

Phase Diagram of Electron Doped Dichalcogenides

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Using first principle calculations, we examine the sequence of phases in electron doped dichalcogenides, such as recently realized in field-gated MoS₂. Upon increasing the electron doping level, we observe a succession of semiconducting, metallic, superconducting and charge density wave regimes, i.e. in different order compared to the phase diagram of (semi-)metallic dichalcogenides such as TiSe₂. Both instabilities trace back to a softening of phonons which couple the electron populated conduction band minima. The superconducting dome, calculated using Eliashberg theory, is found to fit the experimentally observed phase diagram, obtained from resistivity measurements. The charge density wave phase at higher electron doping concentrations as predicted from instabilities in the phonon modes is further corroborated by detecting the accompanying lattice deformation in density functional based supercell relaxations. Upon charge density wave formation, doped MoS₂ remains metallic but undergoes a Lifschitz transition, where the number of Fermi pockets is reduced.

Introduction: Several materials including graphene or transition metal dichalcogenides can be prepared at monolayer thickness [1]. Because of their low effective dimensionality, there is a lack of screening in these materials, and in addition the band structure shows strong van Hove singularities. This can lead to strong enhancements of scales and result in competing instabilities, such as superconductivity (SC) and charge density wave (CDW) phases [2, 3]. For example, based on Eliashberg theory it has been argued that by doping the structurally related graphene up to its van Hove singularity, the effective electron-phonon coupling can be greatly enhanced, leading to superconducting transition temperatures potentially as high as 30K [4]. Furthermore, the quasi-two-dimensional structure of these compounds allows for a high degree of control via tuning knobs such as pressure, doping and adsorbates, but it also makes these materials more vulnerable to the effects of impurity disorder.

The generic phase diagram of the (semi-)metallic transition metal dichalcogenides features a CDW regime at and close to half-filling, which upon doping or exerting external pressure is suppressed by a competing SC instability [5, 6]. For example, pristine 1T – TiSe₂ undergoes a CDW phase transition at approximately 200K [7]. Upon hole doping via Cu intercalation [8] or application of pressure [9] this phase is suppressed and replaced by competing SC order with transition temperatures \sim 2-5K, leading to a phase diagram topology akin to the high- T_c cuprates, with CDW taking the place of the antiferromagnetic insulator regime in the cuprates. This succession of phases can be modeled by combining first principle calculations with Eliashberg theory, based on a phonon mediated pairing mechanism [10]. Furthermore, since these materials are quasi-two-dimensional, it can be expected that other low-energy modes, such as plasmons, are present and may contribute to the formation of the

SC condensate [6, 11].

In this paper, we focus on the phase diagram of *electron doped* dichalcogenides, which we find to have a different topology, thus leading to an interesting set of predictions that can be experimentally tested. Without loss of generality, we focus on the much studied compound MoS₂ because there already is a wealth of data available which allows to scrutinize our approach. Bulk MoS₂ is a layered transition-metal dichalcogenide with an indirect band gap, whereas monolayer MoS₂ is a direct band gap semiconductor [12, 13]. Its conduction and valence bands are dominated by the d-orbitals of the Mo atoms [14]. Electron doping of thin-flake MoS₂ has recently been achieved by means of combined liquid/solid high-capacitance gates, leading to effective 2D carrier densities of up to $n_{2D} \approx 1.5 \times 10^{14} \text{ cm}^{-2}$. Such doping by field effect gates allows us to access larger carrier concentrations compared to chemical substitution, without substantially deforming the lattice [15]. A field-doping-induced superconducting dome was found with onset at $n_{2D} = 6.8 \times 10^{13} \text{ cm}^{-2}$ and peak with maximum $T_c = 10.8 \text{ K}$ at $n_{2D} = 1.2 \times 10^{14} \text{ cm}^{-2}$. [15, 16]. Using density functional theory calculations, it has been shown that this superconducting dome is consistent with electron-phonon coupling that is doping-dependent due to the change of Fermi surface topology when negative charge carriers are introduced [17]. Here, we push this analysis further and identify a competing CDW phase which occurs at higher doping concentrations. While it may turn out to be difficult to achieve such high doping concentrations in MoS₂ experimentally by back gating [15], this prediction is a generic feature, and thus should hold for other electron doped dichalcogenides as well. Example systems for observing the CDW phase predicted here include chemically doped MoS₂, as e.g. realized by alkali deposition/intercalation [18].

