



Strain-induced modulation of electronic and optical properties in hBN/InSe heterostructure

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Abstract

Our study delves into the nuanced effects of strain on hBN/InSe heterostructures, known for their exceptional wide-spectrum absorption capabilities. Employing uniform biaxial strain in the range of -6% to 6% , our investigation reveals a powerful method for manipulating the band gap. Notably, intense tensile strain leads to the near-complete elimination of the band gap—an outcome with profound implications. Comparison with hBN/InTe and hBN/GaTe heterostructures underscores the unique behaviour of hBN/InSe, showing a striking resemblance to hBN/GaTe but achieving lower band gap values under tensile strain. These findings provide crucial insights for experimental work and serve as a guide for more intricate theoretical explorations. With its outstanding electronic properties, tunable band gap, and remarkable absorption characteristics, hBN/InSe emerges as a key player in the development of future novel devices.

Keywords VdW heterostructures · DFT · InSe · Electronic structure · Optical properties · 2D

1 Introduction

Two-dimensional (2D) materials and van der Waals (vdW) heterostructures (HSs) have captured immense attention within the scientific community in recent years, owing to their distinctive physical properties that distinguish them from their bulk counterparts (Novoselov et al. 2016; Geim and Grigorieva 2013; Liu et al. 2016). Their remarkable electronic, optical, and mechanical attributes open up numerous possibilities for applications in modern devices. The exhaustive research in this field has underscored the special advantage of 2D materials and vdW heterostructures—they offer a plenty of options for customization and precise manipulation of their properties, enabling their use in a wide array of applications including transistors, solar cells, lithium-ion batteries, photodetectors (Liang et al.

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2020; Huo et al. 2014; Furchi et al. 2018; Zhou et al. 2011; Withers et al. 2015; Bag and Lee 2019). The current needs of nanoelectronics, optoelectronics and spintronics necessitate use of materials and components with diverse characteristics, coupled with the imperative of their minimization. In this context, 2D materials and vdW heterostructures emerge as promising contributors to fulfilling these demands.

As for tuning their properties, various effective methods have emerged, including doping and controlled introduction of defects, application of external electric or magnetic fields, and the utilization of strain. Notably, strain has proven exceptionally efficient for the precise control of the electronic and optical properties of 2D materials, offering a means to tailor these properties without fundamentally altering the material's characteristics (Xiong et al. 2020; Postorino et al. 2020). In the realm of van der Waals (vdW) materials and heterostructures, in-plane strain is commonly employed to modulate the electronic band structure. However, its utility extends beyond this, as it has been demonstrated to influence spin-orbit coupling (Zhuang et al. 2016), alter magnetic ordering (Šiškins et al. 2020; Wang et al. 2020; Webster and Yan 2018), and introduce various other novel effects (Miao et al. 2021). This multidimensional impact of strain, giving rise to the evolving field of straintronics, has sparked a new wave of research in the manipulation and optimization of material properties for advanced applications.

Within the 2D materials landscape, group III monochalcogenides have emerged as a focal point of extensive research, distinguished by their unique and promising properties. Recent investigations highlight their high electron mobility, a critical parameter for electronic devices, surpassing $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Chen et al. 2019). Notably, their band gap is easily tunable by adjusting the number of layers or applying strain Song et al. (2018); Li et al. (2018); Ma et al. (2013). Moreover, these materials exhibit substantial optical absorption across the UV, visible, and infrared regions (Wang et al. 2019; Lei et al. 2013; Hu et al. 2012), showcasing their potential in photonic applications. The nonlinear optical properties of group III monochalcogenides have been explored (Jie et al. 2015; Zhou et al. 2015), adding another layer of versatility to their applications. A significant advantage lies in their ease of exfoliation through mechanical or chemical methods (Yang et al. 2017; Aitzhanov et al. 2022; Qi et al. 2021; Harvey et al. 2015; Yang et al. 2023). Notably, InSe, one of the pioneering members, has been extensively studied, revealing a plethora of extraordinary properties. For instance, InSe demonstrates excellent thermoelectric performance (Hung et al. 2017) and high electron mobility (Bandurin et al. 2017; Sucharitakul et al. 2015; Feng et al. 2014), underlining its significance in the realm of 2D materials and beyond.

The exploration of heterostructures based on group III monochalcogenides is a thriving area of research. When combined with graphene, these heterostructures demonstrate exceptional tunable Schottky diode characteristics (Kim et al. 2016; Pham et al. 2019; Zhang et al. 2020). Specifically, InSe/InTe heterostructures exhibit enhanced optical absorption intensity compared to isolated monolayers (Shang et al. 2018). Another noteworthy application is observed in Sb/InSe heterostructures, where practical utilization allows for dipole control of Rashba spin splitting. The incorporation of hBN layers in these heterostructures goes beyond enhancing the inherent properties of monochalcogenides. It provides robust mechanical protection and passivation for the fragile monochalcogenides (Tang et al. 2021; Liu et al. 2013; Li et al. 2014), which are susceptible to oxidation when exposed to air (Guo et al. 2017, 2020). This engineering approach not only improves the performance of the HSs but also ensures the stability and longevity of the delicate monochalcogenide components.

Computational predictions suggest that encapsulating an InSe layer between two hBN capping layers significantly boosts electron mobility compared to pristine InSe films (Kang

et al. 2017). The high mobility and on/off ratio exhibited by InSe/hBN/graphite heterostructures, especially when integrated onto flexible substrates, make them compelling candidates for flexible electronics (Wu et al. 2020).

The theoretical exploration of InSe/hBN heterostructures extends beyond their electrical properties to their optical characteristics. Studies indicate that the construction of the heterostructure enhances absorption, concurrently reducing the band gap (Shen et al. 2022) - The band gap of bulk InSe lies in range from 1.3 to 1.4 eV (Gürbulak et al. 2014; Politano et al. 2017; Sang et al. 2019), but in monolayer, the gap is increased to 2.37 eV (Lei et al. 2014; Zhuang and Hennig 2013), resulting in limited applications for optoelectronic devices, as it is too large to be usable for absorbing IR and visible part of the spectrum. This dual enhancement in optical properties further underscores the multifaceted advantages offered by InSe/hBN heterostructures, making them compelling candidates for diverse applications.

Leveraging these insights, our work aims to comprehensively investigate the impact of strain on InSe/hBN heterostructures. Furthermore, the theoretical findings on the optical properties of InSe/hBN heterostructures, indicating enhanced absorption and a reduced band gap, inspire our exploration into the nuanced effects of strain. Understanding how strain influences the electronic and optical properties of InSe/hBN heterostructures is pivotal for optimizing their performance and unlocking their full potential for future technological applications.

2 Computational Methods

Density functional theory (DFT) were performed in the Quantum Espresso (QE) software package (Giannozzi 2009), based on plane waves and pseudopotentials. The Perdew-Burke-Ernzerhof (PBE) exchange correlation functional (Perdew et al. 1996) is used along with norm-conserving pseudopotentials. The energy cutoff of 90 Ry was set after the convergence tests.

The Monkhorst pack of 16x16x1 mesh for k-point sampling is used in geometric optimisation and total energy calculations. For calculations of p-DOS and optical properties, a refined 48x48x1 mesh is used. The band structure is calculated on 440 k-points along Γ -M-K- Γ direction. A vacuum of 20 Å is added along the z-direction to avoid interactions between the layers and simulate 2D structure. Geometry optimisation of the positions of the atoms and the lattice parameters is performed using the BFGS algorithm, with criteria for the maximum forces allowed between atoms of 10^{-6} Ry/Å. To properly account for van der Waals force effects, the Grimme-D2 correction (Grimme 2006; Barone et al. 2009) was included to obtain more accurate lattice constants and forces. The optical properties were calculated using the epsilon.x code in QE software, based on the random phase approximation (RPA).

3 Results

Similarly to hBN/InTe and hBN/GaTe HSs reported in our previous work (Šolajić and Pešić 2022; Šolajić and Pešić 2023), hBN/InSe HS is modelled as supercell composed of 1x1 unit cell of InSe, with $\sqrt{3} \times \sqrt{3}$ supercell of hBN rotated for 30° on top of InSe. Drawing parallels with our previous studies, this approach ensures consistency in our methodology.

For hBN, the unit cell's lattice constant (a) is $2.51\text{\AA}$, while the constructed $\sqrt{3} \times \sqrt{3}$ supercell has a lattice constant of $4.34\text{\AA}$. Comparatively, the calculated lattice constant for InSe is $4.03\text{\AA}$, closely mirroring the values obtained for GaTe in our earlier research (Šolajić and Pešić 2022), where $a = 4.05\text{\AA}$.

Searching for an energetically most favourable configuration, the constructed heterostructure undergoes relaxation, adjusting both the lattice parameter and atomic positions within the unit cell. The optimized lattice parameter for the hBN/InSe heterostructure converges to $a = 4.29\text{\AA}$. Notably, this relaxation induces a 1% strain on the hBN layer and a 6% strain on InSe. This pattern aligns with observations in our studies of hBN/GaTe and hBN/InTe, where the preference is for GaTe (InTe) to experience more significant strain than the hBN layer. Such strain variation arises from the different elastic properties inherent in the combined materials, providing valuable insights into the mechanical interplay within these heterostructures. Namely, the elastic constants of hBN are roughly 3 times larger than ones of InSe, as well the Young and layer modulus (Li and Li 2015; Šolajić and Pešić 2022), similar as in GaTe, leading to different strain strengths induced in each layer.

The application of uniform tensile and compressive biaxial strain, with a maximum amplitude of 6%, to the heterostructure induces significant transformations in its structural parameters. In the unstrained, relaxed configuration, the distance between the hBN layer and InSe, denoted as d , measures $3.29\text{\AA}$. Under compressive strain, d slightly decreases, reaching $3.26\text{\AA}$ for -6% strain, while under tensile strain, it increases, peaking at $3.30\text{\AA}$ for 6% . The bond lengths also undergo alterations with strain. In the absence of strain, the In-In bond length is $2.82\text{\AA}$, the In-Se bond is $2.73\text{\AA}$, and the In-Se-In angle is 103° . Under compressive strain, these bond lengths reduce: the In-In bond shortens to $2.79\text{\AA}$, the In-Se bond contracts to $2.66\text{\AA}$, and the In-Se-In angle decreases to 98.7° . Conversely, tensile strain leads to elongation of bonds and widening of angles. At 6% strain, the In-In bond extends to $2.85\text{\AA}$, the In-Se bond increases to $2.80\text{\AA}$, and the angle expands to 108° . These variations in geometry and covalent bond distances are anticipated to exert a profound influence on the heterostructure's band structure and band gap, providing crucial insights into the structural modifications induced by strain.

3.1 Electronic structure

In the absence of applied strain, representing the relaxed structure, band gap of hBN/InSe heterostructure is calculated to be $E_g = 0.56\text{ eV}$, which is less than the band gaps observed in both the hBN/InTe and hBN/GaTe heterostructures. To validate our results, we also calculated the band gap of the InSe monolayer, obtaining $E_g = 1.49\text{ eV}$, consistent with previous results using the same methodology (Hu et al. 2017). It is important to note that DFT calculations with standard functionals such as PBE often underestimate the band gap in semiconductors. For a more accurate assessment of the band gap, hybrid functionals (e.g. HSE06) are commonly employed. However, it has been observed that in group III monochalcogenides and related structures, the difference in band structures obtained using PBE and hybrid functionals primarily stems from variations in the width of the band gap, which tends to be larger (and more accurate) with hybrids. Notably, the valence bands remain largely unchanged within both methods, while the conduction bands are shifted upwards, largely preserving their shape. Taking into account the qualitatively similar band structures obtained using both methods, we opted for the PBE functional in this manuscript for our calculations. This decision was made due to the significant computational demands associated with calculations employing hybrid

functionals, especially in studies of systems under strain, where a large number of calculations are necessitated. The estimated error introduced in band gaps in our research is approximately in the range of 0.6–0.9 eV. Specifically, our calculations yield a band gap of 1.49 eV in InSe monolayer and 0.56 eV in hBN/InSe heterostructure without introduced strain; when hybrid functionals are used, band gaps of 2.37 eV and 1.16 eV are obtained for monolayer InSe and hBN/InSe heterostructure, respectively. A similar deviation in the band structure is expected in strained structures.

Figure 1 illustrates the relationship between band gap and strain for the hBN/InSe heterostructure, alongside the previously studied hBN/InTe and hBN/GaTe heterostructures for comparative analysis. In contrast to the behaviour observed in hBN/InTe, where the band gap enlarges up to 2% strain before declining, the band gap in hBN/InSe mirrors the trend observed in hBN/GaTe. Notably, it exhibits an almost linear dependence on applied strain. The widest band gap, $E_g = 1.37$ eV, is achieved under -6% strain. Conversely, tensile strain diminishes the band gap, reaching near-zero values at 6% strain. At this point, the energy level at the bottom of the valley in the Γ point of the valence band aligns closely with the energy level at the top of the conduction band valleys located between the Γ and M point, and between K and Γ point, leaving only the indirect gap between the valleys.

Analysing deeper the behaviour of bands proximate to the Fermi level and the composition of associated states reveals several key features, we present the band structure for different strain values illustrated in Fig. 2. Band structure is calculated along the Γ -M-K- Γ direction, and given that heterostructure consisted only of single-layered hBN and InSe is essentially two dimensional, hence the Brillouin zone is practically flat, and negligible contribution exist in the out-of-plane directions. Primarily, the valence band predominantly comprises states contributed by In and Se. Under compressive strain, the valley in the Γ point expands, while under tensile strain, it contracts, influencing the entire band. The conduction band behaviour is more peculiar. For tensile strain, the top of the conduction band rises, and the band closest to the Fermi level is predominantly composed from In and Se states. Conversely, with compressive strain, where top of the conduction band located between the Γ and M/K points is decreasing, at -4% strain, top of the conduction band relocates to the Γ point, and is predominantly composed of N states.

