

SUPPORTING INFORMATION

Misfit layer compounds: a platform for heavily-doped two-dimensional transition metal dichalcogenides.

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(Dated: September 9, 2020)

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THEORY

Extended technical details

The cell parameters and the atomic positions used in first principles calculations are from the experimental work of R. Roesky *et al.*[1]. We build the starting structure for geometrical optimization by considering the NbSe₂ part and the LaSe part initially separated and then combined together, according to the following procedure:

1. NbSe₂ part: we generate a $\sqrt{3}\times 7\times 1$ supercell of the three atoms unicell cell belonging to the space group C222₁ (a slightly distorted hexagonal unit cell along one direction, see main paper for more informations).
2. LaSe part: we adopt C₁ symmetry for the unit cell and generate a $1\times 4\times 1$ supercell
3. We combine the two parts and re-center LaSe in between the NbSe₂ layers.

The assembled bulk system is composed of 232 atoms, it has P1 symmetry and lattice parameters $a = 6.019$ Å, $b = 24.060$ Å, $c = 36.531$ Å. We repeat this procedure with and without the refinement of the common part (see Ref.[1] for more details), obtaining two different starting atomic arrangements, called S1 and S2 respectively. We then performed structural optimization neglecting spin-orbit coupling.

We used the generalized gradient approximation in the PBE parametrization[2] for the exchange-correlation functional with the following configurations for the pseudopotentials: (i) for Se, norm-conserving pseudopotentials with empty d -states in valence and the following valence configuration $4s^2, 4p^3, 4d^0$, (ii) for Nb, ultrasoft pseudopotentials from Vanderbilt distribution [3] including semicore states and two projectors for s and p channels, (iii) for La, ultrasoft pseudopotentials from the Vanderbilt distributions.

As mentioned in the main text, the kinetic energy cutoff for plane-wave expansion has been set to 45 Ry (537 Ry for the charge density). In the case of

non-collinear spin orbit coupling (SOC) calculations we used an energy cutoff of 75 Ry (537 Ry for the charge density). Integration over the the Brillouin Zone (BZ) was performed using an uniform $4 \times 1 \times 1$ Monkhorst and Pack[4] grid. For all of the calculation we adopt a Gaussian smearing of 0.01 Ry.

The energy difference between the two optimized structures is less then 0.1 meV/Nb, i.e. the two relaxed structures are energetically degenerate. For the purpose of the subsequent calculations we have used the lowest energy one, as the results are very similar for the two cases.

The slab was obtained from the bulk by keeping the same axes and removing half of the cell and replacing it with vacuum. Thus, we remove one layer of LaSe and the two nearest NbSe₂ ones. This new system is composed only of an alternating stacking sequence of NbSe₂, LaSe and NbSe₂ layers along the c-axis with about 21 Å of vacuum between the periodic images, we will refer to this system as the "slab". The atomic position of the slab have been relaxed, but they didn't change.

In Tabs.A and B we report the optimized atomic positions expressed in crystalline coordinates (the atoms with * belong to the slab system). The coordinates of the crystal axes are:

$$a = (6.0191, 0.0000, 0.0000) \text{ Å}$$

$$b = (0.0000, 24.0608, 0.0000) \text{ Å}$$

$$c = (0.0000, 0.0000, 36.5319) \text{ Å}$$

Electronic structure of bulk and surface of the misfit compound

We first compare the bulk and slab electronic structure, without SOC contribution, to monitor the possible existence of surface states. As it can be seen, the two systems show similar band dispersion, the main difference is doubling the number of electronic bands in the bulk (See Fig. S1).