Method: We use the VASP [19, 20] and Quantum Espresso [21] Packages for the density functional theory (DFT) based self-consistent evaluation of the electronic and phononic band structures. Electron doping x (in electrons per primitive MoS₂ unit cell) or $n_{2D} = x/A$ (in electrons per cm², A is the area of the unit cell) is realized by introducing additional electrons along with a compensating jellium background. Care is taken such that no unphysical low energy states are introduced by the positive background charges. The electron-phonon matrix elements are calculated using the Phonon package of Quantum Espresso [27], and the superconducting properties based on Eliashberg theory are obtained via postprocessing [22, 23]. In particular, the Eliashberg spectral function,

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(\epsilon_F)} \sum_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}) \frac{\gamma_{\mathbf{q}\nu}}{\hbar\omega_{\mathbf{q}\nu}}, \quad (1)$$

is evaluated from the electronic density of states at the Fermi level $N(\epsilon_F)$, the phonon frequencies $\omega_{\mathbf{q}\nu}$ and the line widths $\gamma_{\mathbf{q}\nu}$ which contain the electron-phonon coupling matrix elements [23]. The superconducting transition temperatures can then be estimated using the Allen-Dynes formula [22],

$$T_c = \frac{\hbar\omega_{log}}{1.2k_B} \exp\left[\frac{-1.04(1+\lambda)}{\lambda(1-0.62\mu^*) - \mu^*}\right], \quad (2)$$

where $\lambda = 2 \int d\omega \alpha^2 F(\omega)/\omega$, and $\omega_{log} = \exp[2/\lambda \int d\omega \alpha^2 F(\omega) \log(\omega)/\omega]$. Here, the effective Coulomb repulsion μ^* is set to a typical value of 0.1 [10, 24]. The emerging CDW at higher electron concentrations is identified by (i) the occurrence of an unstable phonon mode, (ii) by spontaneous deformation of the honeycomb lattice, as well as (iii) by comparison of energies of the deformed lattice with the unperturbed lattice [28].

Results: The evolution of the electronic band structure in MoS₂ upon electron doping is shown in Fig. 1 (a). Similar to other dichalcogenides, the low-energy properties are dominated by minima in the conduction band at lattice vectors K and Σ , which have predominantly Mo d_{z²}-orbital (K) and Mo d_{xy}- and d_{x²-y²}-orbital (Σ) character [12]. Upon electron doping, the Σ valley moves towards lower energies, whereas the K valley is less affected [17]. The doping levels shown here correspond to the metallic regime, the SC phase, and the CDW phase. These instabilities are discussed in more detail below. We note that once the material enters the SC regime with onset at $x \sim 0.05$, both valleys at K and Σ are occupied.

In Fig. 1 (b) the phonon dispersions of MoS₂ are shown for the same electron doping concentrations as in Fig. 1 (a). Similar to graphene, pristine MoS₂ has one quadratic and two linear acoustic phonon branches which flatten out around the K and M points in an energy window $\sim 180 - 240$ cm⁻¹. They are energetically separated

