Anisotropic point defects in rhenium diselenide monolayers

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Highlights
Low-symmetrical ReSe$_2$ provides much more degrees of freedom for defect engineering
Isoelectronic substitution of chalcogen atoms contribute to defects recovery in ReSe$_2$
Antisite defects introduce local magnetic field in ReSe$_2$

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Anisotropic point defects in rhenium diselenide monolayers

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SUMMARY
Point defects in 1T′′ anisotropic ReSe2 offer many possibilities for defect engineering, which could endow this two-dimensional semiconductor with new functionalities, but have so far received limited attention. Here, we systematically investigate a full spectrum of point defects in ReSe2, including vacancies (VSe1-4), isoelectronic substitutions (OSe1-4 and SSe1-4), and antisite defects (SeRe1-2 and ReSe1-4), by atomic-scale electron microscopy imaging and density functional theory (DFT) calculations. Statistical counting reveals a diverse density of various point defects, which are further elaborated by the formation energy calculations. Se vacancy dynamics was unraveled by in-situ electron beam irradiation. DFT calculations reveal that vacancies at Se sites notably introduce in-gap states, which are largely quenched upon isoelectronic substitutions (O and S), whereas antisite defects introduce localized magnetic moments. These results provide atomic-scale insight of atomic defects in 1T′′-ReSe2, paving the way for tuning the electronic structure of anisotropic ReSe2 via defect engineering.

INTRODUCTION
Transition metal dichalcogenides (TMDs) are a focus of current research owing to their rich physics and great potential for novel technological applications(Kang et al., 2015; Keum et al., 2015; Manzeli et al., 2017; Novoselov et al., 2016; Wang et al., 2012; Yu et al., 2015). Point defects, prevailing in TMDs, influence their physical properties and thereby impact the performance of TMD-based devices. For example, sulfur vacancies in monolayer MoS2 are reported to introduce localized states in the energy gap (Hong et al., 2015; Zhou et al., 2013). The concentration of sulfur vacancies is predicted to adjust the semiconductor characteristics of MoS2 to vary between n-type and p-type (Yang et al., 2019a). Sulfur vacancies are also observed to drastically enhance the photoluminescence intensity in monolayer MoS2 (Tongay et al., 2013). On the other hand, point defects can be intentionally introduced into TMD films to trigger new properties. In particular, the hydrogen evolution reaction performance of MoS2 can be finely tuned by varying the concentration of sulfur vacancies (Wang et al., 2020; Yang et al., 2019b). Furthermore, Mo vacancies in MoS2 are predicted to exhibit ferromagnetism (Koos et al., 2019). However, hexagonal TMDs with three-fold symmetry have only one type of nonequivalent chalcogen and metal sites, which limit the degree of freedom to regulate their properties via defect engineering. Additionally, previous reports about the oxidation of TMDs (Kotsakis et al., 2019; Mirabelli et al., 2016; Sar et al., 2019) suggest the possible inclusion of oxygen impurities in the TMDs lattice. Unfortunately, it is rather challenging to reliably identify the presence of oxygen atoms in TMDs with atomic precision.

Unlike 1H- or 1T-phase TMDs, which largely exhibit isotropic properties, rhenium-based TMDs (denoted as ReX2, X = S, Se) with a T′′-phase structure show distinctive in-plane anisotropic properties. The T′′-phase structure of ReX2 can be regarded as a distorted T phase where four Re atoms undergo a 2×2 reconstruction, resulting in a cluster with a diamond-like shape (denoted as 4Re). These 4Re clusters are interconnected with each other along the c axis and form an overall triclinic structure (Lamfers et al., 1996; Whangbo and Canadell, 1992). This unique 2×2 superstructure contains four nonequivalent X sites and two nonequivalent Re sites in one unit cell, which are denoted as Xm (m = 1, 2, 3, 4) and Ren (n = 1, 2) exemplified by the ReSe2 model shown in Figure 1D, providing more opportunities to finely tune the electronic structure of ReX2. Owing to the Peierls distortion from the 1-T phase, for instance, the ReX2 gives rise to a much weaker interlayer coupling. As a result, the electronic and optical properties of ReX2 are largely independent of the layer thickness (Tongay et al., 2014). The anisotropic optical absorption edge of ReSe2 single layer isScience 24, 103456, December 17, 2021 © 2021 The Author(s). This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
crystals are observed when linearly polarized light is perpendicularly incident to the base plane of materials (Ho et al., 1998). Although some reports have already studied point defects in ReSe2 and ReS2 (Horzum et al., 2014; Lin et al., 2015), systematic understanding of all types of point defects and the corresponding property modulations are still lacking.