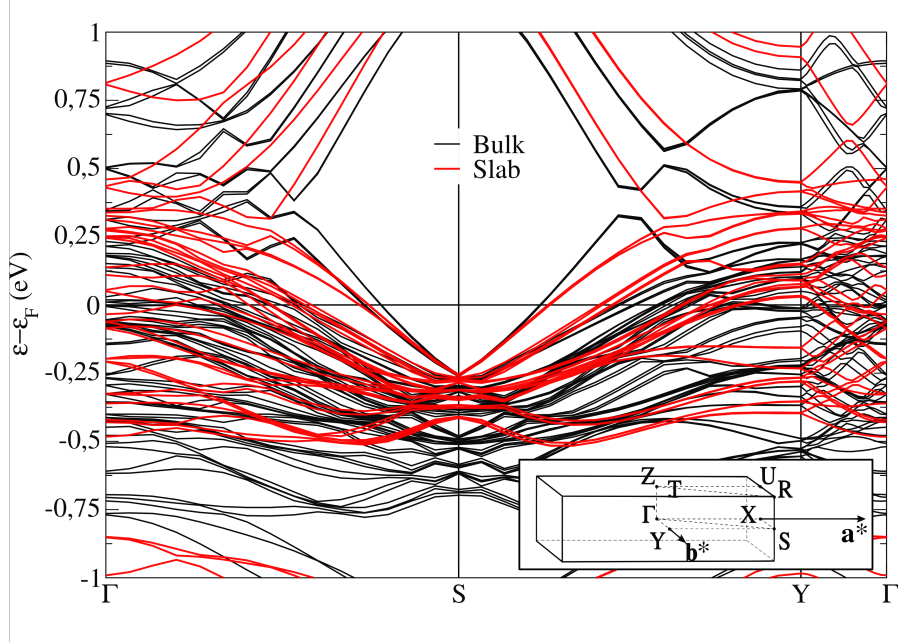


FIG. S1: Electronic band comparison between the bulk (black) and a slab composed by an alternatig sequences of LaSe and NbSe₂ layers along the c-axis, with about 21 Å of vacuum between the periodic images (in red, labeled slab). In the inset we report the bulk Brillouin Zone with special points.

Electronic structure of the misfit compound surface as a single layer NbSe₂.

We unfold the electronic bands (computed with SOC term) of the slab onto those of a C222₁ NbSe₂ monolayer unit cell by means of the Bands-UP software[5, 6], obtaining Fig. 4 in the main text showing a very similar electronic structure to that of a single layer NbSe₂ with C222₁ unit cell. A similar message can be obtained by directly comparing the electronic bands of the slab with those of a $\sqrt{3} \times 7$ supercell of the NbSe₂ C222₁ single-layer unit-cell. We thus plot in Fig. S2, both electronic structures in the Brillouin zone of the $\sqrt{3} \times 7$ supercell. In this case for semplicity, the calculation have been carried out without SOC contribution. The only appreciable effects of LaSe are (i) rigid doping of the NbSe₂ layer and (ii) a small hybridization between La states and NbSe₂ states close to zone center.

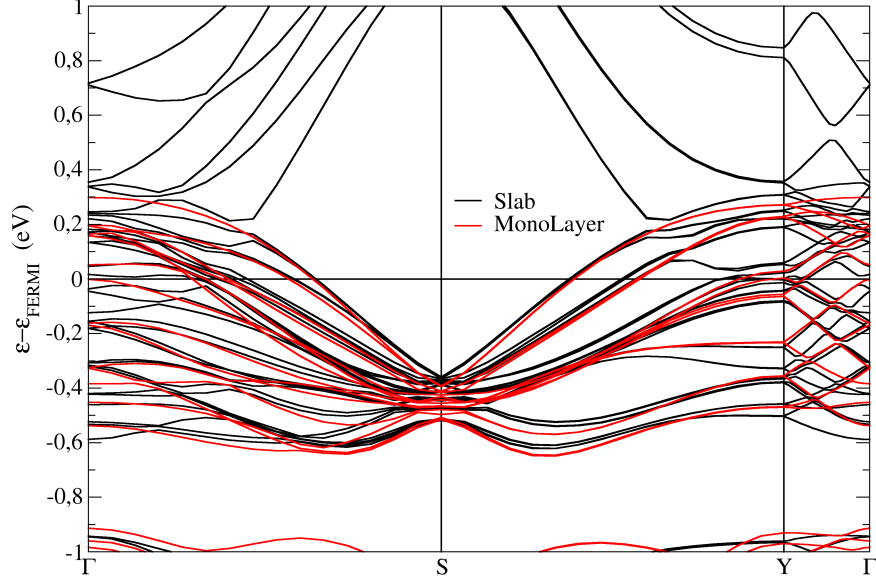


FIG. S2: Comparison between the electronic structure of the slab (black) and that of a NbSe₂ single-layer (red). The NbSe₂ single layer bands have been rigidly shifted by -0.30 eV.