The projected density of states illustrated in Fig. 3 is showing more clear picture of atoms/states composition near the Fermi level. Near the Fermi level we predominantly

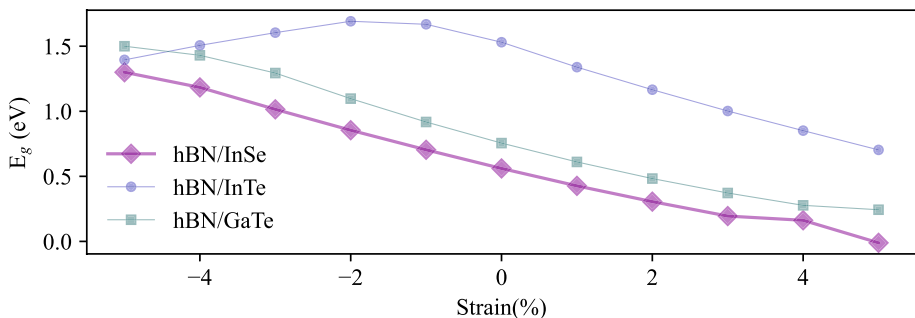


Fig. 1 Band gap as a function of strain for hBN/InSe (purple line with rhomboid markers), along with hBN/InTe (green line and square markers) and hBN/GaTe (blue line, circle markers) for comparison

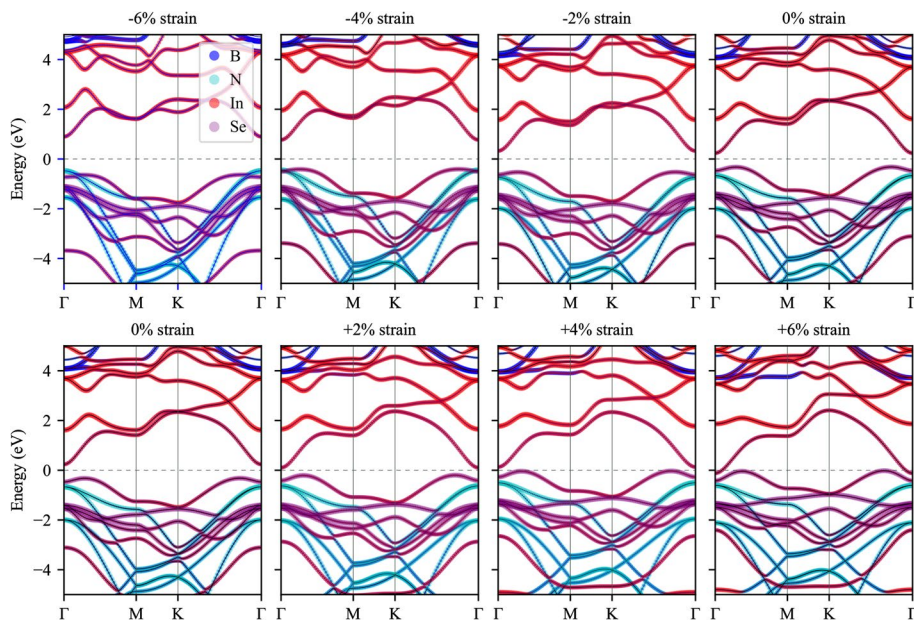


Fig. 2 Projected bandstructure of hBN/InSe HS for different values of applied strain, from -6% to $+6\%$. Contribution from different atoms/states are represented in different colours as in legend

observe Se p and In s states, for strain strengths in range of -4% to $+6\%$. For compressive strain of -4% and stronger, N p states are dominant below the Fermi level, and above the Fermi level, group of In p states is moved closer to the bottom of valence band.

3.2 Optical properties

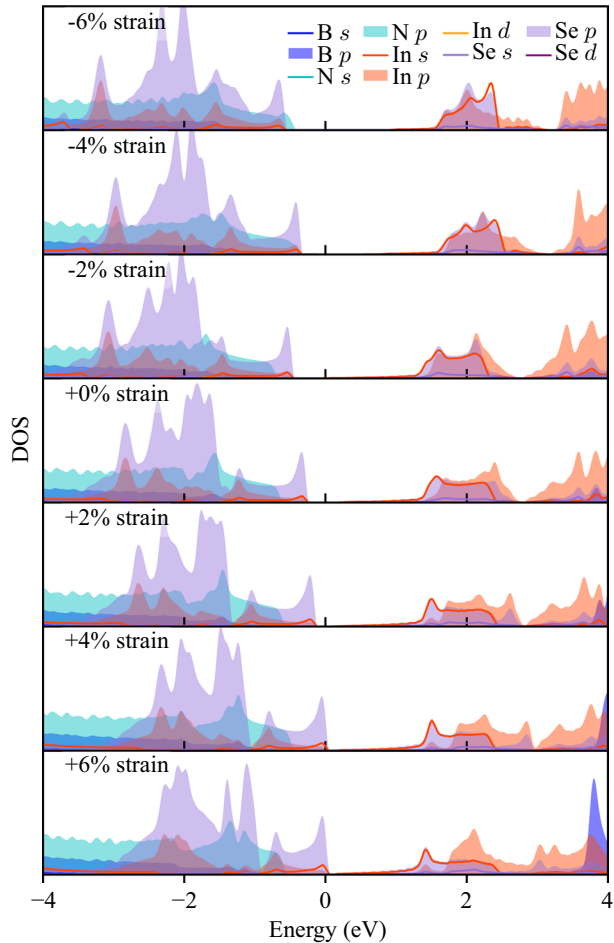
Consistent with our previous research, the optical properties were calculated within the random phase approximation (RPA). We were mostly interested to study how does the strain influence the absorption of heterostructure, and RPA was previously displayed as good performer for qualitative description of optical properties (Jalilian and Safari 2017; Liao et al. 2020; Zólyomi et al. 2014; Shang et al. 2018; Do et al. 2021; Sengupta et al. 2019). The complex dielectric function $\epsilon(\omega) = \epsilon_R(\omega) + i\epsilon_I(\omega)$ is calculated first. From there, we can get the absorption function as follows:

$$\alpha(\omega) = \sqrt{2} \frac{\omega}{c} \sqrt{\epsilon_R^2(\omega) + \epsilon_I^2(\omega)} - \epsilon_I(\omega). \quad (1)$$

Real and imaginary part of dielectric function are presented in Figs. 4 and 5.

In general, both the real and imaginary components of the dielectric function undergo shifts to the right under negative strain and to the left under positive strain, accompanied by alterations in peak amplitudes. However, notable deviations become evident. Under positive strain, specifically at $+4\%$ and beyond, the imaginary part of the dielectric function diverges to infinity at 0 eV. Concurrently, at the same energy, the real part of the dielectric function diverges towards $-\infty$, indicative of a transition towards a metallic character. In

Fig. 3 Projected density of states of hBN/InSe for different strain values. States from different atoms are presented as in legend



the case of z polarization, additional peaks in the imaginary part of $\epsilon(\omega)$ emerge above +4% strain at approximately 0.5 eV, subsequently dropping to zero at 1.25 eV and 3.75 eV. These distinct features in the dielectric response under strain provide valuable insights into the evolving electronic structure and the potential transition towards metallic behaviour.

Building on prior investigations of hBN/InSe (Shen et al. 2022), which showcased exceptional absorption across a broad spectrum comparable to hBN/InTe and hBN/GaTe, our focus turns to manipulating these properties through strain-induced enhancements. Figure 6 presents the absorption profile of the hBN/InSe heterostructure, considering in-plane (xy) and out-of-plane (z) polarizations. The observed behavior is in agreement with our findings in previously studied heterostructures. Our results affirm the outstanding wide-spectrum absorptive capabilities of hBN/InSe, consistent with the reported values in (Shen et al. 2022), where absorption peaks reach up to $8 \times 10^5 \text{ cm}^{-1}$, as well with hBN/In(Ga) Te HSs which showcase similar magnitude. In the xy polarization, compressive strain enhances absorption in the part of UV spectrum (6 eV to 11 eV), while the peak at 15 eV slowly diminishes. Conversely, tensile strain shifts this peak towards the left without losing its amplitude. Notably, tensile strains of +5% and above introduce a small peak in

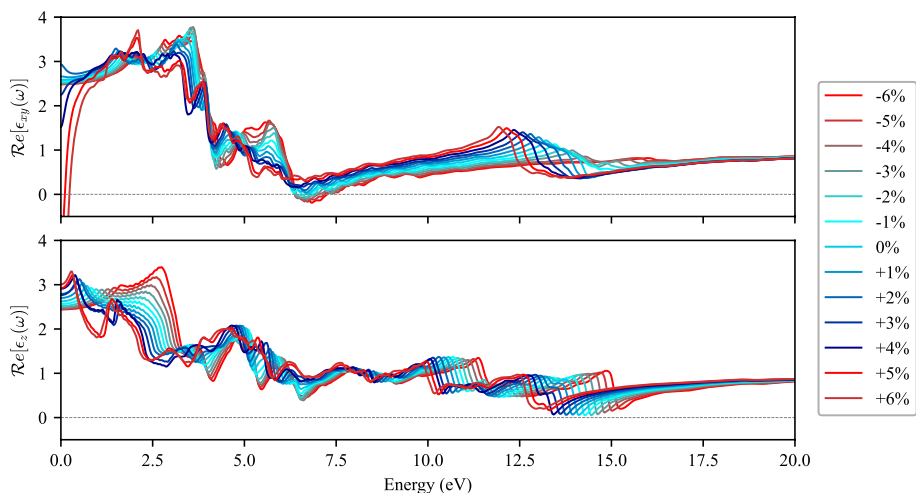


Fig. 4 Real part of complex dielectric function for (a) xy and (b) z polarization, for different values of strain

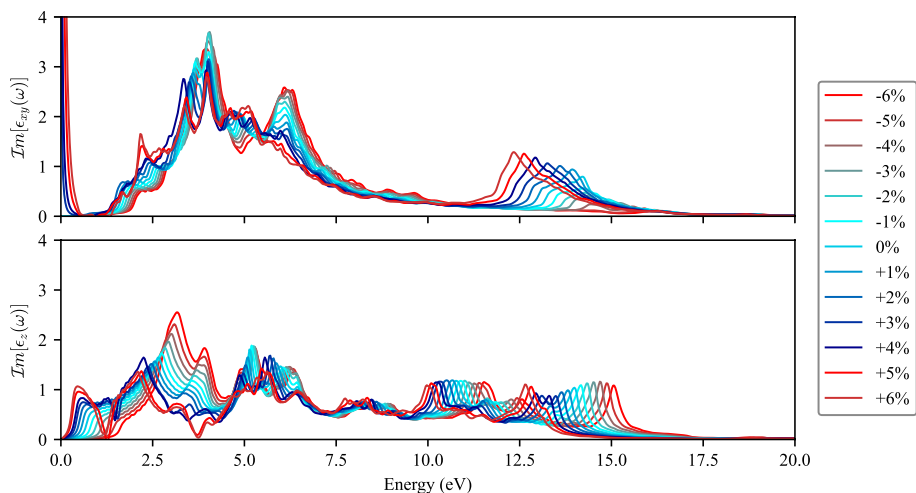


Fig. 5 Imaginary part of complex dielectric function for (a) xy and (b) z polarization, for different values of strain

the IR spectrum and enhance absorption in the visible range. In out-of-plane polarization, tensile strain shifts the absorption function leftward, slightly improving absorption in the visible spectrum, while compressive strains enhance the 2.5 eV to 4.5 eV region. However, stronger tensile strains of 5% and 6% result in a drop to zero absorption at 1.5 eV and 3.8 eV, a feature which is not observed in previously studied HSs. Most of those effects are ascribed to the change in the band gap as a function of strain, but also to different behaviour of specific band and the shape of their valleys, e.g. rising of Np states near the Fermi level at strong compressive strain. These substantial changes in absorption as a function of

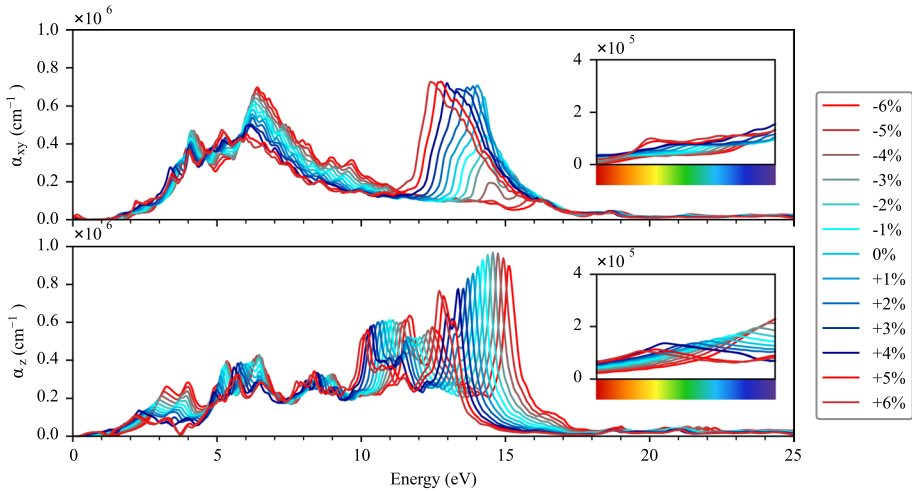


Fig. 6 Absorption function of hBN/InSe for xy and z polarization, for different values of strain. The inset shows the enlarged part within the visible-light part of the spectrum

strain offer a promising avenue for tailoring the properties of hBN/InSe for specific applications, particularly in the development of sensors and detectors.

4 Conclusion

In conclusion, we systematically explored the impact of strain on hBN/InSe heterostructures—an already established exceptional wide-spectrum absorber. Recognized for its promising electronic and mechanical properties, hBN/InSe emerges as a strong contender for future electronic and optoelectronic devices. Applying uniform biaxial strain in the range of -6% to 6% , our results unveil a highly effective method for manipulating the band gap, showcasing a particularly noteworthy outcome: near-complete elimination of the band gap under intense tensile strain. Comparing our findings with previous investigations on strain effects in hBN/InTe and hBN/GaTe heterostructures, hBN/InSe exhibits a striking resemblance to hBN/GaTe. However, the hBN/InSe system demonstrates a distinct trend of reaching lower band gap values under tensile strain, concurrently enhancing absorption in the low-energy spectrum. These outcomes bear considerable significance for guiding subsequent experimental endeavours and serve as a roadmap for more intricate theoretical explorations. With its established outstanding electronic and transport properties, coupled with highly tunable band gap and remarkable absorption characteristics, hBN/InSe stands poised to make a substantial impact on the advancement of future novel devices.

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Author's contribution AS performed calculations and prepared figures. Both authors wrote and reviewed the manuscript.

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Data availability Statement The datasets generated during and/or analysed during the current study are available from the corresponding author on request.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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Negative longitudinal magnetoresistance in the Dirac semimetal PtSe₂: Kondo effect and surface spin dynamics

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The emergence of negative longitudinal magnetoresistance in the topologically nontrivial transition-metal dichalcogenide PtSe₂ is studied. Low- T , high- $\mu_0 H$ transport is performed for arbitrary field directions, and an analytical framework is established. The source of the negative longitudinal magnetoresistance is identified as the Kondo effect stemming from Pt vacancies contributing an uncompensated spin exclusively at the sample surface. The concentration of vacancies and the sample thickness are identified as tuning parameters. The findings are substantiated by density functional theory, which corroborates the proposed Pt-vacancy model.

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I. INTRODUCTION

Beyond graphene [1], transition-metal dichalcogenides (TMDs; e.g., PtSe₂, NiTe₂, PdTe₂, WTe₂) support a plethora of exploitable features, such as the chiral magnetic effect (CME) [2,3], thickness-dependent semiconductor-to-semimetal transition [4], type-II Dirac cones breaking the Lorentz invariance [5], and topologically nontrivial surface states [6].

The presence of topological features is a consequence of TMDs possessing a Weyl- or Dirac-semimetallic nature, which opens avenues towards prospective computing practices [7,8] and a window to high-energy physics phenomena through the lens of quasiparticles at low temperatures [9–11]. Specifically, the materials host at least one pair of Weyl points (WPs) in their Brillouin zone. The WPs have a chiral charge of ± 1 , with the total chiral charge over the whole Brillouin zone vanishing. Weyl and Dirac semimetals can be distinguished according to symmetry: A Dirac semimetal hosts at least one Dirac point (DP) and preserves both the time-reversal symmetry (TRS) and inversion symmetry (IS), while for a Weyl semimetal at least one of these symmetries is broken and a pair of WPs emerges [12]. A DP can then be described as consisting of a pair of WPs with opposite chirality at the same momentum; thus, the DP is not chiral. A linear dispersion relation, $E \propto |\mathbf{k}|$, is found to connect the charge carrier energy E to the momentum $\mathbf{k}$ around the DP or WP, wherein charge carriers have zero effective mass. This linear band dispersion around a DP generates a Dirac cone. If the dispersion is

anisotropic with respect to $\mathbf{k}$, i.e., it is linear only along certain directions, the Dirac cone is type II tilted. In this case, the resulting surface states (boundary to trivial topology) are also anisotropic.

