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Experimental and Theoretical Study of Possible Collective Electronic States in Exfoliable Re-Doped NbS₂

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ABSTRACT: Metallic transition-metal dichalcogenides (TMDs) are rich material systems in which the interplay between strong electron–electron and electron–phonon interactions often results in a variety of collective electronic states, such as charge density waves (CDWs) and superconductivity. While most metallic group V TMDs exhibit coexisting superconducting and CDW phases, 2H-NbS₂ stands out with no charge ordering. Further, due to strong interlayer interaction, the preparation of ultrathin samples of 2H-NbS₂ has been challenging, limiting the exploration of presumably rich quantum phenomena in reduced dimensionality. Here, we demonstrate experimentally and theoretically that light substitutional doping of NbS₂ with heavy atoms is an effective approach to modify both interlayer interaction and collective



electronic states in NbS₂. Very low concentrations of Re dopants (<1%) make NbS₂ exfoliable (down to monolayer) while maintaining its 2H crystal structure and superconducting behavior. In addition, first-principles calculations suggest that Re dopants can stabilize some native CDW patterns that are not stable in pristine NbS₂.

KEYWORDS: transition metal dichalcogenides, NbS₂, substitutional doping, interlayer interaction, atomic structure, superconductivity, charge density waves

ransition metal dichalcogenides (TMDs) offer an ideal platform to study a wide range of electronic systems in two dimensions.¹⁻⁹ In particular, the family of superconducting TMDs, in which Cooper pair condensation may coexists with charge density waves (CDWs), is of great interest.^{10,11} Within this group, 2H-NbS₂ is an intriguing system where charge ordering is absent due to strong anharmonic effects that stabilize the lattice and prevent the CDW formation.^{11–13} Recently, the existence of an incommensurate CDW stabilized by atomic impurities (such as vacancies) has been reported in 2H-NbS2.¹⁴ NbS2 has been much less studied in the mono- and few-layer limits when compared to other TMDs due to challenges in sample preparation. Previous attempts to mechanically exfoliate bulk NbS₂ crystals using the scotch tape method to the monolayer limit have not been successful. Owing to the strong interlayer interaction in NbS₂, such methods yield at best flakes several nanometers thick. 15,16 However, we recently showed that strong alloying of NbS2 with ReS2 results in a 50-50 layered semiconductor crystal, Nb_{0.5}Re_{0.5}S₂, that can be exfoliated down to a monolayer.^{17,18}

Here, we study the NbS₂ system in the extremely low dopant concentration regime and demonstrate that light substitutional doping of NbS₂ with heavy Re atoms (Re < 1%) is an effective route for modifying both interlayer interaction and collective electronic states in NbS₂. Lightly Re-doped NbS₂ (hereafter referred to as Re-NbS₂) can be easily exfoliated using the common scotch tape method, much like pure ReS₂ or other semiconducting TMDs (MoS₂, WSe₂) (see Figure S1). Aberration-corrected annular dark-field scanning transmission electron microscope (ADF-STEM) imaging combined with STEM image simulation reveals the detailed atomic structure and stacking order of Re-NbS₂. Similar superconducting behavior, as in pure NbS₂, is experimentally observed in Re-

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Figure 1. Exfoliable Re-doped NbS₂. Optical images of (a) NbS₂ and (b) Re-NbS₂ crystals exfoliated using the same approach (*i.e.*, exfoliating onto PDMS stamps). On the basis of the optical contrast, mono- and few-layer crystals can be seen in the Re-doped NbS₂ sample while the exfoliated NbS₂ flake seems to be tens of nanometers thick. (c) Atomic-resolution ADF-STEM image of Re-NbS₂ showing both bilayer and trilayer regions with the corresponding FFT (inset). (d) Higher magnification ADF-STEM image of the bilayer Re-NbS₂ crystal and (e) its corresponding line scan intensity profile, showing the presence of a Re atom in the lattice. (f) Computed interlayer energy for Nb_{1-x}Re_xS₂ (0 < x < 1) in the 1H (violet) and 1T' (distorted 1T) (navy) crystal structures, using the trivial stacking sequence. The vertical dashed line denotes the phase transition between the 1H and 1T' phases on the basis of their total energies in the monolayer. For each composition, all low-energy configurations are included as separate data points. (g) Calculated interlayer energy for NbS₂ and Nb_{0.5}Re_{0.5}S₂ in their stable phase, as well as 2H–Nb_{15/16}Re_{1/16}S₂, which approximates the synthesized Re-NbS₂ crystal.

 NbS_2 . In addition, first-principal calculations suggest that Re dopants may stabilize CDW distortions in NbS_2 that are otherwise not observed in the pristine crystal.

RESULTS AND DISCUSSION

We synthesized pure NbS₂ and lightly Re-doped NbS₂ using chemical vapor transport. Using the scotch tape method, we attempted to exfoliate the crystals; the results are presented in Figure 1a,b. Consistent with previous studies, ^{15,16} we were able to cleave NbS₂ to thicknesses of several nanometers, but no thinner (Figure 1a). In sharp contrast, we readily cleaved Re-NbS₂ to few-, bi-, or monolayer form (Figure 1b and Figures S1b and S2).