NbSe₂ dynamical properties as a function of doping

As the electron-doped single layer and the slab show very comparable electronic structure, we study the dynamical stability of a single layer NbSe₂ having C222₁ unit cell as a function of electron-doping. We keep the lattice parameters locked at the experimental parameters of the NbSe₂ layers in the slab structure. The structure is then strained along the *b*-axis (0.8% with respect to the ideal high-symmetry case) according to the misfit between the two different layers.

Phonon modes, in this distorted structure, are calculated in linear response theory[7, 8] using a uniform 12×12 phonon-momentum grid and a uniform 21×21×1 reciprocal space mesh[4] for sampling the electronic state, without the SOC contribution. A Gaussian smearing of 0.01 Ry is adopted.

The evolution of phonon dispersion as a function of electron doping is reported in Fig. S3. As it can be seen, electron doping first shifts the instability to the M-point and then it removes it completely. At the estimated doping of 0.6 electrons

per Nb, the instability disappears.

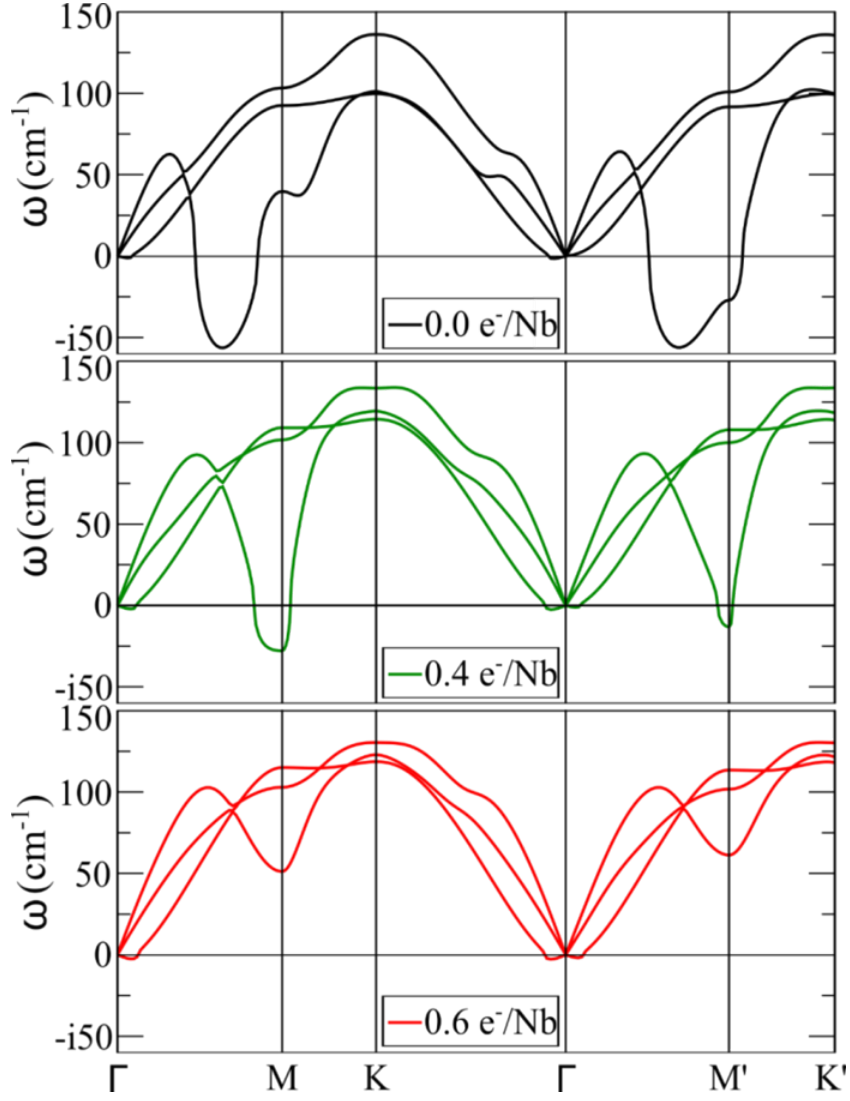


FIG. S3: Phonon dispersion for single layer H-NbSe₂ at the experimental strain as a function of doping.

Nb* 0.48728 0.08890 0.58713	Nb 0.00368 0.12715 0.08717	Nb* -0.00859 0.12785 0.91604
Nb 0.50261 0.08856 0.41650	Se* 0.15678 0.08845 0.54159	Se 0.33713 0.12831 0.04221
Se* 0.15782 0.05623 0.96108	Se 0.33052 0.12962 0.13306	Se* 0.15466 0.08884 0.63418