This occurs in PtSe₂, which hosts DPs located at the $\overline{\Gamma A}$ axis, around which the respective Dirac cones are type II tilted with respect to the selfsame $\overline{\Gamma A}$ axis. Strictly speaking, the DPs are established only in the bulk limit. Monolayers and bilayers of PtSe₂ are semiconducting [4,13], while a transition to a semimetallic behavior takes place for a thickness of three monolayers. Bulk PtSe₂ is AA stacked and is C_3 symmetric with respect to the out-of-plane axis $\overline{\Gamma A}$. This symmetry protects the accidental band crossing forming the type-II DPs. The projection of the bulk DPs onto the boundary between the Dirac semimetal and trivial topology is predicted to result in helical surface states along the edges of the crystal if the Fermi level is sufficiently close to the DP energy level [12,14]. These topological characteristics, combined with high electronic mobility, significant spin-orbit coupling, and stability under ambient conditions, make semimetallic PtSe₂ a top contender for employment in electronic [15], spintronic [16], and photonic [17] devices. Recent developments also point to PtSe₂ as a candidate for the experimental observation of the orbital Hall effect [18,19].

Here, low- T , high- $\mu_0 H$ transport in PtSe₂ is carried out in order to gain insight into the electronic properties of the system. In particular, the origin of the negative longitudinal magnetoresistance (NLMR) detected at temperatures $T \leq 2.5$ K [3,20] is explored. The presence of a Kondo effect is identified and is heralded by a global nonzero-temperature resistance minimum and a NLMR. The origin and the observed thickness dependence of the Kondo effect are elucidated via *ab initio* calculations.

II. EXPERIMENT

The PtSe₂ flakes considered in this work were obtained by mechanical exfoliation from a bulk crystal grown by HQ Graphene [21], instead of by direct selenation of Pt.

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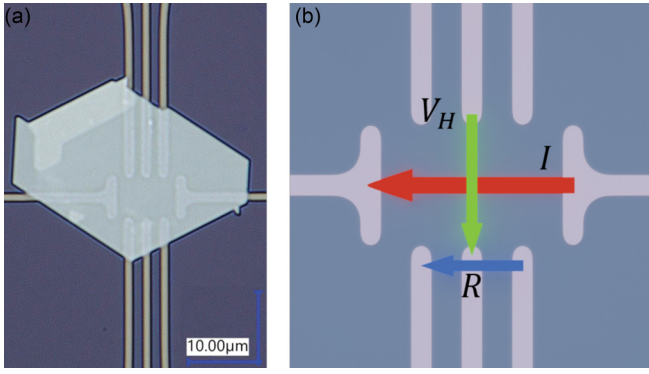


FIG. 1. (a) Optical image of sample B. (b) Schematic of the Hall bar with the current density direction I (thick red arrow). The thinner arrows represent the selection of voltage terminals for a measurement of the longitudinal resistance R (blue) and of the Hall voltage V_H (green).

This ensures high crystallinity and long-range order, as confirmed by optical microscopy, shown in Fig. 1(a), along with atomic force microscopy and Raman spectroscopy, depicted in Figs. S1 and S2, respectively, in the Supplemental Material [22]. The optical microscopy shows that the angles between flake edges comprise $n \times 60^\circ$, $n \in \mathbb{N}$. Atomic force microscopy additionally resolves the flake facets are flat. Raman spectroscopy confirms the expected structural phase. Three representative PtSe_2 samples, labeled A, B, and C, with thicknesses in the range of 20 nm are listed in Table I. The selected 20 nm regime provides a bulk band structure while allowing a spread of surface-to-bulk ratios from 18 to 26 nm. The flakes are placed onto Pt contacts, which are patterned by electron-beam lithography. Sample A has a six-terminal Hall-bar design with a $3 \times 5 \mu\text{m}^2$ measuring area. Sample B has an eight-terminal Hall-bar design with a $5 \times 7 \mu\text{m}^2$ measuring area, rendered in Fig. 1(b), where the current density direction and exemplary voltage terminal selections for the measurement of the longitudinal resistance and the Hall voltage are marked. An optical image of sample B is shown in Fig. 1(a). The superseding eight-terminal design is introduced because of symmetry considerations for terminal pairs normal to the source drain and increased fault tolerance via redundancy. For sample C a design identical to that of sample B is chosen. Finally, Au wires are bonded to the Pt contact pads using In as a solder agent. The low- T , high- $\mu_0 H$ transport measurements are then carried out in a Janis Super Variable Temperature 7TM-SVM cryostat equipped with a 7 T superconducting magnet and a homemade rotatory sample holder (SH) with two angular degrees of freedom. A lock-in amplifier ac technique at 277 Hz is employed to measure the

TABLE I. Considered PtSe_2 samples together with thickness and Hall-bar geometry.

Sample	Thickness t (nm)	Hall-bar design
A	18	Six-terminal
B	20	Eight-terminal
C	26	Eight-terminal

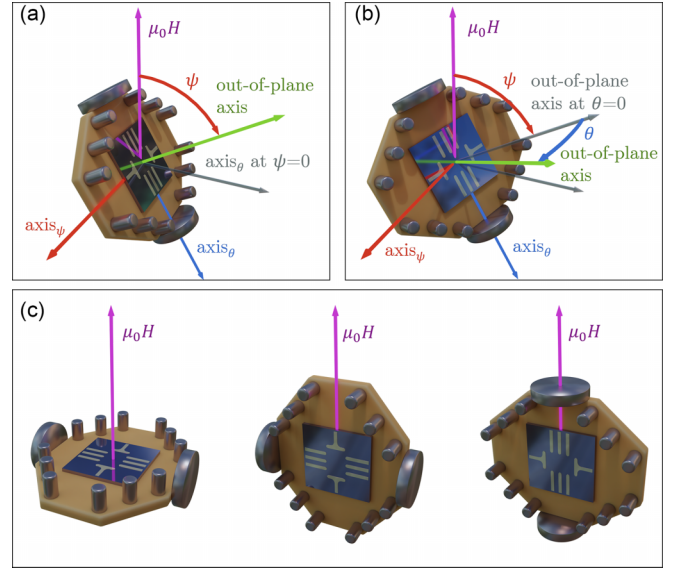


FIG. 2. Sketch of the SH and of the substrate with the Hall bar, showing the rotation axes axis_θ and axis_ψ and the respective angles θ and ψ , as well as the applied magnetic field and the SH out-of-plane axis. (a) A rotation around axis_ψ puts the SH into a $(0, \psi)$ orientation. (b) An additional rotation around axis_θ results in a (θ, ψ) orientation. (c) The $(0,0)$ orientation (left), $(90,0)$ (middle), and $(90,90)$ (right).

magnetotransport properties of the exfoliated PtSe_2 flakes. The SH allows rotation along the axis_ψ , a static axis normal to $\mathbf{H}$ (the vector of applied magnetic field), and ψ is the angle measured between the SH out-of-plane axis and $\mathbf{H}$ [Fig. 2(a)]. The substrate is mounted onto the SH such that, in the $(0,0)$ orientation, the current density direction coincides with the axis_ψ . An additional rotation along the axis_θ is available, with axis_θ being normal to the axis_ψ and rotating with the SH. The resulting angle θ is measured between the out-of-plane axis of the SH and the plane spanned by $(\mathbf{H} \wedge \text{axis}_\theta)$, depicted in Fig. 2(b). The orientation of the SH is thus defined by (θ, ψ) , with θ and ψ given in degrees. In Fig. 2(c), the orientations $(0,0)$, $(90,0)$, $(90,90)$ are depicted (from left to right). The specification of θ and ψ differs from the conventional designation of spherical coordinates by the fact that the axis_θ itself rotates along with ψ . For samples with IS, such as PtSe_2 , $\psi \rightarrow -\psi$ and $\theta \rightarrow -\theta$ are expected to be unity operations. For sample A, the rotation is monitored using the sample's Hall voltage as well as that of a graphite Hall bar mounted at an angle of 90° with respect to the SH out-of-plane axis. For samples B and C, the orientation is established via increments driven by the stepper motors responsible for the ψ and θ rotations.

III. RESULTS AND DISCUSSION

A. Temperature dependence of the resistance

To obtain the longitudinal resistance, voltage probing terminals are chosen on the same side of the drain-source centerline of the Hall bar. Zero-field-cooled (ZFC) measurements are carried out by cooling the sample in the absence of a magnetic field. The ZFC behavior of the resistance as

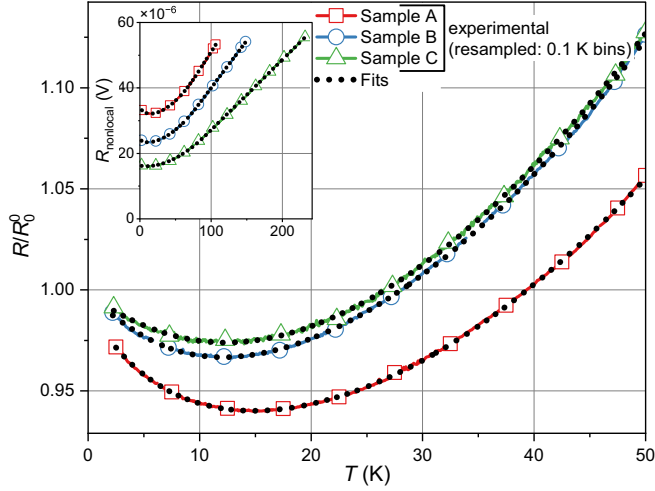


FIG. 3. Resistance ratio $\frac{R}{R_0^0}$ over temperature at zero magnetic field for the considered samples. The respective fits are shown as dotted lines. Inset: The resistance R increases $\propto T$ for $T > T_{\text{lin}} \approx 80$ K. The fitting parameters are available in Tables S1 and S2 of the Supplemental Material [22].

a function of temperature for the three samples is shown in Fig. 3: The resistance ratio to the theoretical zero-field zero-temperature resistance, R/R_0^0 , initially decreases with temperature, as shown in the inset, and a minimum resistance is found at $T \sim 12$ K for all samples. As the temperature is further reduced, the resistance increases again. The data are resampled into 0.1 K bins (evaluated as the average of all data points inside the bin). The absolute resistance R over a larger temperature range is provided in the inset of Fig. 3.

This characteristic is the consequence of two features: (1) The semimetallic nature of PtSe₂ gives rise to a Fermi-liquid behavior and a lattice vibration term at low temperatures, and (2) a Kondo effect causes an increase in resistance for $T \rightarrow 2$ K. The Kondo effect describes scattering processes in which the charge carrier spin is exchanged with the spin of a magnetic impurity (twice), altering the wave vector of the charge carrier. This leads to a logarithmic correction to the resistance. A minimum-resistance temperature is obtained for antiferromagnetic (i.e., negative) coupling of the charge carrier spin to the impurity spin [23]. The resistance is not assumed to diverge for $T \rightarrow 0$ because the impurity spins are screened by interacting charge carriers for $T \lesssim T_K$, with T_K being the Kondo temperature. The Kondo effect also acts in the case of magnetic moments resulting from vacancies, and both Pt and Se vacancies are, indeed, observed in PtSe₂ [24,25]. On the sample surface, these Pt vacancies contribute an uncompensated spin density. Consequently, the thinnest sample, sample A, reaches the lowest $\frac{R}{R_0^0}$ value, while the thickest sample, sample C, exhibits the highest minimum $\frac{R}{R_0^0}$ value.

The semimetallic resistance R_{SM} accounting for the Fermi-liquid behavior (electron-electron coupling) and the electron-phonon coupling is given by

$$R_{\text{SM}}(T) = R_{\text{res}} + A_F T^2 + A_{\text{ph}} T^5, \quad T \leq T_{\text{lin}}, \quad (1)$$

where $T_{\text{lin}} \approx 80$ K is the transition temperature from the regime in which the resistance is given by the sum of the quadratic Fermi-liquid behavior and the $\propto T^5$ lattice vibration term to the linear regime. The theoretical residual resistance at $T = 0$ (without the contribution of the Kondo effect) is R_{res} , and A_F and A_{ph} are prefactors of the Fermi liquid and the lattice vibration resistance, respectively. For $T_K \ll T_{\text{lin}}$, the linear regime is not relevant for the analysis of the Kondo effect. The expression for $R_{\text{SM}}(T)$ at arbitrary temperatures is given in Eq. (S2) in the Supplemental Material [22].

Analytical descriptions of the Kondo effect are elusive and often valid only over a limited range of parameters [26]. In particular, temperature ranges around $T \approx T_K$ are challenging to treat. An expression for the Kondo resistance is adapted from Ref. [27], in that the prefactor $\frac{1}{2}R_{K0}$, with R_{K0} being the (maximum) Kondo resistance, is introduced to account for the nonlocal resistance differing from the local resistance by a constant factor. The original prefactors are contained in R_{K0} . The expression for the Kondo resistance then becomes

$$R_K(T) = R_{K0} \frac{1}{2} \left(1 - \frac{\ln(T/T_K)}{\sqrt{\ln(T/T_K)^2 + S(S+1)\pi^2}} \right). \quad (2)$$

Here, The Kondo temperature is given by T_K , and S is the impurity spin. Strictly speaking, S is not a good quantum number since it models the spin of hybrid orbitals and should thus not be understood as an actual spin quantum number.

The zero-field resistance $R(H = 0, T)$ is obtained as

$$R(H = 0, T) = R_{\text{SM}}(T) + R_K(T) \quad (3)$$

and is employed to fit the obtained ZFC data, which are shown in Fig. 3 as dotted lines. The total resistance at zero field and zero temperature is given by $R_0^0 = R(H = 0, T = 0) = R_{\text{res}} + R_{K0}$, and H is the magnitude of the magnetic field $|\mathbf{H}|$. The observation of a global resistance minimum R_{min} is an indication of the onset of the Kondo effect. As the thickness t of the samples increases ($t_A < t_B < t_C$), the Kondo resistance R_{K0} decreases, which can be explained by considering the system as a bulk conductance channel, except for the surface, where Pt vacancies form uncompensated spins which yield a Kondo resistance. The retrieved values of S are given in Table S1 in the Supplemental Material [22] and are comparable to those reported in Ref. [25].

B. Magnetic field dependence of the resistance

The (longitudinal) magnetoresistance (MR) is probed by choosing voltage probing terminals on the same side of the drain-source centerline but keeping the temperature constant while sweeping the magnetic field. A NLMR is observed for all samples when taking the MR in the (90,0) orientation, as depicted in Fig. 4, which shows the resistance $R - R(H = 0)$ decreasing for increasing H . The onset of saturation is observed for $\mu_0 H > 4$ T. The relative magnitude of the NLMR is greatest for the thinnest sample, sample A, and diminishes with sample thickness.