In this work, by combining aberration-corrected scanning transmission electron microscopy (STEM) imaging and DFT calculations, we systematically investigate a full spectrum of point defects in monolayer ReSe2. We observe both O and S substitutions at four nonequivalent Se sites (OSei, i = 1, 2, 3, 4; SSej, j = 1, 2, 3, 4), where vacancies (VSek, k = 1, 2, 3, 4) should have previously formed. In addition, we analyze antisite defects at two types of Re sites (SeRep, p = 1, 2) and antisite defects at four different Se sites (ReSeq, q = 1, 2, 3, 4). Statistical counting results reveal that O and S atoms are prone to occupy Se1 sites, whereas vacancies tend to occur at Se4 sites, in line with the DFT calculations. Phase imaging via four-dimensional scanning transmission electron microscopy (4D-STEM), showing superior advantages in identifying light elements, is applied to unambiguously confirm the presence of isoelectronic substitutions of S and O atoms at Se sites. The measured concentrations of antisite defects, namely 0.07/nm² for SSe2 and 0.007/nm² for ReSe3, are in accordance with the trend of DFT-calculated formation energies, that is, SSe2 is lower in formation energy than ReSe3. The influence of these native point defects and several impurities on the electronic structure of monolayer ReSe2 is further explored by DFT calculations. We find that vacancies in Se sites notably introduce in-gap states, whereas the in-gap states are largely quenched upon isoelectronic substitutions (O and S). Therefore, the electronic structure modifications induced by Se vacancies are healed by isoelectronic substitutional impurities, and the band structure reveals indiscernible variations compared to the pristine ReSe2 monolayer. It is also

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**Figure 1. The morphology and crystal structure of monolayer 1T-ReSe2**

(A) Optical image of a typical monolayer ReSe2 grown by CVD on SiO2 substrate.

(B) Atomic-resolution HAADF image of monolayer ReSe2.

(C) Top view and side view along the b axis of the crystal model of monolayer ReSe2. The gray and orange balls represent Re and Se atoms, respectively. The green-filled parallelogram covers the unit cell of monolayer ReSe2.

(D) Enlarged atomic model of the unit cell marked in (C) showing the two characteristic Re sites and four Se sites. The distances between adjacent Re1 and Re2 in one unit cell are marked (in nm). Scale bars: (A) 5 μm and (B) 1 nm.
noteworthy that antisite defects at Re and Se sites induce local magnetism with values of 3 μB at Re1, Re3, and Re4 sites, and 1 μB for Re2, Se1, and Se2 sites. Charge density maps indicate that the magnetism mainly stems from the Re atoms, that is, from ReSe or from Re atoms in the vicinity of SeRe.

RESULTS AND DISCUSSION
Morphology and crystal structure of monolayer 1T-ReSe2

Unlike conventional TMD materials in the 1-H and 1-T phases, which exhibit triangular or hexagonal morphology (Zhou et al., 2018), ReSe2 in the 1-T phase shows a unique petaloid-like shape (Chen et al., 2020), as displayed in Figure 1A. Figure 1B shows an experimental STEM high-angle annular dark-field (HAADF) image of monolayer ReSe2. Plane-view and side-view atomic models are provided in Figure 1C. The unit cell of monolayer ReSe2 possesses lattice constants of |a| = 0.671 nm, |b| = 0.659 nm, and |c| = 0.672 nm (Lamfers et al., 1996). The angle between a[100] and b[010] axes is 118.9°. The lattice spacing between two adjacent 4Re diamonds in the Re-chain is 0.323 nm. The lattice spacing between two Re-chains is 0.379 nm. The Re1–Re2 bond length in the 4Re diamonds is 0.287 nm along the b direction and 0.284 nm along the [110] direction, respectively, as highlighted in Figure 1D. The atomic spacing differences between two adjacent 4Re diamonds from different directions are responsible for the anisotropic structural features of ReSe2. Note that the space volumes where the four nonequivalent Se atoms are located are quite different, as reflected by the surrounding Re1–Re2 distances (see Figure 1D). Specifically, Se sites have space volumes with a descending order of Se4, Se3, Se2, and Se1 (see more details in Figure S1).

Formation energy of point defects in ReSe2

Given the anisotropic structure of monolayer ReSe2, we consider a full spectrum of point defects ranging from vacancies to isoelectronic substitutions, including four types of Se vacancies (VSe1, VSe2, VSe3, and VSe4), O substitution of Se atoms (OSe1, OSe2, OSe3, and OSe4), and S substitution of Se atoms (SSe1, SSe2, SSe3, and SSe4). In addition, antisite defects are considered, i.e., Se substituting Re atoms (SeRe1 and SeRe2) and Re replacing Se atoms (ReSe1, ReSe2, ReSe3, and ReSe4). Because metal vacancies are extremely rare owing to the typical chalcogen-rich chemical vapor deposition (CVD) growth environment for TMD materials (Zhou et al., 2018), Re vacancy sites (VRe1 and VRe2) are not discussed here. It should be stated that in this work, we employ the notation of VSe, OSe, SSe, and ReSe without specifying the exact site number (see all values in Tables S2A and S2B). In contrast, VSe, OSe, SSe, and ReSe all have positive formation energies under both Se-rich and Re-rich conditions. The formation energies discussed below are all based on Se-rich conditions unless specified otherwise.