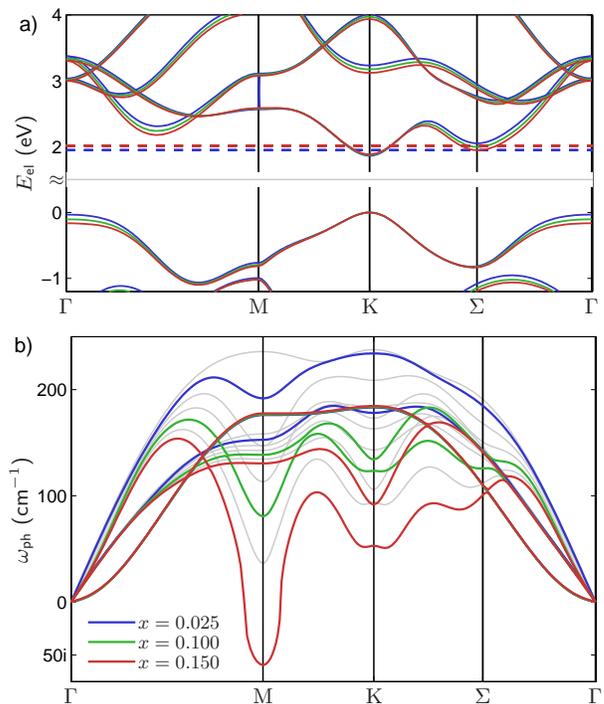


Figure 1: (Color online) (a) Electronic and (b) acoustic part of phononic band structure of MoS₂ as a function of electron doping. Dispersions are shown along a cut Γ -M-K- Σ - Γ of the Brillouin zone for electron doping concentrations $x = 0.025$ (blue), $x = 0.100$ (green), and $x = 0.150$ (red), corresponding to the metallic, superconducting and charge density wave regimes respectively. The electronic band structures are aligned to the maximum of the valence bands. The corresponding Fermi levels are indicated by dashed lines. The phononic band structures are completed by several doping levels inbetween the range of $x = 0$ to $x = 0.15$ (grey).

from the optical branches which fall into the energy range $\sim 300 - 500$ cm⁻¹. Upon doping, the acoustic in-plane branches soften. The parabolic out-of-plane phonons are odd under mirror transformation with respect to the Mo plane and do not couple the conduction band minima at K and Σ . There is thus no Kohn anomaly (or related phenomena) leading to softening of these phonons upon electron doping. The optical branches also move towards lower energies, but are less dramatically affected by doping (not shown). As we will see below, the flat regions of the acoustic branches dominate the formation of the SC condensate, with $\omega_{typ} \sim 2\pi k_B T_c$. At a critical electron concentration $x_c \sim 0.14$ one of the acoustic modes develops an instability at the M point, indicating the onset of a CDW regime. At this point the phonon frequency of this mode becomes imaginary, illustrated by a “drop below zero” in Fig. 1 (b) [10]. This behavior is reminiscent of TiSe₂, where a CDW-SC transition can be tuned by pressure or Cu intercalation [9]. However, the CDW regime in TiSe₂ already occurs in its pristine state, and is suppressed by pressure or hole-doping, giving way to

SC, whereas the sequence of phases we observe in MoS₂ is reversed.

Let us now turn our focus toward the SC regime at intermediate concentrations. We examine the lattice dynamics encoded in the phonon density of states and the Eliashberg function. The phonon density of states, shown in Fig. 2 (a), has a rich peak structure, with the largest contributions stemming from the regions where the phonon dispersion flattens, leading to characteristic van Hove enhancements. While the high-energy optical branches lead to the strongest peaks in the phonon density of states, it turns out that they do not contribute significantly to the formation of the SC condensate. Instead, we observe that the SC response encoded in the Eliashberg function is dominated by the flat regions (around the M and K points) of the acoustic phonon branches. These features are inherited by the Eliashberg function (Fig. 2 (b)), which includes weighting by the electron-phonon coupling matrix elements. As the acoustic phonon mode with minimum at the M point softens, the evolution of the Eliashberg function displays a maximum integrated intensity at $x = 0.125$. However, this concentration does not correspond to maximum of $T_c(x)$ since next to the Eliashberg function $\lambda(x)$ and $\omega_{log}(x)$ have to be considered as well. As it can be seen in the inset of Fig. 2 (b) $\omega_{log}(x)$ decreases with increasing doping. Thus, we find a optimum doping concentration of $x \approx 0.1$, which agrees with the experimentally optimum of $n_{2D} = 1.2 \times 10^{14} \text{ cm}^{-2}$ [15].