Since NbS₂ crystals have been reported to be air sensitive,^{16,19} we exfoliated and transferred Re-NbS₂ samples for electron microscopy and transport studies in a glovebox. Figure S2 shows an optical microscope image of a bilayer Re-NbS₂ crystal transferred onto a transmission electron microscope (TEM) grid. To identify the number of layers (*i.e.*, thickness), we used a focused electron beam to remove atoms layer-by-layer and create a hole in the crystal. Figure S3 shows a sequence of ADF-STEM images taken during the removal process, which clearly confirms this suspended Re-NbS₂ sample to be a bilayer crystal. Figure 1c shows an aberrationcorrected ADF-STEM image of the bilayer Re-NbS₂ crystal. The fast Fourier transform of the ADF-STEM image in Figure 1c (inset) reveals the hexagonal symmetry of the lattice. As observed in the ADF-STEM image, some of the lattice sites for metal atomic columns have a higher intensity. Owing to the Z-contrast mechanism, the brighter spots in the ADF-STEM image correspond to the atomic columns with heavier atoms (*i.e.*, Re in this case). This can be seen in the higher magnification ADF-STEM image of the bilayer Re-NbS₂ crystal presented in Figure 1d. The corresponding line scan intensity profile (Figure 1e) shows a greater intensity for the atom marked by the light blue arrow, suggesting the presence of Re atoms in the lattice of NbS₂. In addition, ADF-STEM images suggest that the concentration of Re dopants in Re-NbS₂ is less than 1%.

The observation that even a low concentration of Re dopants enables the exfoliation of NbS₂ has important implications for further experimental study and applications. To understand how Re dopants can change the interlayer interaction in NbS₂, we turned to first-principles calculations. We used a semiempirical van der Waals correction based on two-body and three-body interactions (DFT-D3),²⁰ which leads to more accurate predictions than the more common DFT-D2 van der Waals correction. In our previous study of the Nb_{0.5}Re_{0.5}S₂ alloy, we theoretically investigated intermediate compositions of Nb_{1-x}Re_xS₂ in their monolayer form, where *x* is between 0 and 1 and changes with a step size of 1/16.¹⁷



Figure 2. Atomic structure, stacking sequence, and phase of Re-NbS₂. (a) Top-view and side-view atomic models of bilayer NbS₂ in the 2H1 phase. (b) Atomic-resolution ADF-STEM image of the exfoliated Re-NbS₂ crystal (bilayer) and (c) the simulated STEM image for bilayer NbS₂ in the 2H1 crystal structure. (d) Line scan intensity profile comparison of the experimental image of bilayer Re-NbS₂ (orange) and simulated STEM images of bilayer 2H-NbS₂ (blue) along the dashed boxes. (e) ADF-STEM image of a trilayer Re-NbS₂ crystal and (f) the simulated STEM image for trilayer NbS₂ in the 2H1 phase. (g) Line scan intensity profile comparison of the experimental (orange) and simulated (blue) STEM images along armchair directions indicated by the dashed boxes.

Here, we extended that study to many-layer (*i.e.*, bulk) properties in order to better understand exfoliation receptivity.

A few points are worth mentioning. First, since pristine NbS₂ and ReS2 adopt the 1H and 1T' (distorted 1T) crystal structures in the monolayer form, respectively, we investigated both of these structures for all compositions. Second, for most compositions, multiple doping configurations are possible on the basis of the positions of the dopants in the lattice. Therefore, we theoretically investigated all likely configurations and eliminated those that did not lie within 0.5 eV (per 4×4 cell) of the ground state configuration for each composition. Third, we must consider different stacking sequences. Pristine NbS₂ has been observed in a 2H-type stacking^{14,21,22} that is named 2H1 in Figure S4. As will be shown later, 2H1 is also the stacking type we observed for Re-NbS₂. On the contrary, $Nb_{0.5}Re_{0.5}S_2$ has been reported to occur in a different 2H-type stacking^{17,18} (named 2H0 in Figure S4). For ReS₂, no specific stacking sequence has been observed because of the lower crystal symmetry of the monolayer and the layers are able to slide almost entirely freely,²³ which also agrees with our calculations. Therefore, in order to reduce the computational cost, we considered the trivial stacking sequence where the 1layer calculation cell simply repeats along the out-of-plane direction, resulting in 1H and 1T' stackings.

In Figure 1f, we show how the interlayer energy, defined as the difference between the energy of a layer in bulk and the energy of an isolated layer, changes as a function of composition. The absolute value of the interlayer energy corresponds to the energy required to separate a layer from the bulk. We also demonstrate the optimized interlayer distance for these configurations versus composition in Figure S5. Multiple data points for a given composition correspond to multiple dopant configurations within 0.5 eV (per 4 × 4 cell) of the lowest-energy configuration. For the monolayer Nb_{1-x}Re_xS₂, we recently demonstrated that the 1H phase is more stable when the Re concentration is less than 68% and the 1T' phase is more stable otherwise.¹⁷ Therefore, a dashed vertical line is printed on the plots to establish this transition point. Best-fit lines are also included and fit the trend fairly well. We found that interlayer energy and distance increase nearly monotonically as the composition changes from NbS₂ toward ReS₂. For simplification, in Figure 1g, we only included the calculated interlayer energies for 2H-NbS2^{15,16} and 2H-Nb_{0.5}Re_{0.5}S₂^{17,18} that have been reported experimentally before, as well as 2H-Nb_{15/16}Re_{1/16}S₂, which approximates the synthesized Re-NbS₂ sample in this study. It is evident that the layers of pristine NbS2 attract each other the most, and as Re is introduced into the lattice, this attraction diminishes, enabling the exfoliation of layers from bulk. When we used a nonlocal van der Waals density functional (optB86),^{24,25} the three values plotted in Figure 1g changed from (-0.223,-0.217,-0.186) to (-0.285,-0.278,-0.236), demonstrating that this trend is robust with respect to the treatment of van der Waals interactions. This finding agrees well with the earlier reports demonstrating the exfoliation of Nb_{0.5}Re_{0.5}S₂ and pure ReS₂ down to a monolayer.^{17,18,23,26}

