Fermiology and electron-phonon coupling in the 2H and 3R polytypes of NbS$_2$

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We investigate the electronic structure of the 2H and 3R polytypes of NbS$_2$. The Fermi surfaces measured by angle-resolved photoemission spectroscopy show a remarkable difference in size, reflecting a significantly increased band filling in 3R-Nb$_{1+x}$S$_2$ compared to 2H-NbS$_2$, which we attribute to the presence of additional interstitial Nb which act as electron donors. Thus we find that the stoichiometry, rather than the stacking arrangement, is the most important factor in the difference in electronic and physical properties of the two phases. Our high resolution data on the 2H phase shows kinks in the spectral function that are fingerprints of the electron-phonon coupling. However, the strength of the coupling is found to be much larger for the the sections of bands with Nb 4$d_{x^2−y^2,xy}$ character than for the Nb 4$d_{3z^2−r^2}$. Our results provide an experimental framework for interpreting the two-gap superconductivity and "latent" charge density wave in 2H-NbS$_2$.

The transition metal dichalcogenides (TMDs) are well-known for hosting a variety of instabilities arising from the interplay of electron-electron and electron-phonon coupling. Particularly rich phenomena are found in the metallic (V,Nb,Ta)(S,Se,Te)$_2$ family, including Mott-insulating phases, superconductivity, and numerous charge density waves (CDW) [1–4]. As a well-known example, 2H-NbSe$_2$ exhibits a $\sim 3 \times 3$ CDW and also superconducts at 7.2 K [5–8]. Several of these layered van der Waals materials favor the trigonal prismatic coordination of the transition metal, but there is an additional degree of freedom in the inter-layer stacking pattern (e.g. 2H, 4H, 3R polytypes [9]), leading to further variety of the novel electronic ground states.

Unlike most other members of the (V,Nb,Ta)(S,Se,Te)$_2$ family, 2H-NbS$_2$ does not undergo any structural instability [10]. Nevertheless, a phonon mode exhibits significant softening with temperature [11], and 2H-NbS$_2$ can be viewed as being close to a lattice instability. This presents an interesting theoretical challenge, as naive Density Functional Theory (DFT) calculations would predict a lattice instability [12], and the absence of any CDW phase is attributed to the anharmonic phononic effects [11, 13]. 2H-NbS$_2$ is also a prototypical two-gap superconductor below $T_c = 6.2$ K, as evidenced by tunneling spectroscopy [14], Andreev reflections [15], and heat capacity measurements [16]. Despite this, the experimental electronic structure of bulk 2H-NbS$_2$ has been hardly explored [17]. Meanwhile, an alternative stacking structure, the non-centrosymmetric 3R phase, has been reported for some time [18, 19], but little is known about its electronic structure, or how and why its properties differ from the 2H phase.

Here, we examine the low-energy electronic structure of 2H-NbS$_2$ and 3R-Nb$_{1+x}$S$_2$ combining Angle-Resolved Photoemission Spectroscopy (ARPES) and density functional theory (DFT) calculations. The measured Fermi surfaces reveal a striking difference in size, implying a significantly greater band filling in the 3R phase. We attribute this difference to additional Nb interstitials in the 3R phase, which act as electron donors. This difference is likely to move the 3R phase away from any latent instabilities and may explain the absence of superconductivity in this phase. Finally, the high-resolution data on the 2H phase reveals that the electron-phonon coupling is highly dependent on the orbital character of the bands, which naturally links to the two-gap superconductivity.

DFT calculations were performed within the Wien2k package [20], accounting for spin-orbit coupling and using the modified Becke-Johnson (mBJ) functional [21]. ARPES measurements were performed at the I05 beamline of Diamond Light Source [22], at temperatures below 10 K. Single crystals were obtained commercially (HQ Graphene, Groningen).