Since in this orientation there are no magnetic field components normal to the electric field $\mathbf{E}$, orbital magnetoresistance can be ruled out. The NLMR is attributed to the Kondo effect: With the application of a magnetic field, the spin-flip

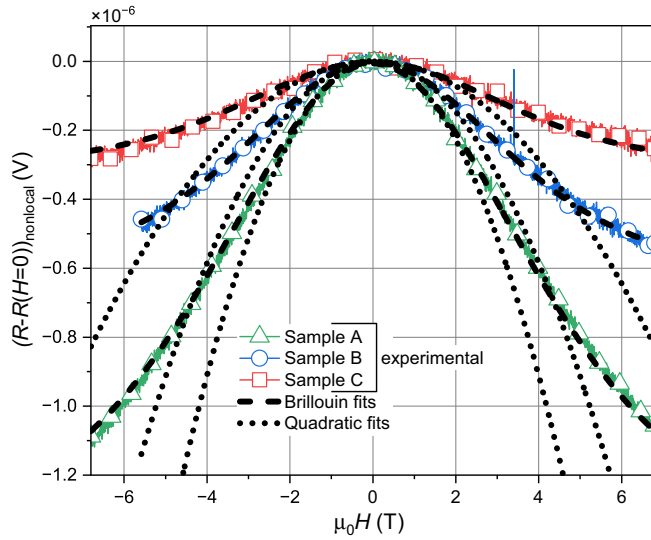


FIG. 4. Resistance $R - R(H = 0)$ over applied magnetic field for all samples in the (90,0) orientation, isolating the Kondo effect from any orbital magnetoresistance. Dotted lines: Quadratic fits. Dashed lines: Fits performed according to Eq. (4). The resulting parameters are available in Tables S3 and S4 in the Supplemental Material [22].

scattering, which is the cause of the Kondo resistance, is inhibited via polarization of the impurity spins and of the charge carrier spins. The slope of $R(H, T)$ plateaus for $H \rightarrow \infty$ due to saturation of the polarization. This effect is assumed to take place isotropically for any direction of $\mathbf{H}$.

Without detailed knowledge of the orbital nature of the uncompensated spins at the surface of the PtSe₂ flake and thereby of the coupling of the vacancy spins with the conduction electrons or their magnetization $\mathbf{M}(\mathbf{H})$, the magnetic field dependence of the Kondo resistance $R_K(H, T)$ cannot be described rigorously at arbitrary temperatures and fields. Analytical descriptions are challenged in the regime where H induces a partial, but non-negligible, polarization of the impurities.

A quadratic dependence $R(H) \propto -\alpha(\mu_0 H)^2$, $\alpha > 0$, is obtained by approximating a low-spin-density expansion around $H = 0$ [25,28], which can be fitted satisfactorily to the data for $\mu_0 H < 2$ T. The fit is shown by the dotted lines in Fig. 4.

In order to take the magnetization saturation into account, the model has to be modified for magnetic fields higher than $\mu_0 H \approx 2$ T. Thus, Eq. (2) is complemented by an impurity spin polarization factor, which accounts for the charge carrier spins aligning with the impurity spins. At $H \rightarrow \pm\infty$, the polarization saturates [29,30]:

$$R_K(H, T) = R_K(T) \left[1 - \mathfrak{B}_J \left(\frac{g\mu_B \mu_0 H}{k_B(T + T_K)} \right)^2 \right], \quad (4)$$

where $\mathfrak{B}_J$ is the Brillouin function for the total angular momentum magnitude $J = \frac{1}{2}$, g is the Landé g factor, μ_B is the Bohr magneton, and μ_0 is the vacuum permeability. It can be seen from the Brillouin fits in Fig. 4 (dashed lines) that this model reasonably fits the data, accounting for the required saturation behavior.

A CME (or Adler-Bell-Jackiw anomaly) may also be considered as a source of the NLMR, as previously reported for PtSe₂ [3,20]. In the context of solid-state physics, a CME describes the generation of a chiral current, usually in Weyl and Dirac semimetals [9,12]. In the case of Dirac systems, the DP has net-zero chirality, and the breaking of symmetries is required for the CME to occur: If the TRS is broken via the application of an external magnetic field $\mathbf{H}$, the chiral degeneracy of the (quadruply degenerate) DP is lifted, and the DP splits along $\mathbf{H}$ into a pair of (doubly degenerate) WPs. By applying an electric field $\mathbf{E}$ parallel to $\mathbf{H}$, a chemical potential difference $\Delta\mu$ is established between the WPs, effectively pumping chiral charge carriers by moving them from one WP to the one with opposite chirality. The system still possesses net-zero chirality, and the chiral charge conservation leads to the chiral charge carriers having to relax at the opposite WP (or via scattering). Resulting from the chemical potential difference $\Delta\mu$ between the WPs, a chiral current density emerges. Since the chiral charge carriers have an electric charge, an electric current density is established concurrently with the chiral one, resulting in a NLMR. This effect requires components of $\mathbf{E} \parallel \mathbf{H}$, and the chiral current density $\mathbf{J}_C$ diminishes according to

$$|\mathbf{J}_C| \propto [\cos \angle(\mathbf{E}, \mathbf{H})]^2. \quad (5)$$

Because the obtained NLMR in the examined samples is robust with respect to $\angle(\mathbf{E}, \mathbf{H})$ and persists even at the $(\pm 90, \pm 90)$ orientations ($\mathbf{E} \perp \mathbf{H}$ and $\mathbf{H}$ in plane), a CME does not conform to the acquired data. The observed modulation of the Kondo effect by sample thickness also cannot be understood in the frame of a CME. A contribution to the already-negative MR in the $\mathbf{E} \parallel \mathbf{H}$ configuration should not be excluded, but it cannot be the dominant effect causing the detected NLMR and cannot explain the increase in resistance observed for $T \rightarrow 0$.

Further, it is unclear whether the type-II DP in PtSe₂ can make a reasonable contribution to the conductivity since the DP is found ≈ 1.2 eV below the Fermi energy E_F [31]. From the calculated band structures, type-I DPs above E_F can also be considered [31,32]. It was shown that the CME conductance is $\propto (E_F - E_{DP})^{-2}$ [33], with E_{DP} being the energy at the DP. This lessens the need for DPs close to E_F in order to obtain a significant conductivity contribution. Another option is to consider defects which modify E_F , potentially bringing it closer to a DP and, again, increasing the CME contribution to the conductivity. It is therefore realistic that PtSe₂ could host a CME.

Since the MR remains negative even in the $(\pm 90, \pm 90)$ orientations, current jetting [34] is an unlikely source of NLMR since it should scale with $\propto [\cos \angle(\mathbf{E}, \mathbf{H})]^2$. Additionally, the well-defined Hall-bar geometry should not enable current jetting at arbitrary angles. Furthermore, current jetting explains neither the saturation of the NLMR for $H \gtrsim 4$ T nor the increase in resistance observed for $T \rightarrow 0$.

In the (0,0) orientation, the MR is positive for all samples and varies only slightly over the measured temperatures for $T \leq 50$ K. The resistance $R - R(H = 0)$ over applied magnetic field in the (0,0) orientation is given in Fig. 5 for sample A and in Fig. S10 in the Supplemental Material [22] for samples B and C.

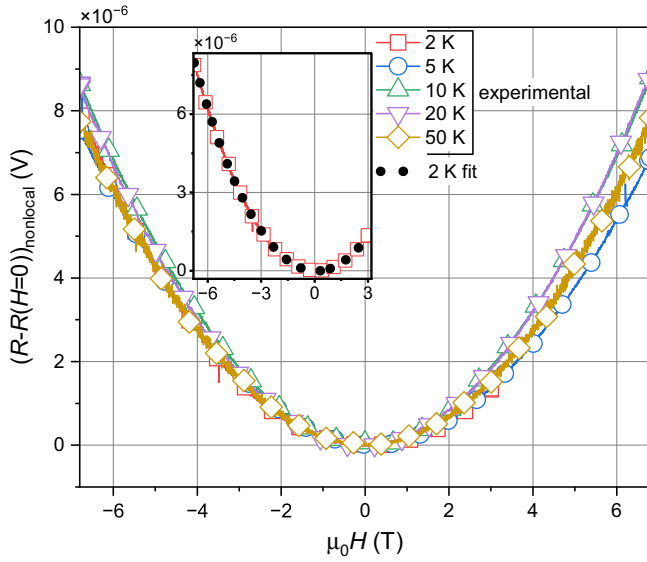


FIG. 5. Resistance $R - R(H = 0)$ of sample A over applied magnetic field in the (0,0) orientation over a temperature range of 2–50 K. Inset: Fit (dotted line) at 2 K. The obtained parameters are provided in Table S5 in the Supplemental Material [22].

The observed evolution of the resistance is $\approx (R \propto H^2)$, pointing at a system dominated by orbital MR. The weak temperature dependence can be explained by the fact that all data lie in the Fermi-liquid regime for $T < T_{\text{lin}} \approx 80$ K. The magnetic field components $\mathbf{H} \parallel \mathbf{E}$ do not contribute any orbital MR, given that the resulting Lorentz force is zero. Due to the finite sample thickness and to the crystalline anisotropy inherent in PtSe₂ [35], components of $\mathbf{H}$ out of plane and in plane give rise to distinct orbital MR effects. It is worth noting that because of the isotropic nature of the Kondo effect, the orbital MR cannot be singled out in the temperature range around T_K .

The orbital MRs thus require separate fitting parameters for the orientations

$$\mathbf{o} \in \{\perp, \parallel\} = \{\text{out of plane, in plane}\}. \quad (6)$$

This treatment is similar to the introduction of an anisotropic electron mass [36]. The description of the orbital MR $R_{\text{orb},\mathbf{o}}$ in orientation $\mathbf{o}$ is given by

$$R_{\text{orb},\mathbf{o}}(H) = M_{\mathbf{o}} |\mu_0 H|^{p_{\mathbf{o}}} + k_{\mathbf{o}} \mu_0 H, \quad \mathbf{o} \in \{\perp, \parallel\}. \quad (7)$$

Here, the parameter $M_{\mathbf{o}}$ models the magnitude of the MR, $p_{\mathbf{o}}$ is the power with which the MR scales ($p_{\mathbf{o}} = 2$ for a Fermi liquid), and $k_{\mathbf{o}}$ is a linear correction term to account for temperature gradients and imperfect geometry of the contacts to the flake. The fit for the total resistance of sample A in the (0,0) orientation at $T = 2$ K, shown in the inset of Fig. 5, is as follows:

$$R(H) = [R_{\text{SM}}(T) + R_K(H, T)]|_{T=2\text{ K}} + R_{\text{orb},\mathbf{o}}(H), \quad (8)$$

with $R_{\text{SM}}(T) + R_K(H, T)$ determined by fitting the field cooling of sample A in the $(-90, 0)$ orientation (which has no orbital effect components). The weak temperature dependence of $R_{\text{orb},\mathbf{o}}$ and the reduced magnitude of $M_{\parallel}$ versus $M_{\perp}$ can

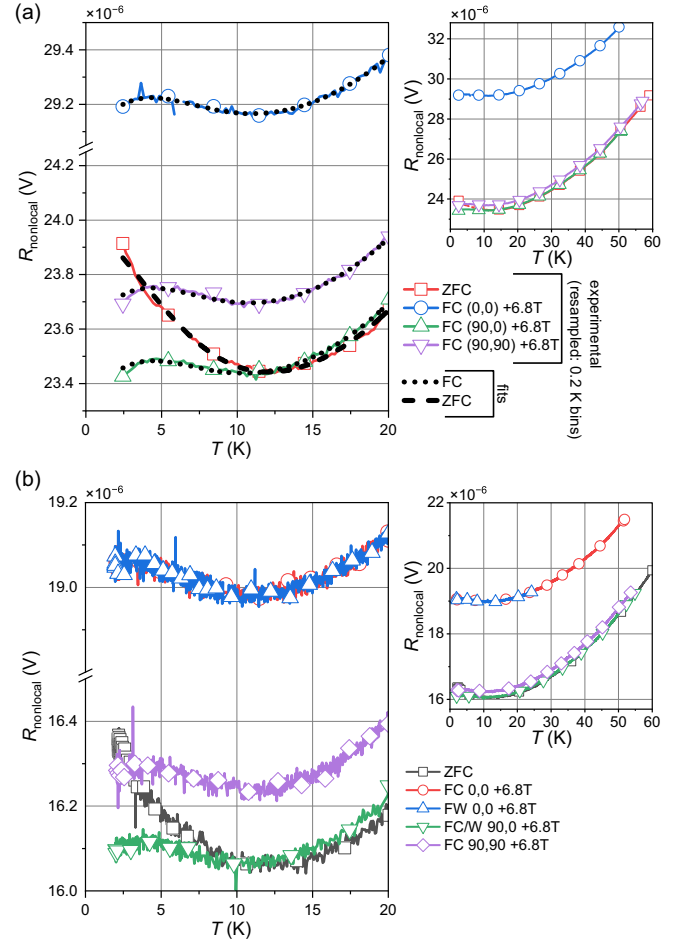


FIG. 6. Resistance over temperature curves [zero-field cooling and field cooling/field warming (FW)]. (a) Sample B. Left panel: Over a temperature range of $T < 20$ K, including an axis break. Dotted lines: Fit of the field cooling. Dashed lines: Fit of the zero-field cooling. The resulting fit parameters are given in Table S6 of the Supplemental Material [22]. Right panel: Over a temperature range of $T < 60$ K. (b) Sample C. Left panel: Over a temperature range of $T \leq 20$ K, including an axis break. The FW in the (0,0) orientation is indistinguishable from the respective field cooling. Right panel: Over a temperature range of $T < 60$ K.

also be gleaned from Figs. 6(a) and 6(b), where the resistance-over-temperature (R - T) curves for samples B and C are given.

C. Unified transport model

The stability of the NLMR with respect to T and ψ at $\theta = \pm 90^\circ$ ($\mathbf{H}$ rotating in the sample plane) is explored in order to discriminate the Kondo effect from a CME: For sample B at 2 K, the NLMR persists for arbitrary ψ , as depicted in Fig. 7, where the resistance $R - R(H = 0)$ over H is shown at specific values of ψ . Larger ψ angles result in higher resistances towards high fields. In the orientation $(-90, 15)$, sample A shows a resistance minimum for $\mu_0 H \approx \pm 5$ T at 2 K, as seen in Fig. 8(a), depicting the resistance $R - R(H = 0)$ over H at specific temperatures. Upon increasing T , the NLMR diminishes, transitioning to a purely positive MR between 3 and 4 K.

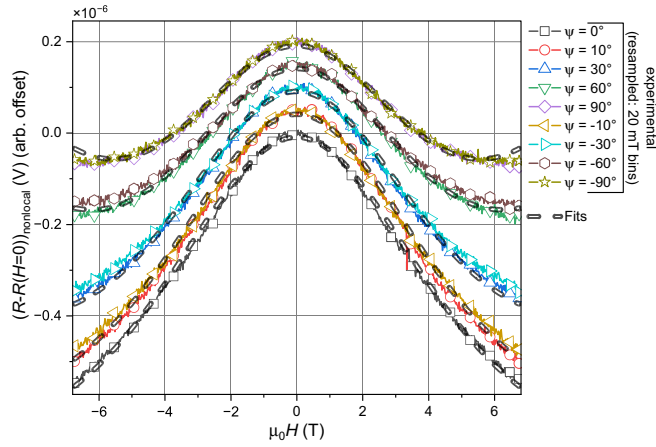


FIG. 7. Resistance over applied magnetic field curves of sample B at 2 K for orientations (90° , $(-90^\circ \leq \psi \leq 90^\circ)$), including fitting functions. Arbitrary offset. Data are resampled every 20 mT, and linear components are disregarded to better compare them to the fit. The parameters are available in Table S7 in the Supplemental Material [22].