To check whether these trends are independent of the stacking sequence for Re-NbS₂, we also computed the bulk structures of NbS₂ and Nb_{15/16}Re_{1/16}S₂ in their high-symmetry stacking sequences (Figure S4). Tables S1 and S2 list the calculated total energy of each stacking sequence with respect to 1H, the interlayer energy as defined above, and the interlayer distance, for DFT-D3 and vdW DF (optB86), respectively. It shows that, when Re is introduced into the system, the interlayer energy and distance increase in most stacking sequences and remain the same for the rest.

We also investigated the effect of substitutional Re dopants on the electronic structure of NbS_2 and found that it is minimally affected by ultralow concentrations of Re dopants. Because Re has two more valence electrons than Nb, it acts as



Figure 3. Superconductivity in Re-NbS₂. (a) Optical microscope image of the Re-NbS₂ thin flake device capped with h-BN. (b) Temperature dependence of R_{xx} for the Re-NbS₂ sample with a thickness of ~14 nm (Figure S7) measured at various out-of-plane magnetic fields. The superconducting transition temperature T_c (defined as the position corresponding to 50% of the normal state resistance) is at ~4.8 K. (c) R_{xx} of the same device versus out-of-plane magnetic field measured at different temperatures.

an electron dopant and raises the Fermi energy by 0.04 eV with respect to deep core levels in the case of 1/16 doping. Additionally, as seen in the projected densities-of-state plots for this composition presented in Figure S6, the states around the Re atom do not significantly contribute to the DOS at the Fermi level as opposed to the Nb atoms in the system.

In addition to the often observed 2H phase (here called 2H1), NbS₂ has another stable structure that can crystallize at room temperature: the 3R phase. While the 2H1 phase consists of S-Nb-S sandwich layers in which transition metals are aligned with each other in the out-of-plane direction and the surrounding chalcogens are aligned with the hollow sites of the neighboring layers (Figure 2a), the 3R phase is formed by stacking three monolayers with in-plane translation (Figure S4f). Among the two polytypes, 2H-NbS₂ is superconducting.^{16,27} Here, we combined atomic-resolution imaging with STEM image simulations to unambiguously identify the atomic-scale crystal structure and stacking order of the synthesized Re-NbS₂ crystals. Parts b and c of Figure 2 demonstrate an atomic-resolution ADF-STEM image of a bilayer Re-NbS2 crystal and a simulated STEM image of bilayer NbS₂ in the 2H1 crystal structure, respectively. They show a hexagonal structure with two distinct lattice sites with different intensities. Figure 2d compares the line intensity profile along the dashed boxes in the experimental (Figure 2b) and simulated (Figure 2c) images. Similarly, we imaged a trilayer Re-NbS₂ crystal and compared the atomic column intensity ratios along the dashed box in the experimental ADF-STEM image (Figure 2e) and that of the simulated STEM image of trilayer NbS₂ in the 2H1 phase (Figure 2f) in Figure 2g. The match between the experimental and simulated images for both bilayer and trilayer crystals suggests that the Re-NbS₂ crystal is in the 2H1 phase.

In order to determine if superconductivity, which is observed in NbS₂, persists in Re-NbS₂, we measured using a four-probe method, the temperature-dependent electrical resistivity of Re-NbS₂. Since superconductivity in few-nanometers thick 2H-NbS₂¹⁶ is sensitive to oxidation-induced disorder, we avoided air exposure of our Re-NbS₂ samples. We transferred an exfoliated Re-NbS₂ flake onto a prepatterned device with Cr/Pd bottom contacts in a glovebox and capped the device with a hexagonal boron nitride (h-BN) crystal (Figure 3a). Figure 3b shows temperature-dependent longi-

tudinal resistance (R_{xx}) for a Re-NbS₂ device with a thickness of ~14 nm (Figure 3a and Figure S7) measured at various outof-plane magnetic fields. As evident in Figure 3b, R_{xx} begins to decrease from the normal state resistance below ~6K at zero magnetic field and drops sharply close to zero with $T_c \sim 4.8$ K (midpoint). Under the application of out-of-plane magnetic field *B*, the superconductivity is gradually suppressed and the superconducting transition temperature decreases (Figure 3b). Figure 3c shows the magnetoresistance of the same device measured at different temperatures. The out-of-plane critical magnetic field is estimated to be ~2 T, above which the magnetoresistance saturates to normal state value. These observations clearly confirm that Re-NbS₂ is superconducting with a T_c close to that of the pristine NbS₂ sample with a similar thickness.¹⁶

Since thin flakes of NbS₂ have been reported to be severely degraded after exposure to air,^{16,19} we tested the air-stability of Re-NbS₂ through imaging two bilayer samples, one fabricated in a glovebox and the other prepared in ambient conditions (Figure S8). While we noticed partial degradation of the sample fabricated under ambient conditions (Figure S8a), it appears that doping with Re lessens the degradation rate of NbS₂ in air. For example, the bilayer Re-NbS₂ crystal was still partially crystalline after several hours of exposure to air (Figure S8a), while NbS₂ samples of 3 nm or thinner were found to be fully oxidized and chemically transformed to an amorphous mixture of NbO_x and NbS_x after exposure to air in a similar time frame.¹⁶