In the 2H phase (space group 194, $P6_3/mmc$), each NbS$_2$ layer is rotated by 180° with respect to the layer below it (Fig. 1(a)). Due to the trigonal prismatic coordination of the Nb, a single layer would not possess inversion symmetry, however in the 2H phase a centre of inversion symmetry exists between the layers [23–25]. Contrastingly, in the 3R phase (space group 160, $R3m$) shown in Fig. 1(e) there is no rotation but rather each layer is translated by a third of a lattice constant in the $b$ direction, with respect to the layer below. This stacking structure does not contain any points of inversion.

In our DFT calculations in Fig. 1(b,f), we find twice as many bands in the 2H phase compared to the 3R phase, since the 2H unit cell contains two formula units, while the 3R phase contains one (in the primitive unit cell). Around the K point, the bands near $E_F$ with Nb 4$d_{x^2−y^2,xy}$ character (red) are split due to combination of interlayer hopping and the spin-orbit coupling, as discussed in numerous studies of 2H-MoS$_2$ [26–28], 2H-WSe$_2$ [25, 29], and 2H-NbSe$_2$ [30]. However the Nb 4$d_{3z^2−r^2}$ orbital (green) is more significantly affected by interlayer hopping terms, leading to a larger band splitting of $\sim 1$ eV at the $\Gamma$ point above $E_F$. For the in-plane S 3$p_{z,y}$ valence bands (yellow), we find a doubling of the band dispersions in the 2H phase, since for these orbitals the interlayer hopping terms are relatively weak compared to the in-plane hoppings. The S 3$p_x$ bands valence bands (blue) are affected by the different geometry: the height of the Brillouin
DFT calculations with orbital character projection of the valence and conduction bands for 2H-NbS$_2$. FIG. 1. Crystalline and electronic structure of 2H-NbS$_2$. (a,e) Crystal structures, showing the different stacking modes. (b,f) DFT calculations with orbital character projection of the DFT band structure along the experimentally-relevant M-K-Γ-K-M (L-H-A-H-L) direction for 2H-NbS$_2$ (c) and 3R-NbS$_2$ (g). (d,h) Overview ARPES spectra showing valence band dispersions. Data measured along Γ-K direction at $h\nu = 79$ eV and $h\nu = 68$ eV for 2H-NbS$_2$ (d) and 3R-NbS$_2$ (h), respectively, using LH ($\rho$) polarized light.

zone in the 2H phase is half that of the 3R phase, leading to an effective backfolding of bands along Γ-A.

In both phases, therefore, there are both quasi-2D and rather 3D valence bands, as highlighted in the $k_z$-projection of the band structure (Fig. 1(c) and 1(g)). This is a helpful representation of the DFT band structure for comparison with ARPES measurements, due to the non-conservation of $k_z$ in the photoemission process, which leads to an effective integration over a range of $k_z$ values [25, 31–33]. In the overview ARPES spectra of the 2H phase in Fig. 1(d), the valence bands closely resemble the $k_z$-projected calculations, including sharp features from quasi-2D states, and broad features from 3D bands. In the case of the 3R phase, however, the agreement is notably worse. First, the data quality in Fig. 1(h) is lower; none of the features are as sharp as in the 2H phase, with a significantly higher background signal. Second, there is evidence for a flat state at $E_F = -1.2$ eV, not present in the calculations, which is indicative of some form of localised impurity-like state. Third, the Nb 4$d$-derived bands at the Fermi level have a substantially larger filling than in the calculation.