This evolution of the Eliashberg function, $\lambda(x)$ and $\omega_{log}(x)$ with electron doping leads to the dome-shaped dependence of the SC transition temperature on the electron doping concentration seen in Fig. 3. Here we show experimental data of Ref. [15] along with results of our numerical simulation. Besides the coincidence in the position of the maximum in $T_c(x)$, we also note that the computed and experimental SC transition temperatures are of the same order of magnitude. This is remarkable, since Eliashberg theory is a rather crude approximation, which does not account for pair-breaking effects, such as impurities, incorporates Coulomb interactions only statically and neglects enhanced phase fluctuations in 2D. It is therefore expected to overestimate $T_c(x)$.

In order to better understand the nature of the SC-CDW phase transition, let us now examine the doping dependence of the CDW-induced lattice distortion α , shown as a red line in Fig. 3. Here, α is defined as the angle between three neighboring Mo atoms subtracted by 60° . For an undistorted honeycomb lattice one finds $\alpha = 0$. By relaxing the atomic structure of a 2×1 supercell, we observe $\alpha \neq 0$ beyond a critical electron concentration of $x = 0.125$, as forces arise from the unstable phonon mode at lattice vector M [25]. These distortion effects, depicted in Fig. 4, become more pronounced with increasing electron doping. We note that in addition to the CDW formation, there is a further homogeneous outward

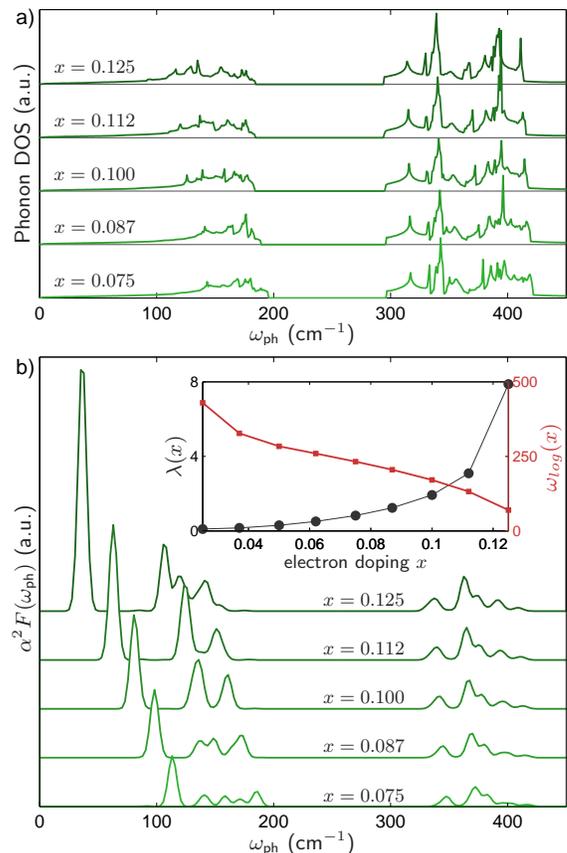


Figure 2: (Color online) (a) Phonon density of states and (b) Eliashberg function of MoS₂ in the SC phase for different doping levels. The inset shows the evolution with electron doping of the electron-phonon coupling and the log-averaged phonon frequency (using a Gaussian smearing of $\delta = 0.005 \text{ Ry}$), determining $T_c(x)$ via Eq. 2.

relaxation of the S atoms upon electron doping.