To understand the improved oxidation resistance of Re-NbS₂, we computed the adsorption energy of oxygen molecules onto undoped and doped monolayers, since oxygen gas is the main contaminant for NbS₂.²¹ As there are no dangling bonds in these layers, oxygen molecules are physisorbed and not chemisorbed. We found the adsorption energies of O₂ for NbS₂, Nb_{15/16}Re_{1/16}S₂, Nb_{0.5}Re_{0.5}S₂, and ReS₂ to be -0.50, -0.40, -0.12, and -0.11 eV per O₂ molecule, respectively. Here, more negative values indicate a stronger adsorption. We observed that only modest Re doping (6.25%) can reduce the absolute value of the adsorption energy by 20%. This may be the main factor responsible for the enhanced air stability of the doped material. This also agrees with recent studies reporting Nb_{0.5}Re_{0.5}S₂ and ReS₂ to be highly air stable.^{17,18,23}

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We next turned to theoretical examinations of Re doping of NbS₂ on charge ordering. Lattice dynamics calculations in the harmonic approximation indicate that NbS₂ should possess CDW configurations, primarily in 3×3 patterns, which are suppressed by anharmonic effects.^{13,14,22,28,29} On the contrary, the closely related material, NbSe₂ exhibits robust CDW configurations.^{4,12,30–38} This is attributed to the fact that Se is heavier than S, diminishing anharmonicity.²⁸ It is also known that the stability of CDWs in NbSe2 is sensitive to small changes made to the system. For example, computational studies have indicated that Na-intercalation suppresses CDWs, and the adsorptions of Co, Mn, K, and Ga unveil CDW configurations not found in the pristine material.^{39,40} Similarly, experimental studies have shown that strain affects the relative stability of various CDWs.^{41,42} A recent study has also found that impurities in NbS₂ may induce CDW patterns around them, which may be incommensurate with the CDW patterns around other impurities.¹⁴

Here, we computationally studied whether a small quantity of Re dopants can stabilize CDWs in NbS₂. We began by determining to which CDW patterns pristine NbS₂ is susceptible. We first computed the vibrational modes of NbS2 and NbSe2 in the full Brillouin zone using density functional perturbation theory, which results in imaginary frequency modes in the vicinity of the q-point that is twothirds of the way from Γ to M. This agrees with previous studies and leads primarily to 3×3 CDW patterns.^{28,30,31,33–35,37–44} Next, we used the frozen phonon method to identify unstable distortions in the 3×3 supercells in NbS₂ and NbSe₂. We found six such modes and then generated initial configurations by displacing the atoms in the original structure in a way that is proportional to these modes. By multiplying the modes by -1, we generated six additional initial configurations. By fully relaxing the atoms and the cells using stringent convergence parameters (see the Methods section for details), we were able to find six distinct 3×3 CDW patterns for both NbS2 and NbSe2 (Figure S9 and Figure 4b,c). The total energy of each pattern relative to the original structure is also printed on the figure for NbS₂ and given in the caption for NbSe₂ (Figure S9). It is clear that the CDW patterns in NbSe2 are more stable than their counterparts in NbS₂ on the basis of their DFT total energies.

Among the CDW patterns presented in Figure S9, most of them have been recognized in previous studies of NbSe₂. Without revealing their full atomic configurations, star, stripe, and triangle CDWs have been detected experimentally. ^{12,30,32,34,35,37,38,41} Additionally, computational studies have described CDW 1, CDW 2, CDW 5, and CDW 6.^{38,40,43,44} However, as mentioned above, in NbS₂, these configurations are typically suppressed by anharmonic effects and therefore not observed experimentally.

Substituting a small percentage of Nb atoms by Re makes no qualitative change to the crystal structure. However, because the Re–Nb bonds are 2% shorter than the Nb–Nb bonds in the lattice, local distortions around Re dopants are expected to affect the stability of CDW patterns. To investigate this, we first relaxed 6×6 supercells of Re-NbS₂ monolayers with 1 Nb atom substituted by Re (*i.e.*, 1/36 or 2.78% doping). Then, in order to generate a reference structure without CDW patterns, we fixed the lattice constants to the relaxed values and relaxed the atoms from their original undistorted positions, allowing only those in the vicinity of the Re dopant (6 Nb atoms and 12 S atoms) to relax. The resulting configuration (Figure 4d) has



Figure 4. CDW patterns in monolayer NbS₂ with 3 × 3 periodicity and monolayer Nb_{35/36}Re_{1/36}S₂ with 6 × 6 periodicity. NbS₂: (a) Configuration with no CDW pattern, (b) CDW 1 (hexagon) and (c) CDW 2 (star). Nb_{35/36}Re_{1/36}S₂: (d) Configuration in which the distortion caused by the introduction of Re is restricted to its vicinity (6 Nb atoms and 12 S atoms), (e) lowest-energy configuration, (f) CDW 1 (hexagon) and (d) CDW 2 (star). Nb, violet; Re, navy; S, light yellow. Covalent bonds between Nb/Re and S atoms are not shown to emphasize the Nb–Nb and Re–Nb distances, which are represented by gray sticks. For each configuration, its total energy relative to the no-CDW configuration (a for NbS₂ and d for Nb_{35/36}Re_{1/36}S₂) is printed at the bottom right corner, in the units of millielectronvolts per 3 × 3 (27-atom) cell.

a higher total energy than the ground state relaxed configuration (Figure 4e). The energy difference divided by four (to ease the comparison with the values in Figure S9) is 14.9 meV. By allowing the next set of atoms around the Re to relax (12 more S atoms), the energy difference reduces to 14.6 meV. The next set of atoms (6 more Nb atoms) reduces the difference to 14.1 meV. Thus, the presented structure provides a reasonable reference structure for Re-NbS₂ in which CDWs are suppressed.