Next, we calculate the thermodynamic stability of the proposed point defects by DFT, as summarized in Figure 2 (more details in Figure S2). In Figure 2A, each characteristic Se and Re site is marked with unique colors. Overall, as shown in Figure 2B, the formation energies of OSe and SSe are negative (see Table S1 for detailed calculations), possessing values from −1.41 eV (Re-rich, i.e., the chemical potential $\mu_{\text{Se}} = -4.096$ eV) to −0.64 eV (Se-rich, i.e., $\mu_{\text{Se}} = -3.544$ eV) and from −1.322 eV (Re-rich) to −0.567 eV (Se-rich), respectively (see all values in Tables S2A and S2B). In contrast, VSe, OSe, and SSe all have positive formation energies under both Se-rich and Re-rich conditions. The formation energies discussed below are all based on Se-rich conditions unless specified otherwise.

Specifically, the formation energies for vacancies at Se sites ($V_{\text{Se}k}$, $k = 1, 2, 3, 4$) differ by as much as 0.97 eV, with the highest at the Se1 site ($2.94$ eV) and the lowest at the Se4 site ($2.07$ eV) (see more details in Figure S2A and Table S2C). In the case of OSe, the formation energy is smallest for OSe1 ($-0.86$ eV) and largest ($-0.64$ eV) for OSe3, as can be seen in Figure 2B. In contrast, O substituting at Se2 and Se4 sites share similar formation energies ($-0.71$ eV for OSe2, -0.72 eV for OSe4), falling between those of OSe1 and OSe3 (Figure 2C). We propose that these unique site-dependent formation energy difference of O impurities stems from their different local chemical bonding environments at each Se site. The spacing volume between adjacent 4Re along the [110] direction is larger than the interspace within 4Re (see Figures 1D and S1B) so that O atoms with much smaller atomic radius compared with Re and Se atoms would preferentially occupy the Se1 site owing to the reduced bond lengths (0.208 nm). Similarly, a higher formation energy of OSe3 may be attributed to longer bond lengths (0.216 nm) between the O atom and its surrounding Se atoms, leading to OSe3 being relatively less stable. The formation energy trend of substitutional S at Se sites is similar to that of O substitution (Figures 2C and 2D). Nonetheless, the relative tendency of the formation energies for O and S substitution at Se2 and Se4 sites is opposite with minor difference, that is, $S_{\text{Se}2} (-0.65$ eV) slightly lower than $S_{\text{Se}4} (-0.61$ eV). With regard to vacancies at Se sites, reasoning along the same lines explains the lower formation energies for $V_{\text{Se}2}$ and $V_{\text{Se}4}$ owing to the larger space volumes at Se3 and Se4 sites.
The formation energies of antisite defects were also calculated, and they are much higher than those of vacancies or isoelectronic substitutions at Se sites (Figure 2B). In the case of ReSe, ReSe4 (6.1 eV) and ReSe3 (5.8 eV) are energetically more favorable than ReSe2 (6.3 eV) and ReSe1 (6.8 eV) (Figure S2C). As a Re atom has a much larger atomic radius than a Se atom, the available spacing is the key factor that determines the thermodynamic stability of ReSe antisites. Because the space volume at Se3 and Se4 sites is much larger than that at Se1 and Se2 sites (see Figure S1B), Re atoms show a tendency to occupy the Se3 and Se4 positions. Comparatively, SeRe shows a lower formation energy than ReSe (Figure 2B). SeRe1 (2.87 eV) with lower formation energy than SeRe2 (3.29 eV) likewise reflects the nonequivalence of two Re sites.

Statistics of primary point defects in ReSe2

In order to verify the relative formation energy trend of these point defects, we carried out statistical defect counting in a monolayer ReSe2 sample grown by CVD under Se-rich conditions (see STAR Methods for details about the sample growth). A large number of atomic-resolution STEM-HAADF images were acquired for point defect statistical analysis. However, the Z-contrast in STEM-HAADF images, that is, \( I \propto Z^{3.3} \) (Pennycook and Boatner, 1988; Pennycook and Jesson, 1990; Treacy, 2011), results in a situation that possible signal from the light O and S atoms would be easily overwhelmed by the strong signal from the heavy Se and Re atoms. Although STEM medium-angle annular dark-field (MAADF) imaging can slightly enhance the contrast of light elements, it is still difficult to identify O atoms in monolayer ReSe2. Given these conditions, we may consider using electron energy loss (EEL) spectroscopy to discern the light elements, but this is challenging here as well. A good signal-to-noise ratio (SNR) EEL spectrum normally requires a much longer acquiring time (about several hundred milliseconds) than HAADF imaging (about several tens of microseconds per pixel). Hence, before generating a satisfactory atomically resolved EEL spectrum, beam-sensitive ReSe2 monolayers would be severely damaged by the impact of the electron beam. Therefore, we use the sign of “USe” to temporarily denote the Se sites with much lower HAADF contrast and the capital “U” stands for undetermined (i.e., the exact identity to be determined). The second step is to determine the density of each point defect in monolayer ReSe2 by an atom-by-atom site location through the center of mass method (Gong et al., 2014; Krivanek et al., 2010). A demonstration of the process is shown in Figure S3.
Figure 3. Main types of point defects and their densities in monolayer ReSe₂

(A) STEM-HAADF images of four types of Uₜₐ in monolayer ReSe₂. The capital letter U means the exact identity remains to be determined.