Se 0.33522 0.01663 0.46126	Se* 0.15359 0.05695 0.86930	Se 0.33167 0.01954 0.36940
Nb* 0.99203 0.01725 0.58691	Nb 0.50497 0.05694 0.08757	Nb* 0.48946 0.05499 0.91554
Nb 1.00369 0.01594 0.41602	Se* 0.65584 0.01691 0.54208	Se 0.83535 0.05617 0.04193
Se* 0.65683 0.01718 0.63205	Se 0.83623 0.08758 0.46143	Se* 0.65685 0.12634 0.96108
Se 0.83897 0.05589 0.13442	Se* 0.65585 0.12691 0.87044	Se 0.82938 0.08660 0.37082
Nb* 0.48793 0.23207 0.58760	Nb 0.00295 0.26988 0.08838	Nb* -0.01021 0.27002 0.91737
Nb 0.49944 0.23087 0.41669	Se* 0.15695 0.23169 0.54227	Se 0.33428 0.27127 0.04282
Se* 0.15710 0.19812 0.96202	Se 0.33851 0.27136 0.13482	Se* 0.15940 0.22826 0.63440
Se 0.33423 0.15946 0.46176	Se* 0.15696 0.20088 0.86941	Se 0.33762 0.15962 0.36921
Nb* 0.98945 0.15958 0.58683	Nb 0.50427 0.19996 0.08762	Nb* 0.48737 0.19839 0.91651
Nb 1.00403 0.15910 0.41613	Se* 0.65550 0.16063 0.54193	Se 0.83623 0.19928 0.04246
Se* 0.66285 0.16093 0.63236	Se 0.83540 0.23070 0.46151	Se* 0.65552 0.26972 0.96226
Se 0.83161 0.19614 0.13406	Se* 0.66307 0.27037 0.87207	Se 0.83491 0.23132 0.37158
Nb* 0.49161 0.37497 0.58816	Nb 0.00451 0.41343 0.08803	Nb* -0.00790 0.41231 0.91692
Nb 0.50246 0.37319 0.41732	Se* 0.15740 0.37372 0.54305	Se 0.33462 0.41338 0.04248
Se* 0.15717 0.34141 0.96250	Se 0.33595 0.41487 0.13513	Se* 0.15603 0.37335 0.63382
Se 0.33437 0.30174 0.46221	Se* 0.15757 0.33977 0.86995	Se 0.33746 0.30261 0.36969
Nb* 0.99032 0.30197 0.58827	Nb 0.50012 0.34257 0.08805	Nb* 0.48771 0.34169 0.91707