The effects of homogeneous S relaxation and CDW formation on the electronic structure are illustrated in Fig. 4 (b) for electron doping $x = 0.2$. In the supercell Brillouin zone, the former band minima at K and Σ are folded almost on top of each other at the supercell K point. In the absence of a CDW, low-energy states originating from K and Σ can be distinguished by their orbital band character. The latter states carry a significant $d_{xy}, d_{x^2-y^2}$ -weight, whereas the conduction band minimum at K has no such admixture. The outward relaxation of the S atoms lowers $d_{xy}, d_{x^2-y^2}$ -derived states from Σ in energy. With increasing CDW amplitude the two bands originating from K and Σ mix, and this hybridization adds to the splitting of the two bands, c.f. Fig. 4 (b). This splitting leads to lowering of the electronic energy if the Fermi level lies sufficiently high in the conduction band. The total energy gain upon CDW formation as function of doping level is shown in Fig. 3 as a blue line. It illustrates that the CDW formation energies

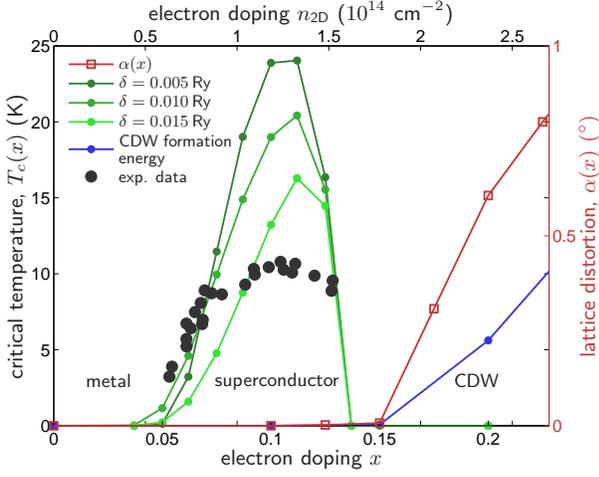


Figure 3: (Color online) Temperature-doping phase diagram of MoS₂. Circles belong to the left axis (K) and squares to the right (°). Green lines are obtained from first principle calculations combined with Eliashberg theory and show the SC critical temperature ($\mu^* = 0.1$ and three choices of the Gaussian broadening used in the calculation of the electron-phonon coupling). Black circles are from experimental data [15]. Also shown is the lattice distortion angle α (red squares) which denotes the onset of the CDW regime at larger electron doping concentrations and the energy gain upon CDW formation (blue circles).

for $x < 0.25$ are comparable to typical Cooper pair condensation energies ~ 5 K (~ 0.5 meV) encountered here, and an interesting competition of the two should emerge.

While the Eliashberg theory of SC order is only applicable as long as the lattice remains stable, it is clear that the competition of CDW and SC order will in any case depend on changes of the Fermi surface due to CDW formation. For the perfect crystal [29] and a doping level of $x = 0.2$, two bands intersect the Fermi level near the supercell K point, and there are thus two Fermi lines around K. Upon formation of the CDW, we observe a Lifshitz transition where one of the Fermi pockets disappears, Fig. 4 (c). The system thus remains metallic in the CDW phase, but the SC transition temperatures should be reduced due to the vanishing phase space for inter-pocket scattering. Persisting metallicity in the CDW phase of MoS₂ is indeed ensured by the “topology” of the inter-mixing bands at K and Σ , Fig. 4 (d). In TiSe₂, CDW bands with opposite slope are folded on top of each other, and a gap can open upon hybridization. However, in MoS₂, the slope of the backfolded bands has the same sign, and avoided crossings do not lead to a full gap, but only reduce the number of Fermi sheets by one.