(B) Antisite defects with Se substitution in Re sites.

(D) Bar graph showing the densities of different point defects in monolayer ReSe₂.
The electron dose so that only vacancies at chalcogen sites could be generated. Figures 5A–5D show creases from 0.7 sequential images of the vacancies generated by the electron beam. As the electron dose gradually increases, the concentration of the dominant vacancies of about 0.14/nm² (Hong et al., 2015). Furthermore, the concentrations of point defects with dim image contrast vary significantly at the four different Se sites and exhibit a trend similar to that of the relative formation energies of four SSe (see Figure 2C) and four OSe (see Figure 2D, if we neglect the 0.01 eV difference between OSe₄ and OSe₂). More experimental evidence is required in order to identify the USe as SSe or OSe, as will be discussed in the latter section.

The presence of antisite defects at Se and Re sites (Figures 3B and 3C) can be readily verified by the STEM-HAADF images (see Figure S4B). The concentrations of Re₄Se₀ and Se₄Re₀ (see Figure 3D) are site-dependent and match well with the formation energy trends. The total concentration of Se₄Re₀ (0.007/nm²) is one order of magnitude lower than U₄Se₀ and Se₄Re₀.

4D-STEM identification of O and S atoms in ReSe₂

In order to determine the possible presence of O or S atoms at the “U₄Se₀” sites, we conducted 4D-STEM experiments. Via phase imaging reconstruction, 4D-STEM is able to greatly enhance the contrast of light atoms surrounded by heavy atoms. Meanwhile, with the aid of a high-performance camera, 4D-STEM imaging could significantly reduce the data acquisition time down to several milliseconds, which greatly minimizes the damage to the sample. We first carry out 4D-STEM phase image simulations on a monolayer ReSe₂ containing three types of defects, that is, V₄Se₀, O₄Se₀, and S₄Se₀ (Figures 4A and 4B). Compared with STEM-HAADF imaging, the reconstructed phase image using the single-side band (SSB) method (See STAR Methods for more details) enhances the contrast of O or S atoms by three to five times (see Figure S5 and Table S3 for more details), making it possible to differentiate O and S atoms from “U₄Se₀” defects.

The experimental 4D-STEM results are displayed in Figures 4C and 4D. According to the simultaneously acquired HAADF image shown in Figure 4D, two patches (number 1# and 2#) containing defects in Figure 4C are selected for analysis. The intensity line profile analysis shown in Figure 4E suggests that the dim contrast at Se sites in the STEM-HAADF image is due to S (at 1# position) atoms and O (at 2# position) atoms, respectively. These results indicate that via 4D-STEM imaging, S and O atoms can be distinguished even in TMD materials such as ReSe₂.

Generation of Se vacancies under electron beam irradiation

The dynamical evolution of the various defects in ReSe₂ monolayer under electron beam irradiation was also surveyed to examine the reliability of the formation energies for vacancies at Se sites. Because the ReSe₂ monolayer is highly sensitive to electron beam irradiation, the probe current was reduced significantly in order to realize a better control of defect propagation (see STAR Methods for more details). We carefully controlled the electron dose so that only vacancies at chalcogen sites could be generated. Figures 5A–5D show sequential images of the vacancies generated by the electron beam. As the electron dose gradually increases from 0.7 × 10⁶ e⁻·nm⁻² to 2.1 × 10⁶ e⁻·nm⁻², as shown in Figure 5E, the density of total vacancies at each Se site rises subsequently except V₅₄Se₁. The decline of V₅₄Se₁ was probably due to the refilling by mobile Se adatoms. More importantly, the ratio of vacancy concentrations at Se₄ sites (marked with green circles in Figures 5A–5D) over the total vacancies at Se sites becomes larger, from 48% to 66%, as shown in Figure 5F. This trend further corroborates the smallest formation energy of V₅₄Se₁ among four V₅₄Seₙ as displayed.

Figure 3. Continued

(C) Antisite defects with Re substitution in Se sites.