The measurements elucidate the competition between the Kondo effect and the orbital effect: While the Kondo effect causes a NLMR and is isotropic, the in-plane orbital effect scales approximately quadratically but requires components $\mathbf{H} \perp \mathbf{E}$, which increase for $\psi \rightarrow \pm 90^\circ$. In sample B, even at $\psi = \pm 90^\circ$, a field of $\mu_0 H = \pm 6.8$ T is not sufficient to reach a regime dominated by the orbital effect. An orientation of $(-90, 15)$ in sample A is employed to shift the minimum resistance below 6.8 T. The contribution from the Kondo effect diminishes with increasing temperature, resulting in the minimum resistance shifting to $H = 0$ as the orbital effect dominates the system. No orbital effect emerges if the sample is rotated to $(\pm 90, 0)$ and the resulting MR is a constant for temperatures $T \geq 5$ K, as seen in Fig. 8(b), where the resistance $R - R(H = 0)$ over H is shown at specific temperatures.

This motivates a description of the resistance for arbitrary values of T , H , ψ , and θ , which requires the consideration of the semimetallic term $R_{SM}(T)$ of the Kondo term $R_K(H, T)$ and of the orbital terms $R_{orb,o}(H)$, which are modulated by an angular dependence:

$$\begin{aligned} R_{orb,\perp} &\propto (\cos \theta)^2 (\cos \psi)^2, \\ R_{orb,\parallel} &\propto [\text{const}(\theta)] (\sin \psi)^2. \end{aligned} \quad (9)$$

To substantiate the angular dependence of $R_{orb,o}$, the orientation of sample B is swept at a constant field of $H = 6.8$ T while the longitudinal resistance is measured. The resistance $R - \langle R \rangle_{\{\theta, \psi\}}$ as a function of ψ or θ is shown in Fig. 9, with $\langle R \rangle_{\{\theta, \psi\}}$ being the average of R over the respective angle θ or ψ . The in-plane sweep results in a minimum resistance for $\psi = 0^\circ$, as depicted in Fig. 9(a), where no (positive) orbital terms are present. The out-of-plane sweep is shown for $\psi = 0^\circ$ in Fig. 9(b), presenting the maximum resistance at $\theta = 0^\circ$, for which the maximum out-of-plane orbital magnitude is expected. The out-of-plane sweep for $\psi = \pm 90^\circ$, also reported in Fig. 9(b), shows an expectedly negligible effect since the sweep corresponds to a rotation axis parallel to $\mathbf{H}$.

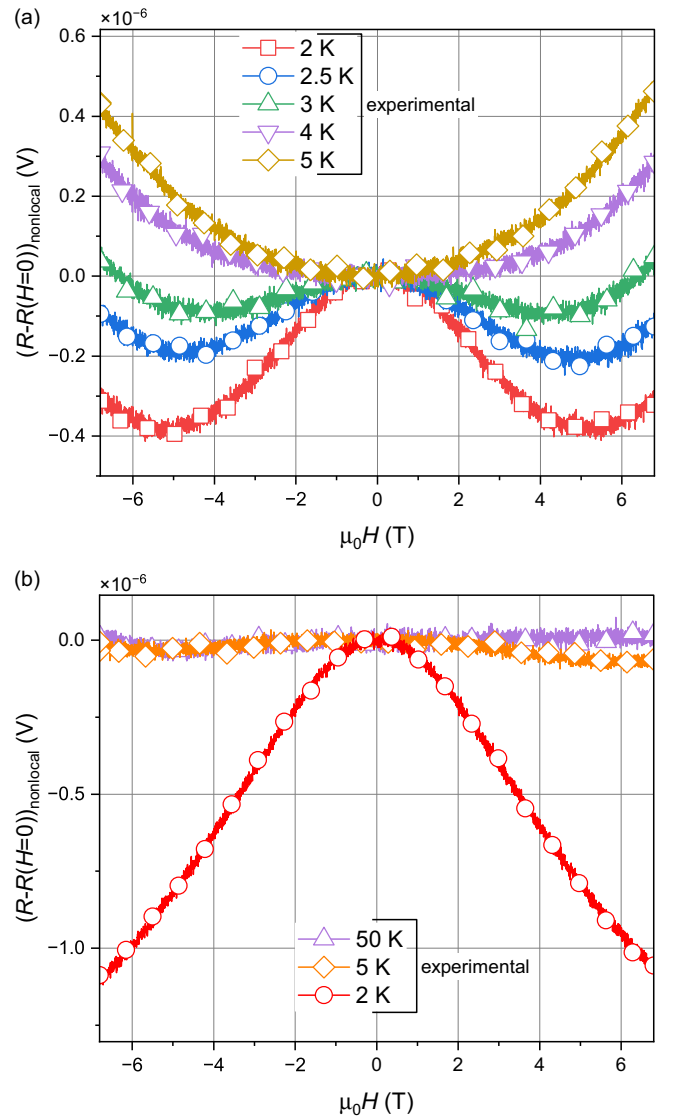


FIG. 8. Resistance $R - R(H = 0)$ over applied magnetic field curves of sample A at various temperatures. (a) For $(-90, -15)$ orientation. (b) For $(-90, 0)$ orientation.

The general description of the longitudinal resistance is given by

$$R(H, T, \theta, \psi) = R_{SM}(T) + R_K(H, T) + \sum_o R_{orb,o}(H, \theta, \psi). \quad (10)$$

The expanded form is provided in Eq. (S3) in the Supplemental Material [22].

The field-cooled (FC) measurements are carried out by cooling the sample in a constant magnetic field while measuring the longitudinal resistance. Using Eq. (10), zero-field coolings and field coolings can be fitted for arbitrary values of θ and ψ , as shown for sample B in Fig. 6(a). The magnetic field direction merely affects the amplitude of the orbital MRs, which are only weakly temperature dependent for $T \lesssim 50$ K. Therefore, FC curves with different orientations differ mainly by a constant offset. In the range of $T < 10$ K, the deviation between the fits and the data is a consequence of all curves

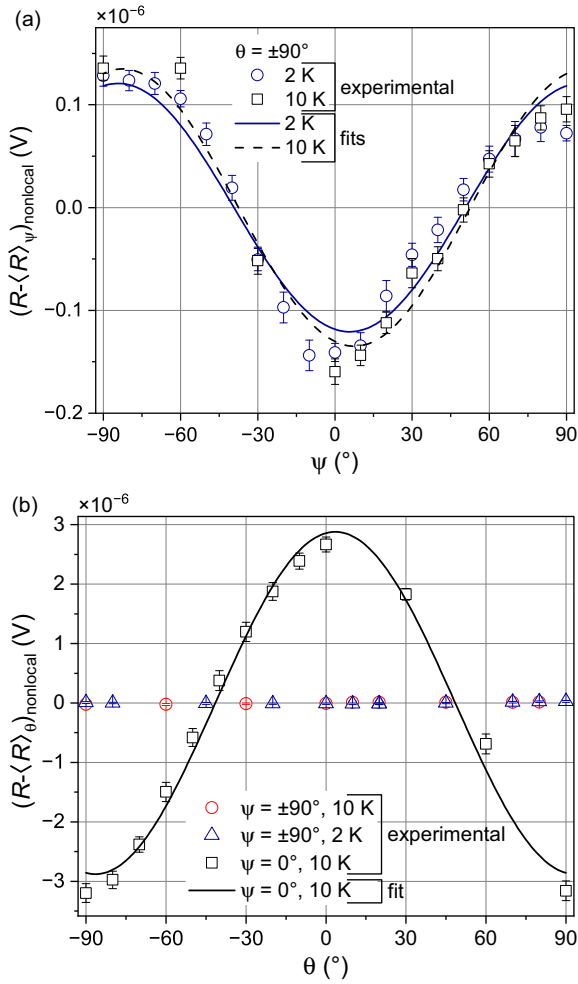


FIG. 9. Resistance upon rotating sample B at 6.8 T for 2 and 10 K. (a) Sweeping ψ at $\theta = \pm 90^\circ$. Solid and dashed lines show fits for 2 and 10 K, respectively. Resistance is given as the deviation from the mean value of the fitting function. (b) Sweeping θ at $\psi = 0^\circ$ and $\psi = \pm 90^\circ$. The line shows the fit for $\psi = 0^\circ$ and 10 K. Resistance for $\psi = 0^\circ$ is given as the deviation from the mean value of the fitting function and for $\psi = \pm 90^\circ$ as a deviation from the mean value. The obtained fit parameters for both (a) and (b) are provided in Table S8 in the Supplemental Material [22].

being fitted with shared values for the parameters T_K and S , resulting in $T_K = 4.59$ K and $S = 0.086$. This suggests that the description can be refined by employing the actual (unknown) magnetization $\mathbf{M}(H, T)$ of the vacancies instead of $\mathfrak{B}_J$.

A visual representation of the magnitude of the Kondo effect is provided in Fig. 10: The rendered $R(H, T, \theta = 90^\circ, \psi = 0)$ surface represents the T and H dependences and includes relevant resistance points that define the shape of the surface in parameter space.

The in-plane behavior observed in Fig. 7 is also fitted satisfactorily. However, for $\mu_0 H \gtrsim 5$ T, it can be gleaned that the curve produced by the fit slightly underestimates the resistance for small ψ and somewhat overestimates it for $\psi \rightarrow \pm 90^\circ$. This again points to a deviation between $\mathbf{M}(H)$ and $\mathfrak{B}_J(H, T)$.

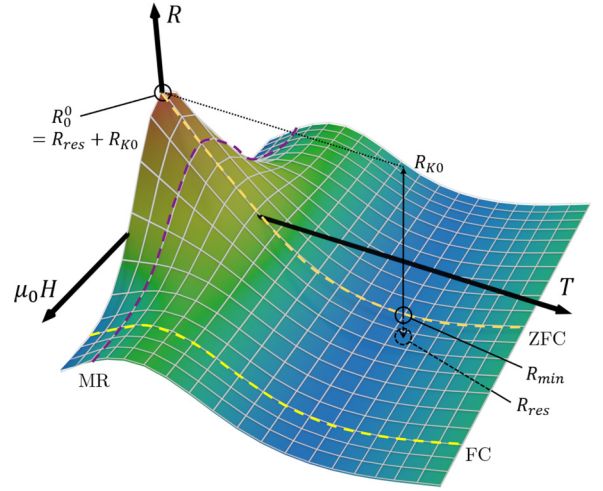


FIG. 10. Visualization of $R(H, T)$ as a function of temperature and magnetic field in the $(90, 0)$ orientation. Relevant resistance points defining the shape of the surface are marked. The point R_{res} corresponds to the minimum resistance without a Kondo effect and lies below the surface. Plot not to scale.

D. Carrier density

For terminals oriented normal to the drain-source direction, a Hall voltage is obtained. Measurements thereof at 2 K in the $(0, 0)$ orientation for samples A, B, and C are reported in Fig. 11, showing the Hall voltage V_H as a function of the applied magnetic field: A linear dependence of $V_H \propto H$ is observed. As sample B is tilted from $(0, 0)$ towards $(90, 0)$, the out-of-plane component of $\mathbf{H}$ is reduced, which in turn reduces the slope of the Hall voltage.

The Hall curves in Fig. 11 yield, at 2 K, charge carrier concentrations $n = \frac{I \mu_0 H}{V_H t q}$ of $(2.33, 7.02, 6.93) \times 10^{20} \text{ cm}^{-3}$ for samples A, B, and C, respectively. Here, the applied current is $I = 10 \mu\text{A}$, and q is the elementary charge. In sample B, the constant offset of $\sim 10 \mu\text{V}$ for zero field does not diminish

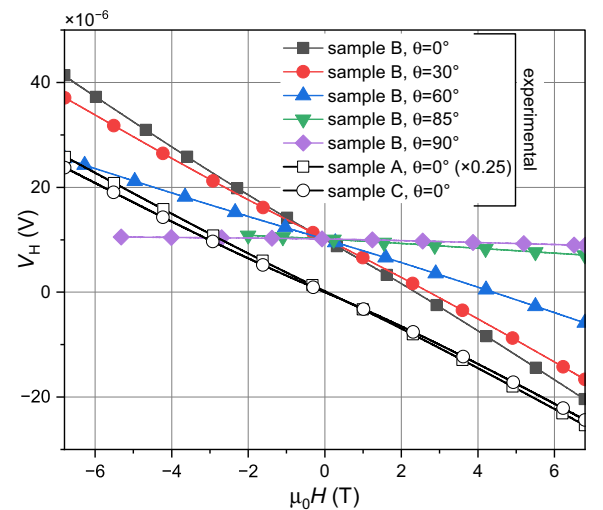


FIG. 11. Hall voltages V_H over applied magnetic field at 2 K in the $(0, 0)$ orientation for samples A, B, and C. For sample B, θ is varied from $(0, 0)$ to $(90, 0)$. Hall voltage of sample A at 1/4 scale.

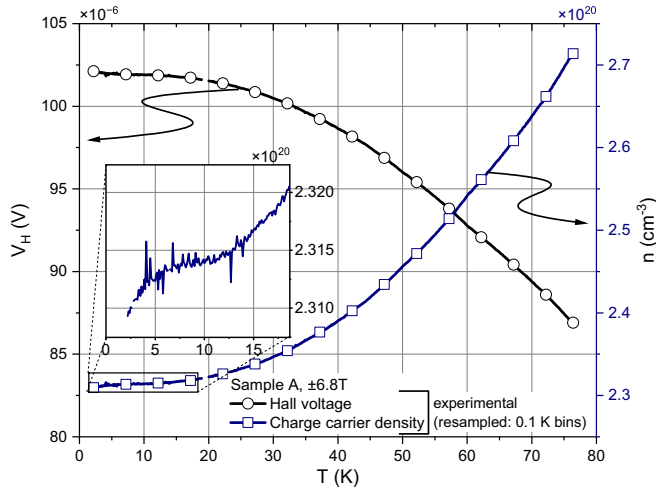


FIG. 12. Computed Hall voltage V_H and charge carrier density n over temperature for sample A. Inset: n for $T < 18$ K.

with θ and is therefore attributed to an asymmetric sample geometry resulting in a longitudinal transport component and thus an apparent V_H at zero field.

For sample A, field coolings in the Hall configuration are obtained at $\mu_0 H = \pm 6.8$ T. The Hall voltage V_H computed according to

$$V_H(H, T) = \frac{1}{2}[V(H, T) - V(-H, T)] \quad (11)$$

is plotted in Fig. 12 together with the carrier density n derived from it.

The carrier density decreases with temperature, plateauing at $T \sim 10$ K. For $T \rightarrow 0$, n drops further, which can be understood in the frame of the strong-coupling Kondo regime wherein the impurity spins pair with charge carrier spins, effectively capturing them. This points to $T_K \approx 10$ K, consistent with the values obtained from the ZFC and FC curves. An extrapolation to higher temperatures yields a charge carrier density ratio $\frac{n(300\text{ K})}{n(2\text{ K})} \approx 9$.

