p-type conductivity mechanism and defect structure of nitrogen-doped $LiNbO_3$ from first-principle calculation

Electronic Supplementary Material

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The selection of pseudopotential

In this supporting information, the test of pseudopotential selection for the atom Nb is discussed. The pseudopotential we employed in the paper is PAW_PBE. The choice for Nb here is Nb_sv and Nb_pv, Nb_sv treats the *s* electrons as the semi-core state, Nb_pv treats the *p* electrons as the semi-core state, and the difference between them is the valence of the Nb element. To find out the suitable pseudopotential of Nb atom in our calculation, we calculated the same $LiNbO_3$ supercell with Nb_sv and Nb_pv, respectively. The results are listed in Table S1. Seen from Table S1, the calculation of Nb_sv and Nb_pv show the different influences on the lattice parameters of $LiNbO_3$. Compared with the experiment results, the calculation with Nb_pv is more convincing to reflect the situation of $LiNbO_3$. Therefore, Nb_pv pseudopotential is employed in this paper.

Table S1. Lattice parameters calculated with Nb_sv and Nb_pv, respectively. The results obtained from experiments are listed here.

	a (Å)	*c* (Å)	*V* (Å^3)
Nb_sv	5.110	13.797	311.964
Nb_pv	5.130	13.890	316.540
Exp. [1]	5.147	13.853	317.873
Exp. [2]	5.151	13.876	318.844

The dispersion effect

In addition, the dispersion effect is considered with DFT-D3. We used the DFT-D3 functional based on the projector augmented wave method to treat the van der Waals interactions in the DFT calculations. To explore the influence of the van der Waals interaction in $LiNbO_3$, we construct two structures calculated with DFT-D3 and normal DFT for comparison. The influence on the lattice of the crystal is shown in Figure S1.

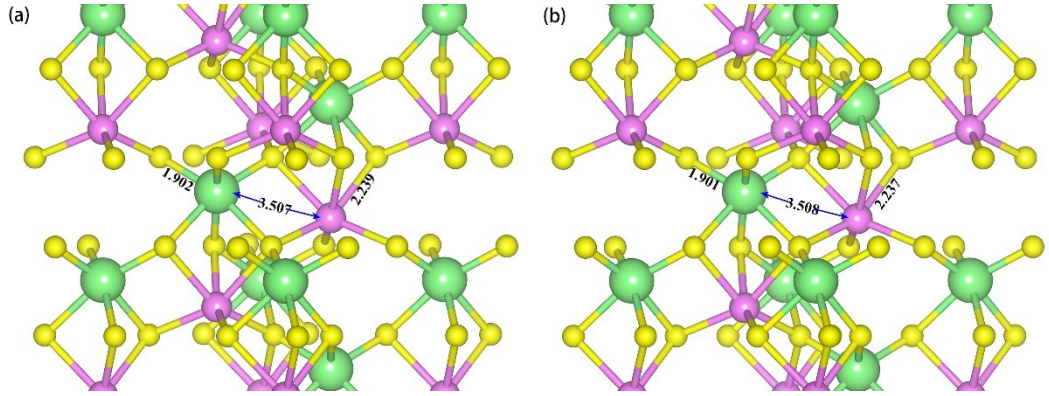

Figure S1. The structure of $LiNbO_3$ calculated with and without DFT-D3 shown in the (a) and (b). The distances between normal Li and Nb, Li and O, Nb and O atoms are labeled on the bond. The unit of these numbers is Å.

Seen from Figure S1, the difference between the two structures is tiny, which means the dispersion effect shows a small influence on the crystal. As we know, there will be a correction energy in the DFT-D3 calculation, which related to the geometry structure of the crystal. While we modeled two structures with No point defect in different sites, the correction energy is -5.41291 eV, and the other one is -5.41293 eV. The differences between these two structures are too small to be considered.

The density of states (DOS) calculated with and without DFT-D3 is shown in Figure S2. Compared with Figure S2(a) and (b), the distribution of Nb, Li, and O features are almost the same; the effect that DFT-D3 brings to the bulk is weak too. Therefore, the dispersion effect can be ignored in the calculation of $LiNbO_3$.

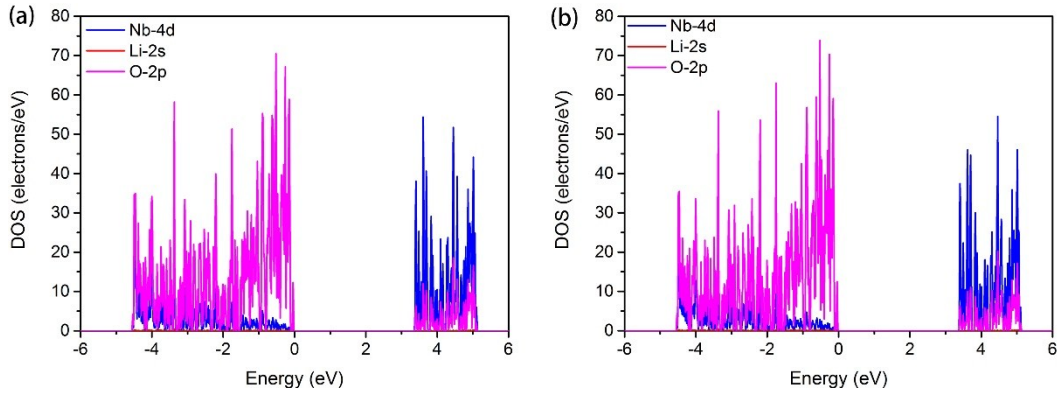

Figure S2. The DOS of $LiNbO_3$ calculated with and without DFT-D3 shown in the (a) and (b).