(D) Statistics of major point defects. In (A)–(C), the upper half shows the experimental images of specific point defects while the corresponding structure models are depicted in the lower panels. These point defects, i.e., U₄Se₀, Se₄Re₀, and Re₄Se₀, are marked with green dashed circles in the HAADF images and the corresponding models, respectively. U₄Se₀ point defects are marked with light blue cross signs in the corresponding structure models. The inset histogram in (D) sums the same type of point defects in Se or Re sites. Point defects in Se sites dominate in ReSe₂. The total area size for statistical analysis is about 2500 nm². Scale bars in (A–C): 0.5 nm. Error bars in (D): 0.011/nm² for U₄Se₀, 0.019/nm² for Se₄Re₀, 0.066/nm² for U₄Se₁, 0.061/nm² for U₄Se₂, 0.036/nm² for U₄Se₃, 0.011/nm² for Se₄Re₁, 0.017/nm² for Se₄Re₂, 0.036/nm² for U₄Se₄, 0.011/nm² for Se₄Re₃, and 0.017/nm² for Se₄Re₄.
The disagreement between the concentration ratios of $\text{VSe}_2$ and $\text{VSe}_3$ with their relative formation energies is likely caused by the dynamic effects such as the moving of the vacancies. DFT calculations also show that in general the total energy of the monolayer ReSe$_2$ only increases slightly (less than 0.1 eV/nm$^2$) with the increasing concentration of Se vacancies (see Figure S6), with the exception of $\text{VSe}_4$, where the total energy decreases by 0.28 eV/nm$^2$ when the concentration of $\text{VSe}_4$ increases from 0.16/nm$^2$ to 0.64/nm$^2$. Note that at all $\text{VSe}_n$ concentrations considered in our calculations, the total energy is consistently lower for cases of $\text{VSe}_3$ and $\text{VSe}_4$ than that for $\text{VSe}_1$ and $\text{VSe}_2$ by $\approx 0.3$ eV. In addition, the overall Re-chain structure of the ReSe$_2$ monolayer and the anisotropy remain unchanged at a relatively high concentration of Se vacancies as shown in Figure S7. These results indicate that vacancies at Se$_3$ and Se$_4$ sites are easier to form as compared with those at Se$_1$ and Se$_2$ sites. Our calculations are in line with previous experimental results reported by Lin et al. that Se atoms at Se$_3$ and Se$_4$ sites are preferentially knocked out under high electron dose irradiation (Lin et al., 2015).

Electronic structure of ReSe$_2$ with point defects

Finally, the effects of the observed point defects on the electronic structure of ReSe$_2$ monolayer are studied. We calculated the density of states (DOS) of all types of point defects mentioned above. Figure 6 lists the representative DOS in each type of point defect, that is, the DOS of $\text{VSe}_1$, $\text{SSe}_1$, $\text{OSe}_1$, $\text{SeRe}_1$, and $\text{ReSe}_1$ (see Figures S9 and S10 for all DOS results). As the density of Se vacancies increases, additional defect states near the Fermi level appear (Figure 6B), similar to previous DFT calculations on defect states in monolayer
MoS$_2$ (Yang et al., 2019a). The calculated DOS of ReSe$_2$ with S and O substitutions at Se sites (Figures 6C and 6D) reveals that the density of states near the Fermi level remains almost the same as in the pristine ReSe$_2$ (Figure 6A) after isoelectronic doping. This phenomenon is consistent with the observation by Tang et al. that oxygen dopants in the form of substitution of chalcogen atoms could reduce the bandgap of intrinsic MoS$_2$ without introducing in-gap states and greatly improve its carrier mobility (Tang et al., 2020). In ReSe$_2$, only a small energy barrier of $\sim$84 meV needs to be overcome to allow external O$_2$ molecules to dissociate when a O$_2$ molecule is adsorbed at a Se vacancy, as shown in Figure S8, suggesting that Se vacancies in monolayer ReSe$_2$ facilitate the dissociation of O$_2$ molecules and subsequently are filled by dissociated O atoms. In light of a usual aging process (Gao et al., 2016; Kotsakidis et al., 2019; Sar et al., 2019) and vacancy-induced oxidation (Liu et al., 2015) in TMD materials, we may expect that slight aging of ReSe$_2$ in ambient conditions would not significantly degrade the in-plane anisotropy and the transport properties.