IV. MODELING

To substantiate the findings, density functional theory (DFT) based calculations for Pt-surface defects within PtSe_2 are carried out. The investigated specimens thereby correspond to a multilayered two-dimensional (2D) system. Notably, PtSe_2 exhibits an indirect band gap exclusively in ultrathin layers, transitioning to a semimetallic state for a thickness greater than or equal to three monolayers. In the semimetallic phase, PtSe_2 exhibits a valence band maximum located at the Γ point, while the conduction band minimum is found between the M and Γ points, as comprehensively demonstrated across layer numbers ranging from 4 to 10 [4] and depicted in Fig. 13(a). A four-layer model, sketched in Fig. 13(b), is considered. The computed Se-Se distance in the four-layer unit cell is $h = 16.37$ Å, with a Pt-atom layer positioned between two Se atom layers, forming a stable 1 T phase characterized by a lattice parameter of 3.74 Å. The presence of Pt defects in the samples was observed experimentally in Ref. [37]. Notably, it has been established that the formation of defects within the bulk does not result in the generation of

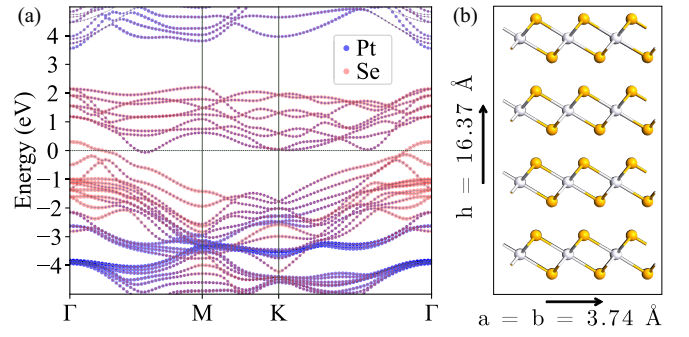


FIG. 13. (a) Band structure of four layers of PtSe_2 with contributions of Pt (blue) and Se (red) atoms. (b) Calculated parameters for the four-layer unit cell of PtSe_2 .

a local magnetic moment [37]. This permits us to focus the computation on the Pt-surface defects within the four-layer model. The inclusion of the Pt-vacancy defect at the surface of the four-layer model results in the generation of a magnetic moment, averaging around $1.3 \mu_B$.

The electronic density of states (DOS) shown in Fig. 14 is given for spin-up states (top panels) and spin-down states (bottom panels). The analysis of the density maps in momentum space (right panels) and the respective DOS over energy (left panels) points at a local magnetic moment originating

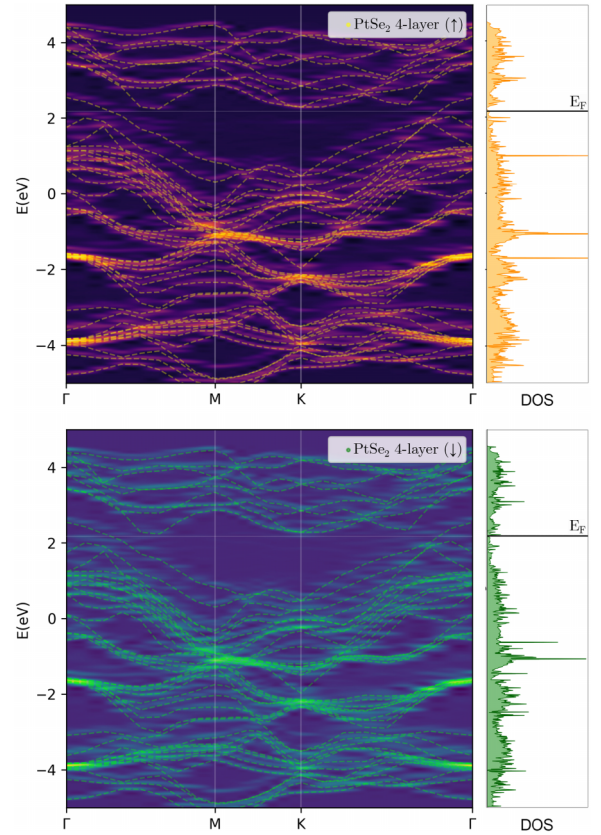


FIG. 14. Electronic DOS in the PtSe_2 four-layer model with Pt vacancy. Top: Spin-up DOS map over momentum and energy (left) and spin-up DOS over energy (right). Bottom: Equivalent plots for spin-down DOS.

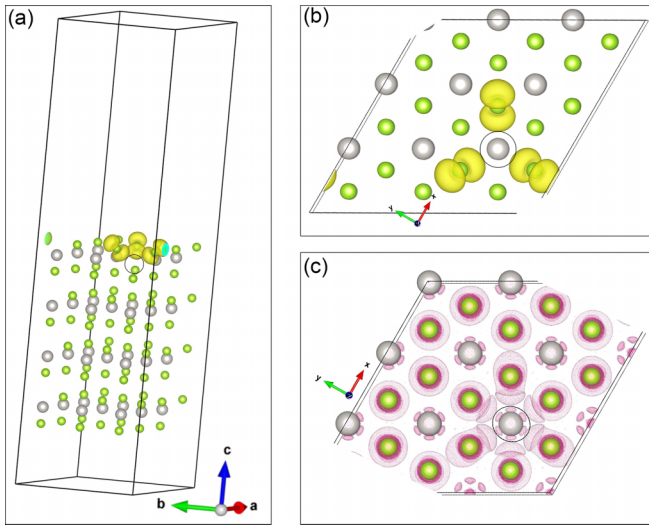


FIG. 15. Spin density (yellow) distribution around the Pt vacancy (circle) in a multilayer model, viewed (a) isometrically and (b) along the out-of-plane axis. (c) Charge density (brown) distribution around the Pt vacancy (circle).

from defect-induced spin-split states that emerge in proximity to the Fermi level (solid line) [37]. The spin density surrounding the defect predominantly concentrates on the adjacent Se atoms within their immediate coordination sphere, as sketched in Figs. 15(a) and 15(b). Additionally, the Pt vacancy is accompanied by a noticeable localization of charge density surrounding it, as shown in Fig. 15(c).

V. CONCLUSION

The electronic structure, in particular the mechanism leading to the observed NLMR for exfoliated PtSe₂ flakes, was

examined. Low- T , high- $\mu_0 H$ magnetotransport is performed, yielding insights via application of analytical fitting functions. The magnetotransport allows for the identification of a Kondo effect present in all considered samples: The observed zero-field behavior can be understood using an analytical formalism, while the field-dependent effects are separated into an isotropic NLMR stemming from the Kondo effect and angle-dependent conventional orbital MR contributions. The attribution of the NLMR to a CME or to current jetting was discussed, resulting in their confutation by considering the angle dependences and the robustness of the observed NLMR. A transport model was formulated to describe the total longitudinal MR in PtSe₂ at arbitrary temperature, magnetic field, and magnetic field direction. The model captures how the Kondo effect emerges at temperatures $T \lesssim 15$ K and how the polarization of the impurity spins reduces Kondo scattering when an external magnetic field is applied. By using DFT in conjunction with transport performed on different flake thicknesses, the origin of the impurity spins was identified in Pt defects, which contribute an uncompensated spin exclusively at the sample surface. The rigorous magnetization function $M(H)$ of the magnetic moments remains to be derived and studied. The results point at a 2D spin density at the surfaces of PtSe₂ flakes and highlight both the sample thickness and the vacancy concentration as tuning parameters for interplay between the Kondo effect and orbital MR. Understanding the dynamics of both the spin and orbital degrees of freedom of the charge carriers in PtSe₂ is fundamental to spintronic applications and detection of an orbital Hall effect.

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Tailoring electronic and optical properties of hBN/InTe and hBN/GaTe heterostructures through biaxial strain engineering

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In this research study, we systematically investigate the electronic and optical properties of van der Waals heterostructures (HSs) consisting of InTe (GaTe) and hBN monolayers, subjected to controlled biaxial strain. Our analysis demonstrates that the application of strain induces noteworthy alterations in the electronic band structure, enabling precise manipulation of the band gap and augmentation of the absorption properties of these structures. Employing density functional theory, we conduct a comprehensive examination of the influence of strain on the electronic and optical characteristics of these HSs. Our investigation showcases the remarkable potential of strain engineering in rendering these heterostructures into efficient and robust wide-range absorbers, particularly optimised for the visible spectrum, underscoring their relevance in various photonic and optoelectronic applications, paving the way for integration into advanced nanodevices.

Van der Waals (vdW) heterostructures (HSs), a class of materials composed of stacked two-dimensional materials held together by van der Waals forces, have attracted significant attention in recent years due to their unique electronic and optical properties^{1–3}. A noteworthy advantage inherent to vdW HSs is their remarkable amenability to precise manipulation and customisation. The weak nature of vdW forces allows the layers to be easily separated and manipulated, allowing the creation of an unlimited number of different structures with precise control over the electronic, optical, and mechanical properties. This makes it possible to design and fabricate materials with specific desired characteristics, offering countless new possibilities for their applications in modern nanodevices⁴. With their high-performance electronic and optical properties, novel HSs can be used for transistors⁵, solar cells^{6,7}, lithium ion batteries^{8,9}, light emitting devices^{10,11}, photodetectors^{12–15}, various sensors^{16–18}, and many more. Recent research has further illuminated their promising potential as candidates for quantum computing applications¹⁹.

Delving deeper into the mechanisms of manipulation for vdW HSs not only enhances their properties but also unlocks a wider array of possibilities for applications in devices that fulfil the growing demands of today's market, such as sensors and switches. The modulation of electrical properties in such structures can be achieved in many ways, with the most common approaches being doping, strain application, or the use of external electric or magnetic field. The study of strain in 2D materials and vdW HSs represents a dynamically evolving research frontier, granting us an additional level of precision in controlling material properties^{20–22}.

Group III–VI monochalcogenide-based HSs have emerged as focal points of research attention, offering substantial promise for a broad spectrum of cutting-edge device applications. They find utility as Schottky barriers, high-performance 2D and flexible electronics, sensors, photodetectors, and more. Materials within the class of two-dimensional III–VI monochalcogenides are known for their high electron mobility, broad absorption spectra, and favourable elastic properties. Notably, the single-layer InTe is predicted to exhibit exceptional thermoelectric performance due to its remarkably low thermal conductance, boasting the highest merit figure, $ZT = 2.03$ at 300 K, among the III–VI monochalcogenide family²³. Recent study was discussing electronic transport and thermoelectric properties of doped InTe, showing that p-type InTe doped with Bi, Ag, Mn, Sn or Sb exhibits the enhanced thermoelectric performance, mainly induced by reduced thermal conductivity²⁴. Additionally, the InTe monolayer demonstrates a broad absorption spectrum, covering the ultraviolet to visible regions, with an absorption coefficient of up to 10^{-5} cm^{-1} . In most recent report, two-dimensional InTe

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was synthesized in large-scale samples, as centimeter-scale 2D films on SiO₂/Si substrates²⁵. InTe also exists in tetragonal phase, and its electronic band structure has a highly anisotropic character²⁶, marking it of high interest for electronic and thermoelectric applications. In that phase, structure has quasi-one-dimensional form, where one-dimensional In¹⁺ chains are observed, and additionally, the presence of In¹⁺ induces a localized gap state, responsible for the high intrinsic p-type doping of InTe²⁷. Similarly to InTe, the monolayer GaTe exhibits comparable absorbing properties²⁸, along with excellent UV light absorption. In the realm of single-layer materials, each member of this material family exhibits remarkable and distinctive properties. Nonetheless, single layer III–VI monochalcogenides possess one noteworthy limitation in their pristine form. The majority of these materials display sensitivity to oxidation upon exposure to ambient air^{29–31}, especially in their single layer form, and need adequate material for passivation and mechanical protection. Non-reactive with most chemicals, stable in air and resistant to oxidation, hBN is already known as an effective coating material in the form of thin films or monolayers^{32–34}, and has been demonstrated successful for protection against oxidation and even for improving the electronic and optical properties of few-layered InSe and GaSe³⁵.

Motivated by these results, in our previous work, we designed and investigated two novel heterostructures, hBN/InTe and hBN/GaTe, as detailed in³⁶. These heterostructures displayed favourable electronic properties and an excellent broad absorption spectrum, enhanced and protected by the hBN layer, making them promising candidates for applications in photodetectors or field-effect transistors. Given the experimentally favourable binding energies and stacking versatility of both hBN/InTe and hBN/GaTe heterostructures, this study further delves into the intriguing potential of fine-tuning their properties through the application of controlled strain. In the following sections, we present a computational study of hBN/InTe and hBN/InTe under biaxial strain. The application of uniform biaxial strain does not alter the symmetry of the structure; instead, it allows us to tune the band structure and optical absorption.

Computational methods

Calculations were carried out using density functional theory (DFT), as implemented in the Quantum Espresso (QE) software package³⁷, based on plane waves and pseudopotentials. In all calculations, the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional³⁸ is used, along with norm-conserving pseudopotentials. The energy cutoff of 80 Ry was set for both structures after the convergence tests.

The Monkhorst pack of $16 \times 16 \times 1$ mesh for k-point sampling is used in geometric optimisation, total energy, and phonon calculations. For calculations of p-DOS and optical properties, a refined $64 \times 64 \times 1$ mesh is used. The band structure is calculated on 440 k-points along Γ -M-K- Γ direction. To simulate the 2D structure, a vacuum of 20 Å was added along the z-direction to avoid interactions between the layers. Geometry optimisation of the positions of the atoms and the lattice parameters is performed using the BFGS algorithm, with criteria for the maximum forces allowed between atoms of 10^{-6} Ry/Å. To properly account for van der Waals force effects, the Grimme-D2 correction^{39,40} was included to obtain more accurate lattice constants and forces. The optical properties were calculated using the epsilon.x code in QE software, based on the random phase approximation (RPA).

Results and discussion

As discussed in our previous work³⁶, the unit cells of InTe and GaTe monolayer are $a = 4.371$ Å and $a = 4.048$ Å, respectively. The unit cell of hBN is $a = 2.515$ Å, and for both structures, constructing the heterostructure consisting of a $\sqrt{3} \times \sqrt{3}$ supercell of hBN rotated for 30° on top of 1×1 unit cell of InTe or GaTe provides an excellent match. After complete optimisation of the lattice parameters and atom positions within the unit cell, the obtained unit cell is hexagonal, with a lattice constant of $a = 4.336$ Å for hBN/InTe and $a = 4.309$ Å for hBN/GaTe. Resulting unit cell of hBN/InTe has induced strain of 0.8% on InTe layer and 0.3% on hBN layer, showing that HS constructed as described is almost an ideal match. The resulting unit cell of hBN/GaTe induces strain of 6% on GaTe and 0.8% on hBN which is slightly less perfect than hBN/InTe HS, but still agreeable. The top view of the structures is presented in Fig. 1. With all three types of stacking being energetically close to each other, we consider H-top stacking (the In(Ga) atom above the centre of the hBN hexagon), which has slightly lower total energy and binding energy compared to the B-top and N-top types. All constituting materials (hBN, InTe, GaTe) exhibit outstanding mechanical properties, demonstrating the ability to withstand significant biaxial strain strengths of more than 10%^{23,28,41}. From an experimental standpoint, achieving a controllable and precise strain beyond a few percent in complex structures like van der Waals (vdW) heterostructures is often challenging, if not impossible. Taking this into account, we chose to set the maximum absolute strain values at 5% even though both systems theoretically possess the capacity for higher strain tolerance. The uniform biaxial strain of -5 to 5% is applied to both structures, with the step of 1%, and the geometry optimisation of the positions of the atoms within the unit cell is performed for all strained structures. The binding energies E_b are calculated for all structures as follows:

$$E_b = E_{\text{heterostr.}} - E_{\text{In(Ga)Te}} - E_{\text{hBN}}, \quad (1)$$

where $E_{\text{heterostr.}}$, $E_{\text{In(Ga)Te}}$ and E_{hBN} represent the total energy of hBN/In(Ga)Te heterostructure, InTe or GaTe monolayer and hBN monolayer, respectively. Total and binding energies, E_{tot} and E_b , along with the distance between the hBN and In(Ga)Te layers d and the width of the layer h are given in Table in the Supplementary file. First, the binding energies are negative in all cases, suggesting that all strained structures are experimentally feasible. It can be seen from and Fig. 2 that the total energy is lowest for HS without strain and increases exponentially with both positive and negative strains, as expected, since the initial system without strain was fully relaxed with respect to the lattice constants and atom positions within the unit cell. The distance between layers and the bond lengths change with different values of applied strain. Although the bonds in the InTe (GaTe) layer are slightly shortened when compressive strain is applied (mainly the In(Ga)–Te bonds), a significant difference

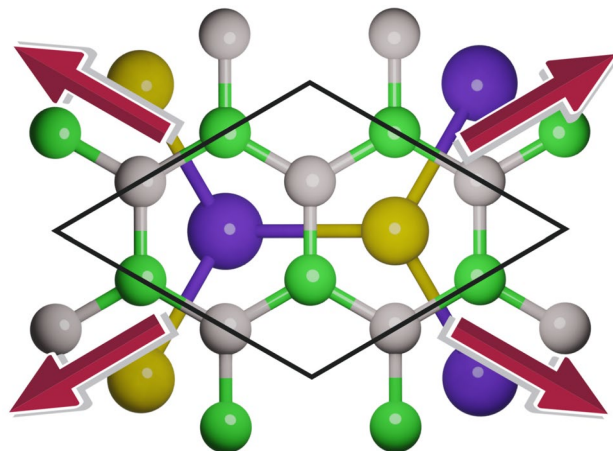


Figure 1. Top view of heterostructures, with arrows showing the tensile biaxial strain. B and N atoms are represented with a grey and green colour, In/Ga and Te atoms are coloured purple and yellow.