The configuration presented in Figure 4e shows that a 6×6 pattern, not native to NbS_2 (it relaxes to the 3 \times 3 CDW 2 pattern in Figure S9), can become stable via substitutional doping. To check whether doping can also increase the stability of native CDW patterns, we generated 6×6 supercell structures from the six 3×3 CDW patterns in Figure S9 and replaced 1 in 36 Nb atoms with Re. Most of these structures relaxed to the one in Figure 4e. However, two of the patterns survived in Re-NbS₂: the metastable CDW 1 (hexagon) and CDW 2 (star) patterns (Figure 4f,g). Relative to the structure without a pattern, these configurations have total energies of -4.2 and -2.5 meV (per 3×3 cell), respectively. Compared to -0.4 meV, their relative total energy for pristine NbS₂ (Figure 4b,c), they are significantly stabilized. Re dopants are therefore expected to help stabilize CDWs in Re-NbS2. We demonstrate the dynamical stability of these CDW patterns in Figure S10. The relative total energies of these patterns are comparable to the computed relative total energies of the triangle CDW patterns in NbSe₂ (-1.8, -2.6 meV, cf. Figure S9). These CDW patterns have been experimentally observed up to 33 K in bulk $NbSe_2^{36-38}$ and may be stable up to 145 K in ultrathin $NbSe_2^{.4}$ Since NbS_2 closely resembles $NbSe_2$ in terms of electronic and vibrational structure, it is reasonable to expect the patterns in Figure 4f,g to also be stable up to similar temperatures. We note that, although the structure in Figure 4e

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has the lowest energy in 6×6 supercells, it is not expected to arise in a lower doping concentration where dopants are not ordered in this specific way. However, since the patterns in Figure 4f,g are also native to the pristine NbS₂, they are likely to occur in Re-NbS₂ at regions with a Re dopant at the center. We also note it is unlikely that potential CDW patterns in Re-NbS₂ play a significant role in easing the exfoliation of the crystals, because these patterns only change M–M distances by less than 2% (in our Nb_{15/16}Re_{1/16}S₂ calculations, changing the relative position of the dopants in adjacent layers modify the interaction energy by less than 0.2 meV/MS₂, which is much less than the effect of doping alone, *i.e.*, 6 meV/MS₂).

CONCLUSIONS

In summary, we have demonstrated a promising avenue for tuning interlayer interaction and electronic ordering in NbS2 through light substitutional doping with heavy atoms. We showed that Re-NbS₂ (Re < 1%) can be easily exfoliated down to mono- and few-layer crystals using the common mechanical exfoliation method. Atomic-resolution microscopy verified the presence of Re dopants in the lattice and the 2H stacking of the synthesized Re-NbS₂ crystals. Temperature-dependent electronic transport measurements indicated a superconducting T_c of ~4.8 K for 2H Re-NbS₂. Theoretical calculations suggested that Re dopant atoms may induce CDW patterns that are otherwise not observed in pristine NbS2. This report represents an effective approach for isolation of mono- and few-layer metallic TMDs with strong interlayer interactions, enabling exploration of rich quantum phenomena in these systems. It also motivates further experimental studies of CDW phases around heavy dopant atoms.

METHODS

Growth of Re-Doped NbS₂ Crystals. Bulk crystals of the rhenium-doped NbS₂ were grown using chemical vapor transport, in a manner similar to our previous reports on the ReS₂–NbS₂ alloy system.^{17,18} Powdered rhenium (Aldrich, 99.995%), niobium (Alfa Aesar, 99.8%), and sulfur (Alfa Aesar, 99.5%) were mixed and sealed into a quartz tube (L = 20 cm, d = 1 cm) under high vacuum (10^{-6} Torr) along with 80 mg of iodine (Alfa Aesar, 99.5%), which acted as a transport agent. The sealed tube was held in temperature gradient ($T_{\text{Hot}} = 960$ °C, $T_{\text{Cold}} = 930$ °C), for 21 days, before cooling naturally. The resulting material was small (<1 mm), silvery platelets. The bulk crystals were stored under a vacuum.

Scanning Transmission Electron Microscopy (STEM) Characterization. Atomic-resolution STEM imaging was performed using an aberration-corrected FEI Titan3 (60–300) operated at 80 kV. ADF-STEM images were acquired using a camera length of 115 mm and a beam current of approximately 50 pA.

STEM Image Simulation. We used MacTempas software for STEM image simulations. Parameters similar to the experiments (*i.e.*, a probe semiangle of 28.9 mrad, 0.05 Å/pixel sampling, and 16 frozen phonon calculations) were used for each simulation.

Device Fabrication and Transport Measurements. We fabricated a four-terminal device using an ultrathin flake of Re-NbS₂ obtained by mechanical exfoliation of the grown bulk crystal. The crystal was exfoliated onto a polydimethylsiloxane (PDMS) film, and the desired flake was identified under an optical microscope by optical contrast. It was then transferred onto prepatterned Cr/Pd (5 nm/20 nm) electrodes on a SiO₂/Si substrate in a glovebox and capped with h-BN. All transport measurements were performed using a Quantum Design Physical Property Measurement System in a high-vacuum mode with external Stanford Research Systems SR830 lock-in amplifiers.

