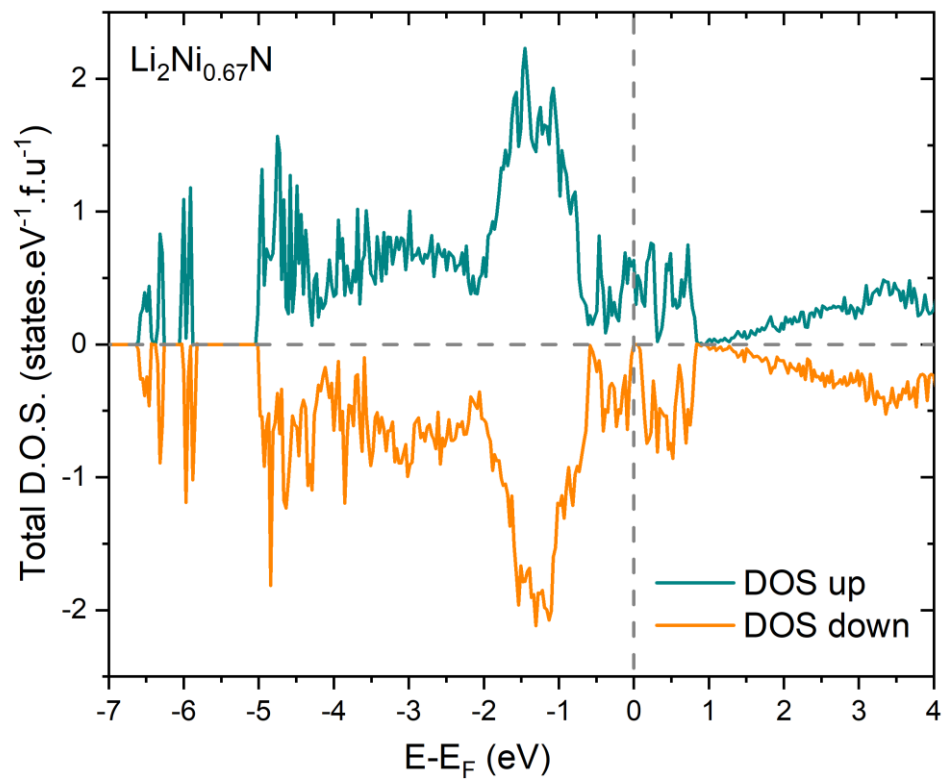


Figure S12: electronic density of states of  $\text{Li}_2\text{Ni}_{0.67}\text{N}$

## References:

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- [1] Brown, I.D.; Recent developments in the methods and applications of the Bond Valence model, *Chem. Rev.* 2009, 109, 6858–6919
- [2] Gagné, O.C.; On the crystal chemistry of inorganic nitrides: crystal-chemical parameters, bonding behavior, and opportunities in the exploration of their compositional space, *Chem. Sci.* 2021, **12**, 4599-4622