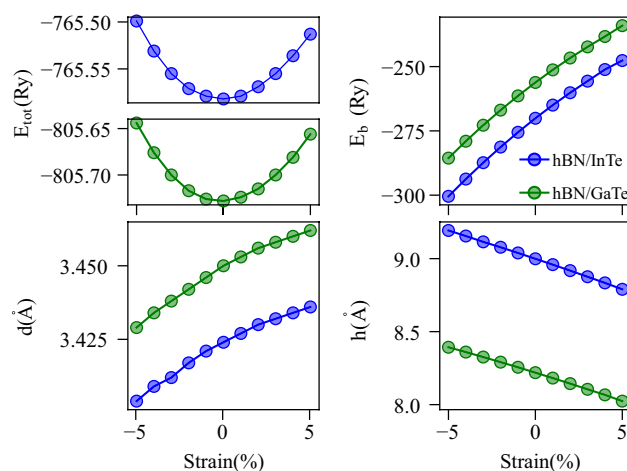


Figure 2. Dependence of total energy E_{tot} , binding energy E_b , distance between the layers d and the thickness of HSS h on applied strain. The blue lines and markers correspond to hBN/InTe, and green lines and markers correspond to hBN/GaTe.

is present in the angle of the In(Ga)–Te bond with respect to the horizontal plane, so the In(Ga)Te layer width is increased, and the inner Te atoms are positioned slightly closer to the hBN layer. In the case of tensile strain, the In(Ga)Te bonds are stretched, causing the layer width to decrease and the distance between the inner Te atoms and the hBN layer to increase. The complete data are given in Table 1 in the Supplementary file.

Before the introduction of strain into any structure, it is essential to conduct a thorough analysis of its mechanical characteristics. We used the Thermo pw code⁴² to compute the elastic constants. The code calculates the non-zero components of the stress tensor for a set of strains and obtains the elastic constants from the first derivative of the stress with respect to the strain. In this way, we can gain a solid basis to understand the relationship between strain and the mechanical reaction of the structure. For 2D systems, nonzero elastic constants follows the Hooke's law under plane stress conditions:

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & 0 \\ 0 & c_{22} & 0 \\ 0 & 0 & c_{66} \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix}. \quad (2)$$

For a hexagonal lattice, $C_{11} = C_{22}$ and $C_{12} = C_{21}$, $C_{66} = (C_{11} - C_{22})/2$, so there are only two independent elastic constants. In that case, Young's modulus, Poisson's ratio, and shear modulus are obtained from the following relations:

$$E_Y = C_{11} - \frac{C_{12}^2}{C_{11}}, \quad \nu_{xy} = \frac{C_{12}}{C_{11}}, \quad G_{xy} = C_{66}. \quad (3)$$

For hexagonal 2D systems, layer modulus that represents the resistance of a sheet to stretching is calculated by following⁴³:

$$\gamma^{2D} = \frac{C_{11} + C_{12}}{2}.$$

(4)

Calculated elastic constants and moduli are given in Table 1. Obtained elastic constants of single layer InTe and GaTe are in range of other III–VI monochalcogenides⁴⁴. Constants $C_{11} = 45.36$ N/m and $C_{12} = 11.76$ N/m for InTe are close to constants of single layer InSe, and $C_{11} = 65.62$ N/m and $C_{12} = 15.30$ N/m for GaTe close to results for single layer GaSe. We calculated the elastic constants of hBN in order to validate our results, and obtained values are in agreement with the literature^{43,45}. When the HSs are formed, all constants and moduli are significantly increased. Elastic constants C_{11} and C_{12} for hBN/InTe are $C_{11} = 338.3$ N/m and $C_{12} = 72.08$ N/m; $C_{11} = 340$ N/m and $C_{12} = 75.48$ for hBN/GaTe, and their values are roughly similar to the sum of individual constants of each layer in the heterostructure. Young modulus is increased to 323 N/m in HSs, which are high almost as in graphene (342–366 N/m for Young modulus and 206–212 N/m for layer modulus, according to the literature^{43,46}), indicating high resistance to unidirectional compression as well to stretching. The results suggest that the presence of the hBN layer in our heterostructures not only shields the delicate monochalcogenide layers from oxidation but also provides effective mechanical protection, at the same time rendering the system more robust and resistant to deformations.

In our investigation, we computed the band structures of both heterostructures (HSs) under various compressive and tensile strain conditions, building upon the foundation laid out in our previous study³⁶. The band structures for HSs under – 4%, 0% and 4% strain are visually represented in Fig. 3. The band structures for all values of strain, from – 5 to 5%, are represented in Figures S1 and S2 in supplementary file. In their pristine, unstrained states, hBN/InTe and hBN/GaTe exhibit band gaps of $E_g = 1.53$ eV and $E_g = 0.76$ eV, respectively. Notably, both HSs display an indirect band gap configuration, with the valence band maximum (VBM) positioned near the Γ point and the conduction band minimum (CBM) precisely at the Γ point.

When the application of strain is introduced, significant alterations occur in both the band gap and the shape of the bands within the heterostructures. In the case of the hBN/GaTe heterostructure subjected to compressive strain, the band gap widens as the strain magnitude increases, reaching a maximum value of $E_g = 1.49$ eV at –5% strain. Importantly, the valence band retains its shape while shifting downward to lower energy levels. In contrast, the conduction band exhibits distinct behaviour: the Γ -valley expands, whereas the energy level of the M-valley remains relatively stable. This results in both valleys having nearly identical energies at –4% strain. Conversely, the introduction of tensile strain leads to a contrasting effect. The upper region of the valence band near the Γ point shifts upward, while the lower region of the conduction band at the Γ point experiences a substantial descent. Consequently, at + 5% strain, the band gap narrows to only 0.24 eV.

The relationship between band gap and strain is systematically explored and plotted in Fig. 6. Remarkably, across the entire range of applied strains, from –5 to + 5%, the dependence closely approximates a linear decrease.

Turning our attention to the hBN/InTe heterostructure, we observe similar trends in band gap modulation under strain. However, a significant disparity arises in the conduction band behaviour, particularly under compressive strain. Here, the valence band also shifts downward as compressive strain intensifies, eventually falling below the group of bands situated around –0.5 eV at the Γ point. Initially, in the relaxed state, the conduction band minimum (CBM) resides at the Γ point, while the bottom of the M valley maintains nearly the same energy. However, as compressive strain is applied, the Γ -valley remains relatively stable in terms of energy, while the M-valley experiences a downward shift. Consequently, the CBM transitions from the Γ to the M-point as strain surpasses –1%. This intricate interplay between the valence and conduction bands results in a band gap expansion, peaking at $E_g = 1.69$ eV at –2% strain before gradually reducing to 1.39 eV at –5% strain.

In the case of tensile strain, the behaviour mirrors that of the hBN/GaTe heterostructure. The valence band shifts upward, and the CBM descends with increasing tensile strain, leading to a reduced band gap, which ultimately reaches a minimum of 0.70 eV at + 5% strain.

The shifts in the position of valleys within the conduction band in response to varying strain values are not uncommon and have been observed in InTe and GaTe monolayers subjected to biaxial strain^{28,47,48}. Furthermore, our analysis of the density of states (DOS) reveals that the bands closest to the Fermi level predominantly arise from the In(Ga) and Te states. DOS for HSs with – 4%, 0% and 4% strain are presented in Figs. 4 and 5. Complete

1	InTe	GaTe	hBN	hBN/InTe	hBN/GaTe
C_{11}	45.36	65.62	290.77	338.30	340.00
C_{12}	11.76	15.30	63.93	72.08	75.48
C_{66}	16.52	25.16	113.42	132.94	132.26
E_y	42.31	62.05	276.41	322.94	323.24
ν_{xy}	0.26	0.23	0.22	0.21	0.22
G_{xy}	16.52	25.16	113.42	132.94	132.26
γ^{2D}	28.56	40.46	177.35	205.19	207.74

Table 1. Elastic constants, Young modulus, Poisson ratio, shear modulus and layer modulus for HSs and pristine InTe and GaTe monolayers. Units are given in N/m.

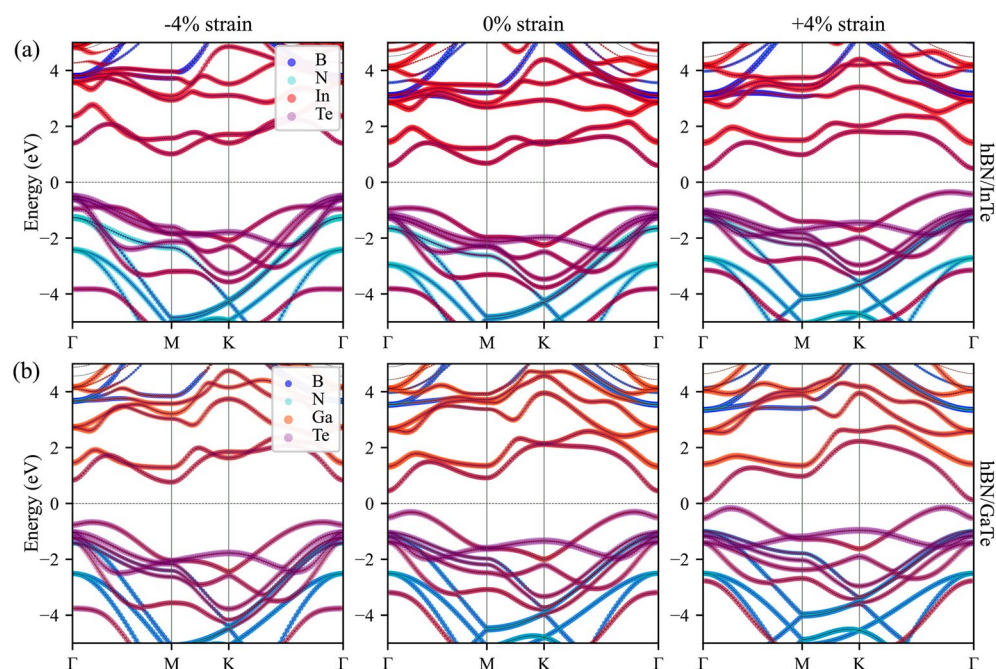


Figure 3. Band structure of (a) hBN/InTe HS and (b) hBN/GaTe. The width of the lines is proportional to the contribution of different atoms/states. The line width is proportional to the magnitude of projections of wavefunctions over atomic orbitals. The contributions from different atomic orbitals are presented in different colours, as shown in the legend.

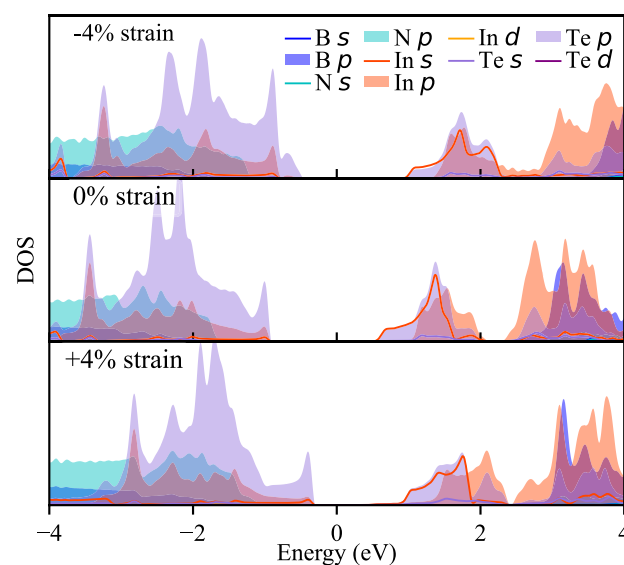


Figure 4. Projected density of states of hBN/InTe HS. Contributions from different atoms and states are represented with colours as in legend.

data with DOS for all strain values are shown in Figure S3 in supplementary file. The uppermost bands below the Fermi level primarily originate from the Te states, while the bands above comprise a combination of In(Ga) and Te states. Consequently, it can be inferred that the changes in the conduction band shape predominantly result from the influence of strain on the InTe(GaTe) layer itself, rather than being an inherent characteristic of the formed heterostructure. These findings underscore the profound influence of strain engineering on the electronic properties of these heterostructures, offering a promising avenue for precise control and modulation of their behaviour for tailored optoelectronic applications.

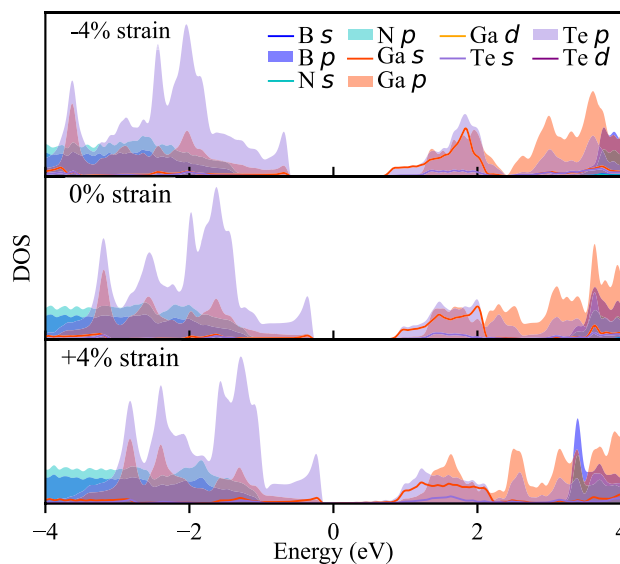


Figure 5. Projected density of states of hBN/GaTe HS. Contributions from different atoms and states are represented with colours as in legend.