Theoretical Calculations. We computed atomic and electronic structures using density functional theory (DFT) in the Perdew-

Burke-Ernzerhof generalized gradient approximation (PBE GGA),⁴⁵ using the QUANTUM ESPRESSO software package.⁴⁶ We employed norm-conserving pseudopotentials with a 80 Ry plane-wave energy cutoff.47 van der Waals interactions were included using the semiemprical DFT-D3 method²⁰ and repeated with the nonlocal van der Waals density functional (optB86) for multilayer calculations.^{24,25} In the case of 1×1 unit-cell calculations, we used a 12 × 12 Monkhorst-Pack k-point mesh to sample the Brillouin zone and adjusted the k-point mesh in the supercell cases.⁴⁸ In twodimensional calculations, periodic copies of the layers were separated by a distance of ~16 Å. Coordinates of all the atoms were relaxed until the forces are less than 10^{-4} Ry/ α_0 in all three Cartesian directions (α_0 : Bohr radius). Also in two-dimensional calculations, a self-consistent dipole correction was applied to prevent spurious electrostatic interactions between periodic copies.49 For chargedensity-wave (CDW) calculations, this cutoff was reduced to the more stringent value of 10^{-5} Ry/ α_0 . We determined the vibrational modes in the full Brillouin zone in the harmonic approximation using density functional perturbation theory (DFPT) with a 6×6 q-point mesh.^{50,51} Further investigation of vibrational modes in supercells of interest was conducted using frozen phonon method with the help of the PHONOPY software package.5

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c07526.

Figures of optical images, ADF-STEM images, highsymmetry stacking sequences, computed interlayer distance, densities-of-states, AFM image, CDW patterns, and dynamical stability of the CDW configurations and tables of energetics of NbS₂ and Nb_{15/16}Re_{1/16}S₂ stacking sequences (PDF)

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Author Contributions

A.A. and A.Z. conceived of the idea. J.D.C. and E.C.G. synthesized the bulk crystals. A.A., X.Y., and K.L. did the sample preparation and device fabrication. A.A. performed STEM imaging and simulations. A.A., K.L., and W.S. carried out the transport measurements. M.D. performed density functional calculations and the theoretical analysis. A.Z. and M.L.C supervised the project. All authors discussed the data presented in the paper.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699– 712.

(2) Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O. V.; Kis, A. 2D Transition Metal Dichalcogenides. *Nat. Rev. Mater.* 2017, *2*, 17033.

(3) Azizi, A.; Eichfeld, S.; Geschwind, G.; Zhang, K.; Jiang, B.; Mukherjee, D.; Hossain, L.; Piasecki, A. F.; Kabius, B.; Robinson, J. A.; Alem, N. Freestanding van der Waals Heterostructures of Graphene and Transition Metal Dichalcogenides. *ACS Nano* **2015**, *9*, 4882–4890.

(4) Xi, X.; Zhao, L.; Wang, Z.; Berger, H.; Forró, L.; Shan, J.; Mak, K. F. Strongly Enhanced Charge-Density-Wave Order in Monolayer NbSe₂. *Nat. Nanotechnol.* **2015**, *10*, 765–769.

(5) Azizi, A.; Wang, Y.; Lin, Z.; Wang, K.; Elias, A. L.; Terrones, M.; Crespi, V. H.; Alem, N. Spontaneous Formation of Atomically Thin Stripes in Transition Metal Dichalcogenide Monolayers. *Nano Lett.* **2016**, *16*, 6982–6987.

(6) Sipos, B.; Kusmartseva, A. F.; Akrap, A.; Berger, H.; Forró, L.; Tutiš, E. From Mott State to Superconductivity in 1T-TaS₂. *Nat. Mater.* **2008**, 7, 960–965.

(7) Azizi, A.; Antonius, G.; Regan, E.; Eskandari, R.; Kahn, S.; Wang, F.; Louie, S. G.; Zettl, A. Layer-Dependent Electronic Structure of Atomically Resolved Two-Dimensional Gallium Selenide Telluride. *Nano Lett.* **2019**, *19*, 1782–1787.

(8) Fatemi, V.; Wu, S.; Cao, Y.; Bretheau, L.; Gibson, Q. D.; Watanabe, K.; Taniguchi, T.; Cava, R. J.; Jarillo-Herrero, P. Electrically Tunable Low-Density Superconductivity in a Monolayer Topological Insulator. *Science (Washington, DC, U. S.)* **2018**, *362*, 926–929.

(9) Sajadi, E.; Palomaki, T.; Fei, Z.; Zhao, W.; Bement, P.; Olsen, C.; Luescher, S.; Xu, X.; Folk, J. A.; Cobden, D. H. Gate-Induced Superconductivity in a Monolayer Topological Insulator. *Science* (*Washington, DC, U. S.*) **2018**, 362, 922–925.

(10) Klemm, R. A. Pristine and Intercalated Transition Metal Dichalcogenide Superconductors. *Phys. C* 2015, 514, 86–94.

(11) Naito, M.; Tanaka, S. Electrical Transport Properties in 2H-NbS₂, -NbSe₂, -TaS₂ and -TaSe₂. J. Phys. Soc. Jpn. **1982**, 51, 219–227.
(12) Guillamón, I.; Suderow, H.; Vieira, S.; Cario, L.; Diener, P.; Rodière, P. Superconducting Density of States and Vortex Cores of

2H-NbS₂. *Phys. Rev. Lett.* **2008**, *101*, 166407. (13) Leroux, M.; Le Tacon, M.; Calandra, M.; Cario, L.; Méasson, M.-A.; Diener, P.; Borrissenko, E.; Bosak, A.; Rodière, P. Anharmonic Suppression of Charge Density Waves in 2H-NbS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 155125.