Conclusions: Electron doped dichalcogenides feature CDW and SC instabilities, driven by the softening of an acoustical phonon mode upon charge doping. Due to the band topology, the M point CDW cannot fully gap the Fermi surface of electron doped MoS₂. Therefore, CDW and SC phases may coexist, albeit with reduced SC

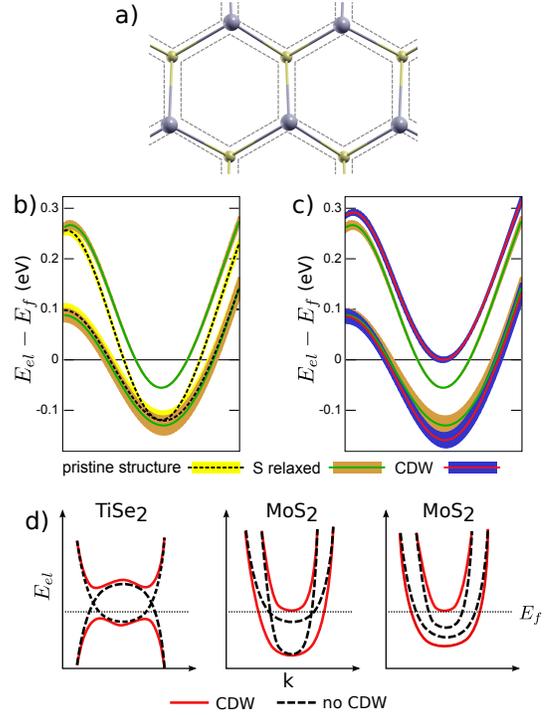


Figure 4: (Color online) Manifestation of the CDW in lattice distortion and band structure. (a) Lattice distortion in MoS₂, observed in ab initio calculations via self-consistent relaxation of 2×1 supercells. (b), (c) Influence of lattice relaxation effects on the band structures of the 2×1 supercells obtained for a doping level $x = 0.2$. The $d_{xy}, d_{x^2-y^2}$ weight of the bands is illustrated by the width of the bands. (b) Effect of homogeneous outward relaxation of the S atoms on the conduction band minima as observable from comparison of the MoS₂ structure with S positions according to undoped and homogeneously relaxed $x = 0.2$ system. (c) Comparison of supercell band structures for homogeneously relaxed MoS₂ and MoS₂ featuring the CDW (fully relaxed) at $x = 0.2$. (d) Comparison of band topologies involved in the CDW formation in TiSe₂ and MoS₂. Only in the TiSe₂ case, CDW formation can fully gap the Fermi surface.

transition temperatures. In any case, the SC and CDW instabilities rely on the energy differences between the conduction band minima at K and Σ . These are highly sensitive to lattice relaxation, and we speculate that adsorption of molecular species on MoS₂ may be useful for tuning superconducting transition temperatures.

Since MoS₂ is optically active, it remains to be seen whether intense photodoping could be a means to trigger the CDW or SC instabilities. This would be a rather unusual effect, since excitations normally suppress order and have been widely used to melt CDWs.

The competition of CDW and SC phases is common in metallic transition metal dichalcogenides, such as TiSe₂, NbSe₂ and TaS₂. All these materials differ, however, from MoS₂ in that the transition metal atoms lack one (Nb, Ta) or two (Ti) valence electrons in comparison to Mo. Thus, entirely different bands are involved in the

CDW/SC instabilities of electron doped MoS₂. It is consequently not surprising that the phase diagram of MoS₂ is reversed compared to materials like TiSe₂.