Nb 1.00398 0.30286 0.41660	Se* 0.65802 0.30360 0.54286	Se 0.83515 0.34166 0.04310
Se* 0.65453 0.30366 0.63443	Se 0.83602 0.37385 0.46227	Se* 0.65721 0.41349 0.96193
Se 0.83559 0.34157 0.13345	Se* 0.65647 0.41354 0.87152	Se 0.82910 0.37582 0.37158
Nb* 0.49005 0.51730 0.58747	Nb 0.00405 0.55681 0.08800	Nb* -0.01192 0.55511 0.91707
Nb 0.50192 0.51575 0.41679	Se* 0.15589 0.51714 0.54260	Se 0.33484 0.55648 0.04261
Se* 0.15786 0.48387 0.96200	Se 0.33360 0.55406 0.13501	Se* 0.16334 0.51662 0.63279
Se 0.33496 0.44482 0.46238	Se* 0.15406 0.48337 0.87014	Se 0.33139 0.44255 0.37055
Nb* 0.98798 0.44531 0.58793	Nb 0.50230 0.48476 0.08747	Nb* 0.48967 0.48524 0.91656
Nb 1.00349 0.44590 0.41715	Se* 0.65730 0.44572 0.54251	Se 0.83644 0.48506 0.04258
Se* 0.65835 0.44788 0.63496	Se 0.83381 0.51700 0.46222	Se* 0.65650 0.55595 0.96232
Se 0.82903 0.48536 0.13278	Se* 0.66030 0.55872 0.87052	Se 0.83739 0.51776 0.37036
Nb* 0.49245 0.65951 0.58824	Nb 0.00170 0.70019 0.08845	Nb* -0.01241 0.69816 0.91682
Nb 0.50402 0.65929 0.41740	Se* 0.15754 0.66053 0.54327	Se 0.33410 0.69860 0.04307
Se* 0.15532 0.62696 0.96237	Se 0.33743 0.69846 0.13461	Se* 0.15669 0.66056 0.63360
Se 0.33472 0.58747 0.46222	Se* 0.16254 0.62538 0.87163	Se 0.33512 0.58749 0.37176
Nb* 0.98812 0.58867 0.58812	Nb 0.50050 0.62716 0.08833	Nb* 0.48905 0.62784 0.91745
Nb 0.99969 0.58868 0.41721	Se* 0.65794 0.58881 0.54260	Se 0.83461 0.62848 0.04320
Se* 0.65684 0.58703 0.63520	Se 0.83492 0.65965 0.46278	Se* 0.65722 0.69915 0.96245