(14) Wen, C.; Xie, Y.; Wu, Y.; Shen, S.; Kong, P.; Lian, H.; Li, J.; Xing, H.; Yan, S. Impurity-Pinned Incommensurate Charge Density Wave and Local Phonon Excitations in 2H-NbS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2020**, *101*, 241404.

(15) Huang, Y. H.; Peng, C. C.; Chen, R. S.; Huang, Y. S.; Ho, C. H. Transport Properties in Semiconducting NbS₂ Nanoflakes. *Appl. Phys. Lett.* **2014**, *105*, 093106.

(16) Yan, R.; Khalsa, G.; Schaefer, B. T.; Jarjour, A.; Rouvimov, S.; Nowack, K. C.; Xing, H. G.; Jena, D. Thickness Dependence of Superconductivity in Ultrathin NbS₂. *Appl. Phys. Express* **2019**, *12*, 023008.

(17) Azizi, A.; Dogan, M.; Cain, J. D.; Eskandari, R.; Yu, X.; Glazer, E. C.; Cohen, M. L.; Zettl, A. Frustration and Atomic Ordering in a Monolayer Semiconductor Alloy. *Phys. Rev. Lett.* **2020**, *124*, 096101.

(18) Azizi, A.; Dogan, M.; Long, H.; Cain, J. D.; Lee, K.; Eskandari, R.; Varieschi, A.; Glazer, E. C.; Cohen, M. L.; Zettl, A. High-Performance Atomically-Thin Room-Temperature NO₂ Sensor. *Nano Lett.* **2020**, *20*, 6120–6127.

(19) Li, Z.; Yang, W.; Losovyj, Y.; Chen, J.; Xu, E.; Liu, H.; Werbianskyj, M.; Fertig, H. A.; Ye, X.; Zhang, S. Large-Size Niobium Disulfide Nanoflakes Down to Bilayers Grown by Sulfurization. *Nano Res.* **2018**, *11*, 5978–5988. (20) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(21) Wang, X.; Lin, J.; Zhu, Y.; Luo, C.; Suenaga, K.; Cai, C.; Xie, L. Chemical Vapor Deposition of Trigonal Prismatic NbS₂ Monolayers and 3R-Polytype Few-Layers. *Nanoscale* **2017**, *9*, 16607–16611.

(22) Leroux, M.; Cario, L.; Bosak, A.; Rodière, P. Traces of Charge Density Waves in NbS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *97*, 195140.

(23) Tongay, S.; Sahin, H.; Ko, C.; Luce, A.; Fan, W.; Liu, K.; Zhou, J.; Huang, Y.-S.; Ho, C.-H.; Yan, J.; Ogletree, D. F.; Aloni, S.; Ji, J.; Li, S.; Li, J.; Peeters, F. M.; Wu, J. Monolayer Behaviour in Bulk ReS₂ Due to Electronic and Vibrational Decoupling. *Nat. Commun.* **2014**, *5*, 3252.

(24) Thonhauser, T.; Cooper, V. R.; Li, S.; Puzder, A.; Hyldgaard, P.; Langreth, D. C. van der Waals Density Functional: Self-Consistent Potential and the Nature of the van der Waals Bond. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 125112.

(25) Klimeš, J.; Bowler, D. R.; Michaelides, A. van der Waals Density Functionals Applied to Solids. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, 83, 195131.

(26) Cui, Q.; He, J.; Bellus, M. Z.; Mirzokarimov, M.; Hofmann, T.; Chiu, H.-Y.; Antonik, M.; He, D.; Wang, Y.; Zhao, H. Transient Absorption Measurements on Anisotropic Monolayer ReS₂. *Small* **2015**, *11*, 5565–5571.

(27) Tissen, V. G.; Osorio, M. R.; Brison, J. P.; Nemes, N. M.; García-Hernández, M.; Cario, L.; Rodière, P.; Vieira, S.; Suderow, H. Pressure Dependence of Superconducting Critical Temperature and Upper Critical Field of 2H-NbS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 134502.

(28) Bianco, R.; Errea, I.; Monacelli, L.; Calandra, M.; Mauri, F. Quantum Enhancement of Charge Density Wave in NbS₂ in the Two-Dimensional Limit. *Nano Lett.* **2019**, *19*, 3098–3103.

(29) Heil, C.; Poncé, S.; Lambert, H.; Schlipf, M.; Margine, E. R.; Giustino, F. Origin of Superconductivity and Latent Charge Density Wave in NbS₂. *Phys. Rev. Lett.* **2017**, *119*, 087003.

(30) Pásztor, Á.; Scarfato, A.; Spera, M.; Barreteau, C.; Giannini, E.; Renner, C. Holographic Imaging of the Complex Charge Density Wave Order Parameter. *Phys. Rev. Res.* **2019**, *1*, 033114.

(31) Calandra, M.; Mazin, I. I.; Mauri, F. Effect of Dimensionality on the Charge-Density Wave in Few-Layer 2H-NbSe₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *80*, 241108.