In the case of antisite defects, the DOS is very different from that of vacancies or O(S) substitutions at Se sites. Because of the unpaired electrons, the antisite defects of Re$_{Se}$ and Se$_{Re}$ introduce magnetic moments into the ReSe$_2$ lattice. Specifically, the total magnetic moment of the ground state of one Re atom is $3 \mu_B$ at Re$_{Se1}$, $1 \mu_B$ at Re$_{Se2}$, $3 \mu_B$ at Re$_{Se3}$, and $3 \mu_B$ at Re$_{Se4}$ antisites, respectively. For antisite defects at Re sites, the calculated magnetic moment is $1 \mu_B$ in both Se$_{Re1}$ and Se$_{Re2}$. To further identify the origin of magnetism, the spin-resolved charge density is calculated, and the representative ones are shown in Figures 6G–6J (see Figure S10 for all the six antisite results). Figure 6I (top view) and 6J (side view) show that, in the case of Re$_{Se1}$, the spin-polarized electrons are mainly localized on the Re atom. In the case of Se$_{Re1}$ as shown in Figure 6G (top view) and Figure 6H (side view), the magnetism of Se$_{Re}$ is mainly contributed by the nearby Re atoms. In pristine ReSe$_2$, the conduction band is composed primarily of the Re $d$-orbitals. Owing to the substitutional Se atom in Se$_{Re1}$, the $d$-orbitals split, and subsequently the spin-polarized electrons are localized on the Re atoms nearby. The coordination geometry of the Re is octahedral in Re$_{Se2}$ while tetrahedral in Re$_{Se1}$, Re$_{Se3}$, and Re$_{Se4}$, resulting in the split $e_g$ and $t_{2g}$ orbitals in Re$_{Se1}$, Re$_{Se3}$, and Re$_{Se4}$, and consequently higher magnetic moments than that in Re$_{Se2}$. In light of the magnetic moment differences between antisite defects at Sem ($m = 1, 2, 3, 4$) sites and Rem ($m = 1, 2$) sites, we may envision building an anisotropically controllable solid-state spin qubit system.
utilizing ReSe$_2$ (Tsai et al., 2021). Alteration of local magnetism of these materials may be realized through changing the density of antisite defects in a ReSe$_2$ film by controlling the growth parameters.

**Conclusions**

In summary, we systematically investigate point defects with anisotropic distributions in monolayer 1T"-ReSe$_2$ and their electronic structures through first-principles calculations and STEM imaging. Because of the anisotropic structure of ReSe$_2$, there are four types of nonequivalent Se sites and two types of
nonequivalent Re sites in one unit cell. We find that point defects at Se sites dominate in pristine monolayer ReSe$_2$, followed by antisite defects Se$_{Re}$ and Re$_{Se}$, that is, 0.71/nm$^2$ for point defects at Se sites, 0.07/nm$^2$ for Se$_{Re}$, and 0.007/nm$^2$ for Re$_{Se}$. Isoelectronic substitutions of O and S atoms at Se sites are preferentially formed within the Re-chains, while Se vacancies tend to appear in the channels between Re-chains. DFT calculations reveal that Se vacancies result in in-gap states, whereas isoelectronic substitution of O and S atoms at Se sites hardly change the band structure near the Fermi level. Moreover, antisite defects of Re$_{Se}$ introduce large site-dependent magnetic moments into this system while Se$_{Re}$ antisite defects induce relatively weak magnetic moments independent of the anisotropy. These results show that the anisotropic structure of 1T-ReSe$_2$ offers extra degrees of freedom to finely tune the physical properties via defect engineering. The often-neglected isoelectronic substitution at chalcogen sites provides an alternative approach to recovering the intrinsic properties of defective 2D materials.

Limitations of the study

Oxygen atoms are commonly present in TMD materials especially in the ambient environment. Although 4D-STEM imaging distinguishes the oxygen atoms in ReSe$_2$, statistical defect analysis via high-throughput 4D-STEM experiment remains challenging, especially for electron-beam sensitive 2D materials.

STAR*METHODS

Detailed methods are provided in the online version of this paper and include the following:

- **KEY RESOURCES TABLE**
- **RESOURCE AVAILABILITY**
  - Lead contact
  - Materials availability
  - Date and code availability
- **EXPERIMENTAL MODEL AND SUBJECT DETAILS**
- **METHOD DETAILS**
  - ReSe$_2$ growth and TEM sample preparation
  - Electron microscopy characterization
  - Density functional calculations
- **QUANTIFICATION AND STATISTICAL ANALYSIS**

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at [https://doi.org/10.1016/j.isci.2021.103456](https://doi.org/10.1016/j.isci.2021.103456).

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AUTHOR CONTRIBUTIONS

W. Zhou and S.X. Du conceived and supervised the project. J.D. Zhou and Z. Liu provided the sample. Y. Zhu and X.Y. Chen designed and conducted the STEM experiments. L. Tao conducted the DFT calculations. Y. Zhu, Y.H. Ma, and S.C Ning analyzed the 4D-STEM data. Y. Zhu and L. Tao wrote the paper. X.X. Zhao, M. Bosman, and S.T. Pantelides contributed to the revision of the paper. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Whangbo, M.H., and Canadell, E. (1992). Analogies between the concepts of molecular chemistry and solid-state physics concerning structural instabilities. Electronic origin of the structural modulations in layered transition metal dichalcogenides. J. Am. Chem. Soc. 114, 9587–9600. https://doi.org/10.1021/ja00050a044.