To further understand the difference between the two phases, in Fig. 2 we consider the Fermi surfaces. The DFT calculations of the Fermi surfaces in the two cases are broadly similar, as in both cases quasi-2D “barrels” appear, centered around the Γ and K points (Fig. 2(a) and 2(e)). The inter-layer hopping in the 2H phase plays an important role in creating a splitting of inner and outer barrels around K. However, there is no such splitting term in the 3R phase, and the splitting is a spin-splitting, allowed due to the absence of inversion symmetry (See Supplemental Material, SM [34]). In Fig. 2(b) and 2(f) we present simulations of the in-plane Fermi surfaces after averaging over the entire $k_z$ axis [35]. The measured Fermi surface in the 2H phase, Fig. 2(c), is broadly comparable with the calculation. Notably, the band splitting around the K barrels is reproduced, and we can also resolve the two separate bands forming the Γ barrel, with the inner displaying a strong hexagonal warping. The most noticeable difference is that experimentally, the triangular barrels around K form closed pockets (similar to 2H-NbSe$_2$ [7, 30]), while in our calculation the outer K barrels connect near the M points. We attribute this to a limit to the accuracy of the functional, rather than any off-stoichiometry of the 2H sample. The more advanced GW calculations of Ref. [36] similarly found smaller, closed, K barrels, along with slightly expanded Γ barrels. Experimentally, we find that the observed Fermi surface appears highly two-dimensional, with very little variation observed in the photon energy dependence in Fig. 2(d).

However, in the measured Fermi map of 3R-NbS$_2$ (Fig. 2(g)), the Γ and K barrels of the Fermi surface are found to be both significantly smaller compared to the calculations.
Phase is reported to exist only as stoichiometric NbS. The difference between the two polytypes is intimately related to the stoichiometry. These Nb interstitials exemplify the mantra of not judging by appearances. Although neither phase undergoes any structural phase transitions, the 2H phase, a sharp doublet is observed, consistent with spin-orbit split $2p_{1/2}$ and $2p_{3/2}$ states from a single chemical site. However, in the 3R phase, there are additional minority peaks, arising from S atoms in a chemical environment with more than the normal 3 nearest-neighbour Nb atoms, due to the interstitial Nb occupancy. The main doublet is also broadened, reflecting electronic inhomogeneity caused by the partial filling of the interstitial sites. Moreover, the main doublet is shifted by $\sim 180$ meV, a chemical shift related to the overall chemical potential and average orbital fillings. It is worth remarking that the two polytypes also have different physical appearances; although both black and metallic-looking, the off-stoichiometric 3R phase forms as beautiful plate-like single crystals with clear crystal facets, while the 2H phase forms thin, flaky samples usually without clear facets. Thus, NbS$_2$ exemplifies the mantra of not judging by appearances.

Although neither phase undergoes any structural phase transition, 2H-NbS$_2$ is considered to be on the brink of a CDW-like transition [11–14, 16, 39–41], while a CDW does stabilise in the closely-related 2H-NbSe$_2$ at 33.5 K. It is generally acknowledged that the charge density waves in this

FIG. 2. Fermiology of 2H-NbS$_2$ and 3R-NbS$_2$. (a,e) calculated 3D Fermi surface of (a) 2H-NbS$_2$ and (e) 3R-NbS$_2$. (b,f) Simulated Fermi surfaces obtained by averaging over the whole Brillouin zone width in the $k_z$ direction for 2H-NbS$_2$ (b) and 3R-NbS$_2$ (f). In the latter, a section is simulated at 250 meV above the natural Fermi level. (c,g) Fermi surface measured at a photon energy $h\nu = 79$ eV (inset, 42 eV) for 2H-NbS$_2$ (c), and $h\nu = 120$ eV for 3R-NbS$_2$ (g). (d) Photon energy-dependent ARPES of 2H-NbS$_2$ from 50 to 130 eV, plotting MDCs at $E_F$ along K-T-K (H-A-H) direction for a function of photon energy, showing the quasi-2D nature of electronic states with a consistently-resolved splitting of the K barrel bands. (h) S 2p core levels of 2H-NbS$_2$ (red) and 3R-NbS$_2$ (blue) using a photon energy $h\nu = 240$ eV, showing clearly additional satellites in the 3R phase. Inset shows microscope images of the single crystals used in this work.
family of materials cannot be explained by electronic “nesting” alone, and it is important to consider the momentum-dependence of the electron-phonon interaction, which itself is related to the orbital character of the bands [5, 7, 8, 42–45]. For the calculated bands along ΓK in Fig. 3(a), there is a crossover in orbital character between the doublets corresponding to the Γ barrels (mainly Nb 4d_{3z^2−r^2}) and the K barrels (mainly Nb 4d_{x^2−y^2,xy}, see also Fig.S2 [34]). The experimental spectral function in Fig. 3(b) shows significantly different impact of electron-phonon coupling at the two pairs of Fermi crossings, with the second pair of crossings (corresponding to the K barrels) exhibiting a clear kink structure, characteristic of a strong electron-phonon interaction, whereas for the first pair (Γ barrels) the effect is much less prominent.