(32) Soumyanarayanan, A.; Yee, M. M.; He, Y.; van Wezel, J.; Rahn, D. J.; Rossnagel, K.; Hudson, E. W.; Norman, M. R.; Hoffman, J. E. Quantum Phase Transition from Triangular to Stripe Charge Order in NbSe₂. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 1623–1627.

(33) Malliakas, C. D.; Kanatzidis, M. G. Nb-Nb Interactions Define the Charge Density Wave Structure of 2H-NbSe₂. J. Am. Chem. Soc. **2013**, 135, 1719–1722.

(34) Dai, J.; Calleja, E.; Alldredge, J.; Zhu, X.; Li, L.; Lu, W.; Sun, Y.; Wolf, T.; Berger, H.; McElroy, K. Microscopic Evidence for Strong Periodic Lattice Distortion in Two-Dimensional Charge-Density Wave Systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 165140.

(35) Arguello, C. J.; Chockalingam, S. P.; Rosenthal, E. P.; Zhao, L.; Gutiérrez, C.; Kang, J. H.; Chung, W. C.; Fernandes, R. M.; Jia, S.; Millis, A. J.; Cava, R. J.; Pasupathy, A. N. Visualizing the Charge Density Wave Transition in 2H-NbSe₂ in Real Space. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 235115.

(36) Chatterjee, U.; Zhao, J.; Iavarone, M.; Di Capua, R.; Castellan, J. P.; Karapetrov, G.; Malliakas, C. D.; Kanatzidis, M. G.; Claus, H.; Ruff, J. P. C.; Weber, F.; van Wezel, J.; Campuzano, J. C.; Osborn, R.; Randeria, M.; Trivedi, N.; Norman, M. R.; Rosenkranz, S. Emergence of Coherence in the Charge-Density Wave State of 2H-NbSe₂. *Nat. Commun.* **2015**, *6*, 1–7.

(37) Ugeda, M. M.; Bradley, A. J.; Zhang, Y.; Onishi, S.; Chen, Y.; Ruan, W.; Ojeda-Aristizabal, C.; Ryu, H.; Edmonds, M. T.; Tsai, H. Z.; Riss, A.; Mo, S.-K.; Lee, D.; Zettl, A.; Hussain, Z.; Shen, Z.-X.; Crommie, M. F. Characterization of Collective Ground States in Single-Layer NbSe₂. *Nat. Phys.* **2016**, *12*, 92–97.

(38) Guster, B.; Rubio-Verdú, C.; Robles, R.; Zaldívar, J.; Dreher, P.; Pruneda, M.; Silva-Guillén, J. A.; Choi, D. J.; Pascual, J. I.; Ugeda, M. M.; Ordejón, P.; Canadell, E. Coexistence of Elastic Modulations in the Charge Density Wave State of 2H-NbSe₂. *Nano Lett.* **2019**, *19*, 3027–3032.

(39) Lian, C.-S.; Si, C.; Wu, J.; Duan, W. First-Principles Study of Na-Intercalated Bilayer NbSe₂: Suppressed Charge-Density Wave and Strain-Enhanced Superconductivity. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96*, 235426.

(40) Cossu, F.; Moghaddam, A. G.; Kim, K.; Tahini, H. A.; Di Marco, I.; Yeom, H.-W.; Akbari, A. Unveiling Hidden Charge Density Waves in Single-Layer NbSe₂ by Impurities. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, 98, 195419.

(41) Gao, S.; Flicker, F.; Sankar, R.; Zhao, H.; Ren, Z.; Rachmilowitz, B.; Balachandar, S.; Chou, F.; Burch, K. S.; Wang, Z.; van Wezel, J.; Zeljkovic, I. Atomic-Scale Strain Manipulation of a Charge Density Wave. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 6986– 6990.

(42) Cossu, F.; Palotás, K.; Sarkar, S.; Di Marco, I.; Akbari, A. Strain-Induced Stripe Phase in Charge-Ordered Single Layer NbSe₂. *NPG Asia Mater.* **2020**, *12*, 24.

(43) Zheng, F.; Zhou, Z.; Liu, X.; Feng, J. First-Principles Study of Charge and Magnetic Ordering in Monolayer NbSe₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *97*, 081101.

(44) Lian, C. S.; Si, C.; Duan, W. Unveiling Charge-Density Wave, Superconductivity, and Their Competitive Nature in Two-Dimensional NbSe₂. *Nano Lett.* **2018**, *18*, 2924–2929.

(45) Perdew, J. P.; Zunger, A. Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1981**, 23, 5048–5079.

(46) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. J. Phys.: Condens. Matter 2009, 21, 395502.

(47) Hamann, D. R. Optimized Norm-Conserving Vanderbilt Pseudopotentials. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2013, 88, 085117.

(48) Cohen, M. L.; Schlüter, M.; Chelikowsky, J. R.; Louie, S. G. Self-Consistent Pseudopotential Method for Localized Configurations: Molecules. *Phys. Rev. B* 1975, *12*, 5575–5579.

(49) Bengtsson, L. Dipole Correction for Surface Supercell Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, 59, 12301–12304.

(50) Gonze, X.; Lee, C. Dynamical Matrices, Born Effective Charges, Dielectric Permittivity Tensors, and Interatomic Force Constants from Density-Functional Perturbation Theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, 55, 10355–10368.

(51) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and Related Crystal Properties from Density-Functional Perturbation Theory. *Rev. Mod. Phys.* **2001**, *73*, 515–562.

(52) Togo, A.; Tanaka, I. First Principles Phonon Calculations in Materials Science. *Scr. Mater.* **2015**, *108*, 1–5.