Yang, H., MacLaren, I., Jones, L., Martinez, G.T., Simson, M., Huth, M., Ryll, H., Soltau, H., Sagawa, R., Kondo, Y., et al. (2017). Electron ptychographic phase imaging of light elements in crystalline materials using Wigner distribution deconvolution. Ultramicroscopy 180, 173–179. https://doi.org/10.1016/j.ultramic.2017.02.006.

Yang, J., Kawai, H., Kong, P.Y., and Goh, K.E.J. (2019a). Electrical doping effect of vacancies on monolayer MoS2. J. Phys. Chem. C 123, 2933–2939. https://doi.org/10.1021/acs.jpcc.8b01049.

Yang, J., Wang, Y., Lagos, M.J., Manichev, V., Fullion, R., Song, X., Voiry, D., Chakraborty, S., Zhang, W., Batson, P.E., et al. (2019b). Single atomic vacancy catalysis. ACS Nano 13, 9958–9964. https://doi.org/10.1021/acs.nano.9b05226.

Yu, Y.J., Yang, F.Y., Lu, X.F., Yan, Y.J., Cho, Y.H., Ma, L.G., Niu, X.H., Kim, S., Son, Y.W., Feng, D.L., et al. (2015). Gate-tunable phase transitions in thin flakes of 1T-TaS2. Nat. Nanotechnol. 10, 270–276. https://doi.org/10.1038/nnano.2014.323.

Zhou, J., Lin, J., Huang, X., Zhou, Y., Chen, Y., Xia, J., Wang, H., Xie, Y., Yu, H., Lei, J., et al. (2018). A library of atomically thin metal chalcogenides. Nature 556, 355–361. https://doi.org/10.1038/s41586-018-0008-3.

Zhou, W., Zou, X., Najmaei, S., Liu, Z., Shi, Y., Kong, J., Lou, J., Ajayan, P.M., Yakobson, B.I., and Idrobo, J.-C. (2013). Intrinsic structural defects in monolayer molybdenum disulfide. Nano Lett. 13, 2613–2622. https://doi.org/10.1021/nl4007479.
STAR★METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE              | IDENTIFIER       |
|---------------------|---------------------|------------------|
| Chemicals, peptides, and recombinant proteins |                      |                  |
| KOH                 | Sigma Aldrich       | CAS: 1310-58-3   |
| KI                  | Sigma Aldrich       | CAS: 7681-11-0   |
| Re powder           | Sigma Aldrich       | CAS: 7440-15-5   |
| Se powder           | Sigma Aldrich       | CAS: 7782-49-2   |
| PMMA                | Sigma Aldrich       | CAS: 9011-14-7   |
| Software and algorithms |                  |                  |
| Digital Micrograph  | Gatan, Inc          | https://www.gatan.com |
| Origin              | OriginLab Corporation | https://www.originlab.com |
| Python              | Python Software Foundation | https://www.python.org |
| VASP 5.5.4          | NA                  | https://www.vasp.at |
| Other               |                      |                  |
| Optical microscopy  | OLYMPUS Corporation | https://www.olympus-lifescience.com |
| Electron microscopy | Nion Co.            | https://www.nion.com |

RESOURCE AVAILABILITY

Lead contact
Further information requests should be directed to the lead contact, Wu Zhou (wuzhou@ucas.ac.cn).

Materials availability
This study did not generate new reagents.

Date and code availability
Data and code used in this paper will be shared by the lead contact upon request. Any additional information required to reanalyze the data reported in this paper are available from the lead contact upon request.

EXPERIMENTAL MODEL AND SUBJECT DETAILS

Our study does not use experimental models typical in the life sciences.

METHOD DETAILS

ReSe₂ growth and TEM sample preparation

The monolayer ReSe₂ samples were synthesized using a molten-salt-assisted CVD process (Zhou et al., 2018), during which a furnace including a quartz tube was employed. Firstly, 1 mg KI powder and 5 mg Re powder were put together into an aluminum oxide boat. A Si substrate with a surface layer of SiO₂ was placed on the aluminum oxide boat with the smooth surface facing the Re source and with one cm distance. Then the aluminum oxide boat was inserted into the center of the quartz tube. Another boat containing the Se powder was deposited on the upstream of the tube furnace. The furnace was heated with a ramp rate of 50°C min⁻¹ to the growth temperature (700-780°C for Re and 300°C for Se) and held for 5 ~ 10 min before cooling down to room temperature naturally. Ar/H₂ with a flow rate of 80/10 sccm was used as the carrier gas.

The TEM samples were prepared with a poly (methyl methacrylate) (PMMA) assisted method. 0.8 μm thick PMMA was spin-coated on the samples deposited on the wafer, and then baked at 180°C for 3 min. After that, the wafer was immersed in the KOH solution (1M) to etch the SiO₂ layer overnight. Afterward, the ReSe₂ film was transferred into deionized water several times to wash away the residual contaminants and then fished by a TEM grid. The transferred specimen was dried naturally, and then dropped into
acetone for a whole night to wash away the PMMA coating layers. The TEM sample was baked in the vacuum at 160°C for 8 ~ 10 hours to reduce the contaminants on the sample before STEM imaging.