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- [1] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, *Proc. Natl. Acad. Sci. USA* **102**, 10451 (2005).
- [2] K. C. Rahnejat, C. A. Howard, N. E. Shuttleworth, S. R. Schofield, K. Iwaya, C. F. Hirjibehedin, C. Renner, G. Aeppli, and M. Ellerby, *Nature Communications* **2**, 558 (2011).
- [3] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nature Nanotechnology* **7**, 699 (2012), ISSN 1748-3387.
- [4] C. Si, Z. Liu, W. Duan, and F. Liu, *Phys. Rev. Lett.* **111**, 196802 (2013).
- [5] A. H. Castro Neto, *Phys. Rev. Lett.* **86**, 4382 (2001).
- [6] J. van Wezel, P. Nahai-Williamson, and S. S. Saxena, *Phys. Rev. B* **83**, 024502 (2011).
- [7] F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, *Phys. Rev. B* **14**, 4321 (1976).
- [8] E. Morosan, H. Zandbergen, B. Dennis, J. Bos, Y. Onose, T. Klimczuk, A. Ramirez, N. Ong, and R. Cava, *Nat Phys* **2**, 544 (2006).
- [9] A. F. Kusmartseva, B. Sipos, H. Berger, L. Forró, and E. Tutiš, *Phys. Rev. Lett.* **103**, 236401 (2009).
- [10] M. Calandra and F. Mauri, *Phys. Rev. Lett.* **106**, 196406 (2011).
- [11] T. O. Wehling, E. Şaşıoğlu, C. Friedrich, A. I. Lichtenstein, M. I. Katsnelson, and S. Blügel, *Phys. Rev. Lett.* **106**, 236805 (2011).
- [12] A. Kuc, N. Zibouche, and T. Heime, *Phys. Rev. B* **83**, 245213 (2011).
- [13] E. S. Kadantsev and P. Hawrylak, *Solid State Communications* **152**, 909 (2012), ISSN 0038-1098.
- [14] G.-B. Liu, W.-Y. Shan, Y. Yao, W. Yao, and D. Xiao, *Phys. Rev. B* **88**, 085433 (2013).
- [15] J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita, and Y. Iwasa, *Science* **338**, 1193 (2012).
- [16] K. Taniguchi, A. Matsumoto, H. Shimotani, and H. Takagi, *Applied Physics Letters* **101**, 042603 (2012).
- [17] Y. Ge and A. Y. Liu, *Phys. Rev. B* **87**, 241408 (2013).
- [18] R. B. Somoano, V. Hadek, A. Rembaum, S. Samson, and J. A. Woollam, *The Journal of Chemical Physics* **62**, 1068 (1975).
- [19] G. Kresse and J. Furthmüller, *Comput. Mat. Sci.* p. 15 (1996).
- [20] G. Kresse and J. Furthmüller, *Phys. Rev. B* p. 11169 (1996).
- [21] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., *Journal of Physics: Condensed Matter* **21**, 395502 (2009).
- [22] P. B. Allen and R. C. Dynes, *Phys. Rev. B* **12**, 905 (1975).
- [23] G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.* p. 966 (1960).
- [24] M. Calandra and F. Mauri, *Phys. Rev. Lett.* **101**, 016401 (2008).
- [25] Y. Ge, W. Wan, W. Feng, D. Xiao, and Y. Yao (????), arXiv:1403.0695.
- [26] J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- [27] The DFT calculations are performed within the local density approximation (LDA) using norm-conserving pseudopotentials. For the electronic calculations a $32 \times 32 \times 1$ k-mesh is used ($64 \times 64 \times 1$ for the calculation of $N(\epsilon_F)$), in combination with a Methfessel-Paxton smearing (0.0075 Ry). The lattice parameter is chosen to be 3.12 Å and adjacent layers are separated by about 13 Å. The geometry of the unit cell is optimized for each electron doping. Phonon band structures and electron-phonon couplings are calculated within the density functional perturbation theory based on the evaluation of the dynamical matrices on a $8 \times 8 \times 1$ q-mesh.
- [28] To this end the PAW method in GGA (PBE) [26] as implemented in VASP is used to calculate the relaxed structures and the total energies of simple 1×1 unit cells and 2×1 supercells for several doping concentrations. Both calculations are performed on $32 \times 32 \times 1$ k-meshes ($16 \times 32 \times 1$ in the case of the 2×1 structures). In the relaxation calculation a smearing of 0.0075 Ry is used, and the tetrathedron method is applied to obtain accurate total energies. The lattice parameter and the layer separation are the same as in the phonon calculations.
- [29] Perfect crystal here refers to an MoS₂ structure which has been relaxed at a charge doping level of $x = 0.2$ where only atomic displacements preserving all lattice symmetries were allowed.