For a more quantitative analysis, we performed a fitting analysis to extract the band positions in Fig. 3(e). From this, we identify a “kink” energy of -15 meV for the K barrels; the deviation of the bands around this energy can also be visualised in the “curvature” plot in Fig. 3(d). Meanwhile the inner bands have a change of slope around ~20 meV, but this is a more subtle effect. A quantitative measure of electron-phonon coupling is the renormalization of the Fermi velocity, \( \lambda = v_F(\text{bare})/v_F(\exp.) − 1 \) [46]. If we assume the \( v_F(\text{bare}) \) values from DFT [47], we find a clear dichotomy between the innermost band 1, with \( \lambda \approx 0.51 \), and the outer crossings of the K barrel with \( \lambda \approx 2.32 \) for band 3 and \( \lambda \approx 2.59 \) for band 4. Additionally, in Fig. 3(f) we show a dichotomy in the energy-dependent linewidths, as the broadening of the K barrels increase much faster with binding energy than the Γ barrels. The outermost band 4 shows the fastest rise, consistent with having the strongest coupling, and also shows a saturation of the linewidth coinciding with the kink energy [46].

Taken together, this evidence strongly suggests that in 2H-NbS\(_2\), the electron-phonon coupling depends crucially on the orbital character of the bands, and for the ΓK dispersion analysed here, the \( \lambda \) value is up to ~4-5 times larger for the section with Nb 4d_{x^2−y^2,xy} character than for the Nb 4d_{3z^2−r^2}. Our experiments are highly consistent with the calculations of Ref. [13], who took the electron-phonon interaction into consideration and also found a significantly larger interaction strength on the sections of the K barrel closest to the K points, correlating closely with the Nb 4d_{x^2−y^2,xy} orbital character. This has important implications for the superconductivity, and our data gives strong experimental support for the scenario of Ref. [13], where the inner Γ sheets with weaker el-ph coupling are "cold" areas corresponding to the smaller gap, while the straight sections of the K barrels are "hot" regions developing a larger gap, explaining the overall gap structure with two characteristic energy scales [14, 15].

Recapping the results on 3R-Nb\(_{(1+x)}\)S\(_2\), we showed that the prevalence of donor-type interstitials leads to a shifted chemical potential, smaller Fermi surfaces and a reduced DOS, moving the doped system away from any structural instabilities [48, 49]. It is this difference, rather than the difference in stacking arrangement, that principally distinguishes the electronic and physical properties of the two phases. If a stoichiometric 3R-NbS\(_2\) existed, our DFT calculations suggest it would have a similar Fermi surface to the 2H phase, and therefore could have similarly interesting properties, potentially including non-centrosymmetric superconductivity. Unfortunately, stoichiometric 3R-NbS\(_2\) is entirely hypothetical, and the only thermodynamic bulk phases are 3R-Nb\(_{(1+x)}\)S\(_2\) and 2H-NbS\(_2\) [18]. However, the monolayer limit provides

![FIG. 3. Electron-phonon coupling in 2H-NbS\(_2\). (a) Calculated band dispersion along ΓK direction (inset: 2D Fermi surface) with orbital character projection. (b) ARPES data of the valence band dispersion along ΓK, measured at a photon energy \( h\nu = 30 \) eV, overlaid with DFT calculations for comparison. (c) Closer look at the data near \( E_F \) and the ‘curvature’ plot of the data, highlighting kinks in the spectral function. (d) Momentum distribution curve (MDC) fitting of the data using a multi-Lorentzian peak function, and (f) peak widths of the four bands.](image_url)
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