TABLE A: List of atomic positions expressed in crystalline coordinates, the atoms with *

belong to the slab system (first part).

Se 0.83626 0.62875 0.13400	Se* 0.65408 0.69856 0.86992	Se 0.83375 0.66126 0.37025
Nb* 0.48833 0.80223 0.58780	Nb 0.00279 0.84252 0.08709	Nb* -0.01269 0.84191 0.91640
Nb 0.50421 0.80258 0.41663	Se* 0.15651 0.80276 0.54259	Se 0.33666 0.84158 0.04217
Se* 0.15597 0.77034 0.96179	Se 0.32934 0.84132 0.13260	Se* 0.16087 0.80621 0.63424
Se 0.33616 0.73141 0.46249	Se* 0.15670 0.76973 0.87183	Se 0.32847 0.73037 0.37232
Nb* 0.98975 0.73232 0.58856	Nb 0.50411 0.77013 0.08784	Nb* 0.49202 0.77014 0.91697
Nb 1.00183 0.73104 0.41761	Se* 0.65833 0.73085 0.54304	Se 0.83501 0.77050 0.04250
Se* 0.65401 0.73077 0.63498	Se 0.83424 0.80300 0.46217	Se* 0.65699 0.84164 0.96200
Se 0.83282 0.77381 0.13465	Se* 0.65399 0.84136 0.86943	Se 0.83497 0.80012 0.36953
Nb* 0.48737 0.94522 0.58746	Nb 0.00033 0.98476 0.08710	Nb* -0.01217 0.98509 0.91609
Nb 0.50220 0.94599 0.41552	Se* 0.15695 0.94575 0.54181	Se 0.33642 0.98515 0.04227
Se* 0.15535 0.91358 0.96160	Se 0.33571 0.98510 0.13223	Se* 0.15378 0.94626 0.63439
Se 0.33453 0.87475 0.46113	Se* 0.16203 0.91420 0.87105	Se 0.33567 0.87394 0.37058
Nb* 0.98867 0.87498 0.58721	Nb 0.50501 0.91327 0.08737	Nb* 0.48888 0.91245 0.91666
Nb 0.99996 0.87316 0.41612	Se* 0.65530 0.87365 0.54224	Se 0.83542 0.91359 0.04181
Se* 0.66179 0.87286 0.63311	Se 0.83374 0.94489 0.46106	Se* 0.65643 0.98445 0.96134
Se 0.83733 0.91317 0.13442	Se* 0.65975 0.98134 0.86944	Se 0.83806 0.94398 0.36925
La* 0.40302 -0.10447 0.70021	La -0.41165 0.10574 0.19998	Se* -0.09285 -0.10439 0.71987
Se 0.08454 0.10575 0.21978	La* -0.10055 -0.10332 0.80416	La 0.09165 0.10506 0.30394
Se* 0.40581 -0.10363 0.78428	Se -0.41422 0.10534 0.28404	La* -0.06644 0.02060 0.69856
La 0.05862 -0.01919 0.19856	Se* 0.42316 0.02112 0.71899	Se -0.43077 -0.01966 0.21904
La* 0.41729 0.02216 0.80323	La -0.42388 -0.02022 0.30314	Se* -0.08373 0.02057 0.78327
Se 0.07681 -0.01905 0.28322	La* 0.39812 0.14657 0.69919	La -0.43910 0.35391 0.20000
Se* -0.09349 0.14617 0.71950	Se 0.07140 0.35543 0.22031	La* -0.07096 0.14439 0.80389
La 0.08968 0.35595 0.30464	Se* 0.41904 0.14610 0.78363	Se -0.41699 0.35582 0.28458
La* -0.08020 0.27220 0.70081	La 0.07965 0.23106 0.20071	Se* 0.41450 0.27071 0.72060
Se -0.42170 0.23004 0.22057	La* 0.39551 0.27092 0.80505	La -0.44241 0.23078 0.30528
Se* -0.09535 0.27120 0.78494	Se 0.06876 0.23065 0.28479	La* 0.42769 0.39439 0.70022
La -0.43574 0.60713 0.20030	Se* -0.07912 0.39634 0.72049	Se 0.07087 0.60507 0.22070
La* -0.06951 0.39772 0.80518	La 0.06145 0.60417 0.30532	Se* 0.42195 0.39591 0.78469
Se -0.43049 0.60601 0.28484	La* -0.10442 0.52093 0.69974	La 0.09647 0.48059 0.19973
Se* 0.40434 0.52098 0.71985	Se -0.41248 0.48066 0.21984	La* 0.41466 0.52052 0.80385
La -0.42411 0.48152 0.30387	Se* -0.08800 0.52141 0.78416	Se 0.07878 0.48037 0.28422
La* 0.43175 0.64760 0.69996	La -0.40600 0.85481 0.19948	Se* -0.07902 0.64603 0.72043
Se 0.08552 0.85532 0.21964	La* -0.09763 0.64582 0.80465	La 0.06247 0.85745 0.30408
Se* 0.40892 0.64584 0.78456	Se -0.42725 0.85568 0.28386	La* -0.08647 0.77038 0.70078
La 0.07111 0.72911 0.20105	Se* 0.41446 0.77136 0.72072	Se -0.42330 0.73075 0.22085
La* 0.43380 0.77090 0.80541	La -0.40383 0.73105 0.30533	Se* -0.07707 0.77103 0.78490
Se 0.08697 0.73062 0.28515		

TABLE B: List of atomic positions expressed in crystalline coordinates, the atoms with *

belong to the slab system (second part).

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