**Electron microscopy characterization**

The STEM-HAADF imaging was conducted on an aberration-corrected Nion U-HERMES100 microscope operating at 60 kV. The probe-forming semi-angle is 32 mrad, and the collection half angle for HAADF imaging is between 75 and 210 mrad. The beam current was about 15 pA for a single shot image with an electron dose rate of ~ 2000 e⁻/Å²/s. The sequential video was acquired in a multi-frame mode with a relatively low electron dose rate (~ 180 e⁻/Å²/s) on the same area where a single shot image was just taken. Images used for point defects statistics were processed by removing the effect of the probe tail to more accurately identify the intensity on each atom position(Krivanek et al., 2010). Each frame of the time-sequence video was filtered using a nonlinear filter to increasing the signal to noise ratio(Du, 2015).

The 4D-STEM experiments were performed on the same microscope with the same settings. Since monolayer ReSe₂ is very sensitive to electron beam irradiation, the experimental parameters for recording the 4D dataset were optimized after multiple attempts. The beam current, scanning pixel size and exposure time were set to 2 pA, 0.3125 Å and 2 ~ 4 ms, respectively. The CMOS camera for recording each convergent beam electron diffraction (CBED) has 2048x2048 pixels, which is cropped and binned to 192x192 pixels to reduce the size of the 4D dataset. The CBED bright field disk was centered and the rotation of CBED was corrected by changing the direction of the scanning using the shadow image approach(Savitzky et al., 2021). 4D-STEM simulations as well as STEM-HAADF image simulations were implemented on monolayer ReSe₂ crystal model containing three types of defects, i.e., VSe, OSe and SSe, using Dr. Probe software(Barthel, 2018). The simulation parameters are set according to experimental conditions. The thermal vibration of the ReSe₂ lattice is considered using the frozen phonon method and 30 phonon configurations are employed.

The phase of monolayer ReSe₂ is retrieved with our custom-written python codes, using a direct ptychographic method called SSB as has been described in Ref(Pennycook et al., 2015; Rodenburg et al., 1993; Yang et al., 2017). The monolayer characteristic of the sample meets the so-called weak phase object approximation (WPOA) that the SSB method is established on. In addition, the aberration-free condition for the SSB method is also largely satisfied in the experiment through the careful alignment and tuning of the microscope with the aid of the aberration corrector and monochromator.

**Density functional calculations**

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projected augmented wave (PAW) method(Blochl, 1994; Kresse and Furthmuller, 1996). Wave functions were expanded in a plane-wave basis set to 400 eV energy cutoff. Exchange and correlation effects were described using the Perdew-Burke-Ernzerh of generalized gradient approximation(Perdew et al., 1996). All structures are modeled by a supercell with a vacuum layer of 15 Å. Point-defect calculations are performed using 2×2×1 supercells in which the interaction between nearby supercells is negligible because the formation energies of vacancies already converge in this condition (see Figure S11 for details). All atoms are fully relaxed until the net force is less than 0.02 eV Å⁻¹. The Brillouin zone is sampled with a 7 × 7 × 1 point. Density of states are plotted using the sigma of 0.01.

The formation energy is a function of the chemical potential:

\[ E_{\text{form}} = E_{\text{defect}} - E_{\text{defect-free}} + \mu_i - \mu_j \]

where \( E_{\text{defect}} \) and \( E_{\text{defect-free}} \) represent the total energies of structure with and without the defect respectively, \( \mu_i \) is the chemical potential of missing atoms, and \( \mu_j \) is the chemical potential of substitutional atoms. The formation energy of a Se vacancy is \( E(V_{\text{Se}}) = E_{\text{defect}} - E_{\text{defect-free}} + \mu_{\text{Se}} \), while the formation energy of an antisite defect at Se site (ReSe) is \( E(\text{ReSe}) = E_{\text{defect}} - E_{\text{defect-free}} + \mu_{\text{Se}} - \mu_{\text{Re}} \) and the formation energy of an antisite defect at Re site is \( E(\text{SeRe}) = E_{\text{defect}} - E_{\text{defect-free}} + \mu_{\text{Re}} - \mu_{\text{Se}} \). For Se-rich conditions, \( \mu_{\text{Se}} \) is the energy of a Se atom in Se₈ molecules. For Se-poor conditions, \( \mu_{\text{Se}} \) is \( [E(\text{ReSe})-E(\text{Re bulk})]/2 \) which corresponds to Re atoms in bulk form.
QUANTIFICATION AND STATISTICAL ANALYSIS

Values shown in Figure 3D are obtained by calculating the concentration of each type of point defects based on a large number of STEM-HAADF images. Error bars in Figure 3D are the standard deviations of the concentrations of each type of point defects. Curves in Figures 5E and 5F are obtained by calculating the number of vacancies in Figures 5A–5D.