The comparison of chemical potential

As we mentioned in the paper, the chemical potentials of Li, Nb, and O depend on the preparation conditions. They cannot be obtained from the crystal or metal directly, which are subject to the thermodynamic conditions. In Table S2, we list the chemical potentials of Li & Nb ions in lithium niobate from different works. And we can find that different functional and different supercell size both affect the chemical potential of Li & Nb ions. Therefore, we calculate the chemical potentials instead of directly citing references.

Table S2. Comparison of the chemical potential in Li-deficient condition between our works and references.

	Chemical potential (eV)			
Method	GGA-PAW[3]	HSE06[4]	GGA-PBE[5]	PAW-PBE (this paper)
Supercells	240-atoms	120-atoms	240-atoms	240-atoms
Li	-4.791	-3.45	-4.37	-3.63
Nb	-19.180	-21.8	-20.19	-18.98

The formation energy of V_{Li}^{0}

Seen from Figure 5 of this paper, the most stable charge state of V_{Li} is -1 in the possible Fermi energy. We also calculated the formation energy of V_{Li}^{0}, and the results are shown in Figure S3. The formation energy of V_{Li}^{0} is about 3.62 eV, which is higher than the formation energy of V_{Li}^{-1} in the possible Fermi range. Therefore, the V_{Li}^{0} point defect is difficult to form in crystals. That coincides with experimental results, till now there are no stable V_{Li}^{0} state in lithium niobate reported.

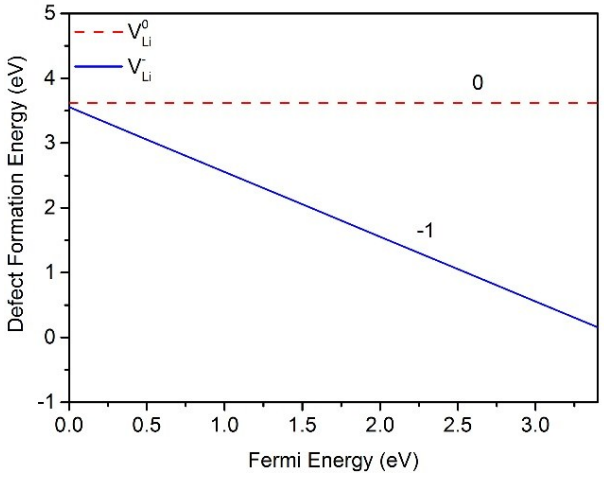

Figure S3. The formation energy of V_{Li} with 0 and -1 charge state.

Reference

[1] S. C. Abrahams and P. Marsh, *Acta Crystallogr., Sect. B: Struct. Sci.* 1986, **42**, 61.

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[4] L. Li, Y. Li and X. Zhao, *Phys. Rev. B* 2017, **96**, 115118.

[5] Y. Li, W. G. Schmidt, and S. Sanna, *Phys. Rev. B* 2014, **89**, 094111.

The structure of the No point defect

The most stable optimized structures of nitrogen-doped $LiNbO_3$ that nitrogen substituting O site is given here. The others can be found in the supplementary materials.

N_O structure
1
10.276204109 0.000000000 0.000000000
-5.138102055 8.899453813 0.000000000
0.000000000 0.000000000 27.826610565
Li O Nb N
48 143 48 1
Direct
0.9996424508 0.9977295549 0.1431896228
0.0186370806 0.9740316274 0.3890901605
0.3247858019 0.1726457856 0.3082890594
0.3279559300 0.1731220568 0.0625088043
0.1744466240 0.3253335724 0.4749394153
0.1863651513 0.3511680149 0.2231589375
0.5128751586 0.0179593951 0.1412616079
0.4805469205 0.9789489235 0.3970187162
0.8282747981 0.1606991565 0.3074374839
0.8261542093 0.1561331500 0.0533851836
0.6549315498 0.3204686124 0.4717960202
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0.0014132354 0.4967044559 0.1422823542
0.0101716690 0.4806124270 0.3909719463
0.3361906925 0.6521948533 0.3039441991
0.3326098996 0.6977230740 0.0601604276
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0.0043377202 0.4900091320 0.6422597744
0.9917620026 0.5051493874 0.8887223652
0.3737143878 0.6890795957 0.8087380383
0.3067662300 0.6470933997 0.5501753476
0.1747628173 0.8506680239 0.9822075651

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