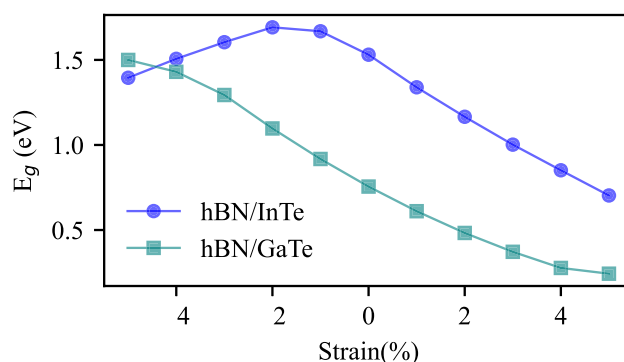


Figure 6. Band gap of hBN/InTe (indicated as blue line and circles) and hBN/GaTe (indicated as green line and squares) as a function of applied strain.

Significant variations in both the band gap and the shape of the bands can drastically alter dielectric function and absorption. The complex dielectric function $\epsilon(\omega) = \epsilon_R(\omega) + i\epsilon_I(\omega)$ is obtained from DFT calculations in the RPA framework. The absorption coefficient $\alpha(\omega)$ is obtained directly from the dielectric function as follows:

$$\alpha(\omega) = \sqrt{2} \frac{\omega}{c} \sqrt{\epsilon_R^2(\omega) + \epsilon_I^2(\omega) - \epsilon_I(\omega)}. \quad (5)$$

Calculation of optical properties were performed within RPA. Optical properties of group III monochalcogenide members and similar structures as well of hBN were previously studied both with GW and RPA based methods, and it is shown that RPA can provide reasonably good results of dielectric function and its qualitative description^{49–53}. In⁵⁴, heterostructure of InSe with silicene, germanene and antimonene, imaginary part of the dielectric function calculated both with RPA over GGA and GW, and main difference observed is the shift of the dielectric function for 0.5–1 eV due to larger calculated band gap. The absorption coefficients of both HSs under different strain strengths are presented in Figs. 7 and 8, respectively. The band gap width variations induced by strain strength exhibit a notable influence on the absorption properties of both HSs. Specifically, compressive strain causes the absorption function to shift towards higher energies, while tensile strain results in a shift towards lower energies, a behaviour consistently observed in both HSs. However, the most striking disparity in absorption behaviour occurs in hBN/InTe, where the application of compressive strain induces the formation of a pronounced peak at approximately 3 eV for z-polarisation. This striking alteration is attributed to the significant reduction of the M-valley in hBN/InTe and is absent in hBN/GaTe under similar strain conditions. This study highlights the intricate interplay between strain and the optical properties of these heterostructures. The observed differences in absorption behaviour underscore the nuanced effects that strain engineering can exert, offering a pathway towards fine-tuning the optical characteristics of these materials for tailored optoelectronic applications.

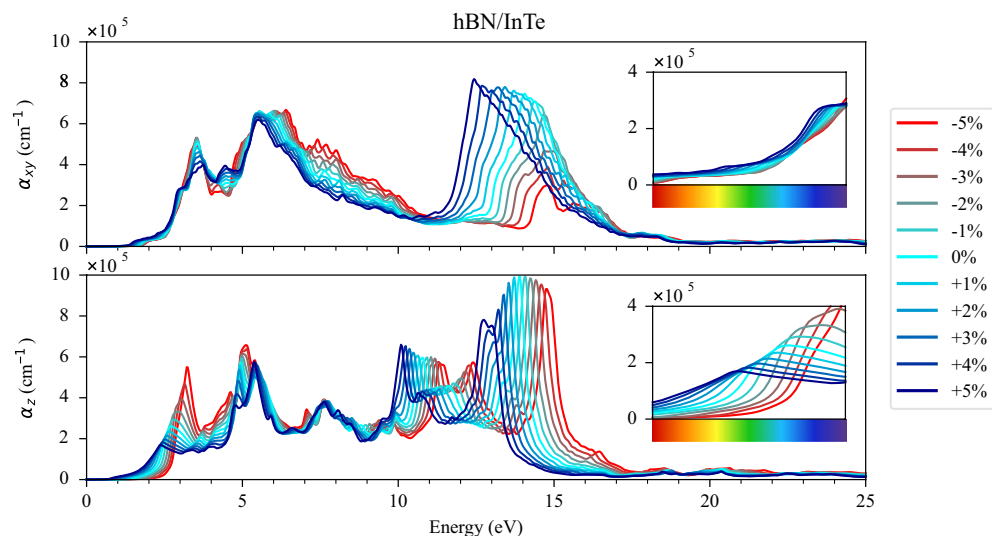


Figure 7. Absorption function of hBN/InTe HS for (a) in-plane (α_{xy}) and (b) out-of-plane (α_z) polarisations. Each colour represents a different value of the induced strain, from red (− 5% of strain) to blue (+ 5% of strain). The visible part of the spectrum is enlarged in the inset.

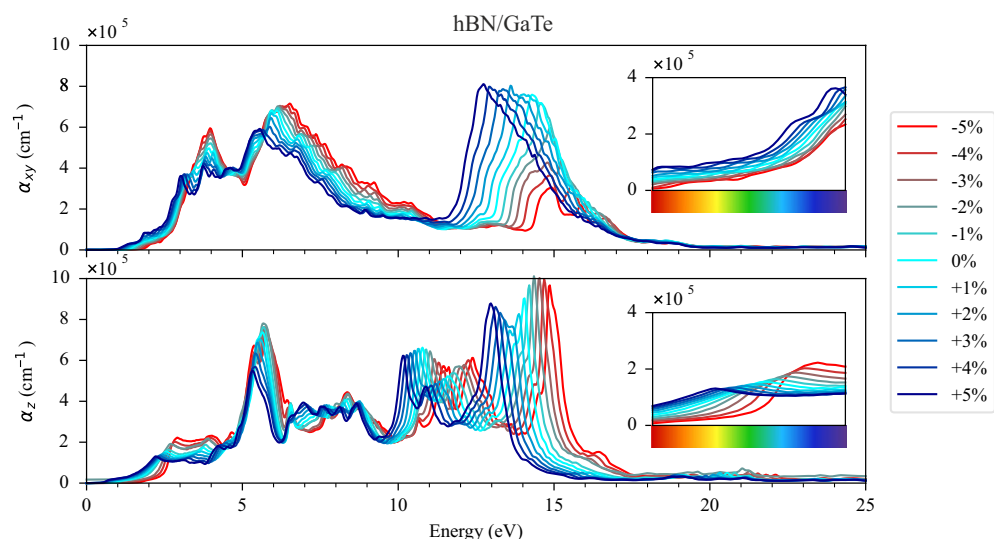


Figure 8. Absorption function of hBN/GaTe HS for (a) in-plane (α_{xy}) and (b) out-of-plane (α_z) polarisations. Each colour represents a different value of the induced strain, from red (− 5% of strain) to blue (+ 5% of strain). The visible part of the spectrum is enlarged in the inset.

Conclusions

In this study, we systematically investigated the impact of biaxial strain on recently designed HSs composed of InTe (GaTe) and hBN monolayers using DFT. All the considered strained structures were found to be experimentally feasible, characterised by negative binding energies. Our band structure analysis revealed that strain offers a powerful tool for the precise manipulation of the band gap in these structures.

In the case of hBN/GaTe, we observed an almost linear relationship between band gap and strain, with band gap values increasing under compressive strain and decreasing under tensile strain. Specifically, the largest band gap of $E_g = 1.49$ eV was achieved at − 5% strain, while it reduced to 0.24 eV at + 5% strain. In hBN/InTe, the manipulation of strain led to a decrease in the M-valley's energy, effectively positioning it below the Γ -valley. This resulted in a band gap that decreased under strain stronger than − 2%, with band gap energies falling within the range of 0.70–1.69 eV.

Additionally, we examined the optical properties by calculating the dielectric functions and found that tensile strain substantially enhanced absorption in the low-energy spectrum, particularly in the visible spectrum.

On the contrary, compressive strain increased absorption at 3 eV, but shifted the absorption function towards higher energies.

Our findings underscore the pivotal role of strain engineering in these HSs, offering precise control over their electronic and optical properties. Furthermore, these tunable properties open up possibilities for their utilisation in various sensor and switch applications.

Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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Author contributions

A.Š. did the calculations and prepared figures. Both authors wrote the main manuscript text and reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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Spin-phonon interaction and short-range order in $\text{Mn}_3\text{Si}_2\text{Te}_6$

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The vibrational properties of ferrimagnetic $\text{Mn}_3\text{Si}_2\text{Te}_6$ single crystals are investigated using Raman spectroscopy and density functional theory calculations. Eighteen Raman-active modes are identified, 14 of which are assigned according to the trigonal symmetry. Four additional peaks, obeying the A_{1g} selection rules, are attributed to the overtones. The unconventional temperature evolution of the A_{1g}^5 mode self-energy suggests a competition between different short-range magnetic correlations that significantly impact the spin-phonon interaction in $\text{Mn}_3\text{Si}_2\text{Te}_6$. The research provides comprehensive insight into the lattice properties, studies their temperature dependence, and shows arguments for the existence of competing short-range magnetic phases in $\text{Mn}_3\text{Si}_2\text{Te}_6$.

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I. INTRODUCTION

Layered magnetic van der Waals materials have lately received widespread attention due to their potential application in spintronics, magnetoelectronics, data storage, and biomedicine [1–7]. Recent experimental confirmation of a long-range magnetism persisting down to a monolayer in CrI_3 [8] further affirmed these materials as a platform for magneto-optoelectronic devices [9], and as candidates for studying low-dimensional magnetism [10].

$\text{Mn}_3\text{Si}_2\text{Te}_6$ single crystals were first synthesized in 1985 [11]. However, few studies were carried out on this compound since. It was only recently that the attention has shifted to them, mainly through comparisons with quasi-two-dimensional materials, specifically CrSiTe_3 . The vast majority of recent studies were focused on explaining the magnetism in $\text{Mn}_3\text{Si}_2\text{Te}_6$ and determining its crystal structure. It was revealed that $\text{Mn}_3\text{Si}_2\text{Te}_6$ crystallizes in a trigonal structure described by the $P\bar{3}1c$ (No. 163) space group [11,12]. According to various magnetization studies, $\text{Mn}_3\text{Si}_2\text{Te}_6$ is an insulating ferrimagnetic with Curie temperature T_c between 74 and 78 K [12–15]. First-principles calculations suggested a competition between the ferrimagnetic ground state and three additional magnetic configurations, originating from the antiferromagnetic exchange for the three nearest Mn-Mn pairs [15]. Additionally, both magnetization and diffuse neutron scattering experiments point at the existence of strong spin correlations well above T_c , which may be associated with

short-range order or to the preserved correlated excitations in the paramagnetic region [12,15].

Here, we present an experimental and theoretical Raman scattering study of $\text{Mn}_3\text{Si}_2\text{Te}_6$ single crystals, with the focus on phonon properties in the temperature range from 80 to 320 K. Out of 18 observed modes, 14 ($5A_{1g} + 9E_g$) are identified and assigned in agreement with the $P\bar{3}1c$ space group. Phonon energies are in a good agreement with the theoretical predictions. Two most prominent Raman modes, A_{1g}^4 and A_{1g}^5 , are used to study the temperature evolution of phonon properties, and reveal three subsequent phase transitions at $T_1 = 142.5$ K, $T_2 = 190$ K, and $T_3 = 285$ K. Furthermore, the A_{1g}^5 mode exhibits strong asymmetry, most likely originating from enhanced spin-phonon coupling. Interestingly, the A_{1g}^5 phonon line is symmetric in the temperature range T_1 – T_2 , while becoming more asymmetric above T_3 , potentially indicating that the strength of spin-phonon interaction changes with temperature. We speculate that the observed phenomenon, shown in the A_{1g}^5 phonon, originates from the shift in dominance between competing magnetic states, that are found to be very close in energy [15].

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

The $\text{Mn}_3\text{Si}_2\text{Te}_6$ single-crystal samples used in this study are prepared according to the procedure described in Ref. [12]. The Raman spectra have been obtained with a Tri Vista 557 spectrometer (Teledyne Princeton Instruments, Trenton, NJ, USA) with a 1800/1800/2400 grooves/mm diffraction grating combination in a backscattering configuration. The 514-nm line of a Coherent Ar^+/Kr^+ ion laser (Coherent, Santa Clara, CA, USA) is utilized as the excitation source. The direction of the incident (scattered) light coincides with

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TABLE I. Wyckoff positions of atoms and their contributions to the Γ -point phonons together with the corresponding Raman tensors for the $P\bar{3}1c$ space group of $\text{Mn}_3\text{Si}_2\text{Te}_6$.

Space group: $P\bar{3}1c$	
Atoms	Irreducible representations
Mn (2c)	$A_{2g} + A_{2u} + E_g + E_u$
Mn (4f)	$A_{1g} + A_{1u} + A_{2g} + A_{2u} + 2E_g + 2E_u$
Si (4e)	$A_{1g} + A_{1u} + A_{2g} + A_{2u} + 2E_g + 2E_u$
Te (12i)	$3A_{1g} + 3A_{1u} + 3A_{2g} + 3A_{2u} + 6E_g + 6E_u$
Raman tensors	
$A_{1g} = \begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}$	
${}^1E_g = \begin{pmatrix} c & & \\ & -c & d \\ & d & \end{pmatrix}$	${}^2E_g = \begin{pmatrix} & & \\ & -c & -d \\ d & & \end{pmatrix}$

the crystallographic c axis. Laser-beam focusing is achieved through a microscope objective with $50\times$ magnification. The temperature-dependent Raman scattering measurements have been performed under high vacuum (10^{-6} mbar), with the sample being placed inside of a KONTI CryoVac continuous helium flow cryostat (CryoVac GmbH & Co. KG, Troisdorf, Germany) with a 0.5-mm-thick window. The samples are cleaved in air before being placed into the cryostat. The obtained Raman spectra are corrected by a Bose factor. The spectrometer resolution is comparable to a Gaussian width of 1 cm^{-1} .

The calculations are based on the density functional theory (DFT) formalism as implemented in the Vienna *ab initio* simulation package (VASP) [16–19], with the plane-wave basis truncated at a kinetic energy of 520 eV, using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [20] and projector augmented-wave (PAW) method [19,21]. The Monkhorst and Pack scheme of k -point sampling is employed to integrate over the first Brillouin zone with $12 \times 12 \times 10$ at the Γ -centered grid. The convergence criteria for energy and force have been set to 10^{-6} eV and $0.001\text{ eV \AA}^{-1}$, respectively. The DFT-D2 method of Grimme is employed for van der Waals (vdW) corrections [22]. The vibrational modes are calculated using density functional perturbation theory implemented in VASP and PHONOPY [23]. Previous DFT results found the energy of the ferrimagnetic state to be well above an eV per Mn below that of the nonmagnetic state [15], thus this configuration is considered in this study.

III. RESULTS AND DISCUSSION

A. Polarization measurements

$\text{Mn}_3\text{Si}_2\text{Te}_6$ crystallizes in a trigonal $P\bar{3}1c$ crystal structure [11,12]. The Wyckoff positions of the atoms and their contributions to the Γ -point phonons, together with the corresponding Raman tensors, are listed in Table I. In total, there are 16 Raman-active modes ($5A_{1g} + 11E_g$) and 17 infrared-active modes ($6A_{2u} + 11E_u$). According to the Raman tensors presented in Table I, in our scattering configuration and with

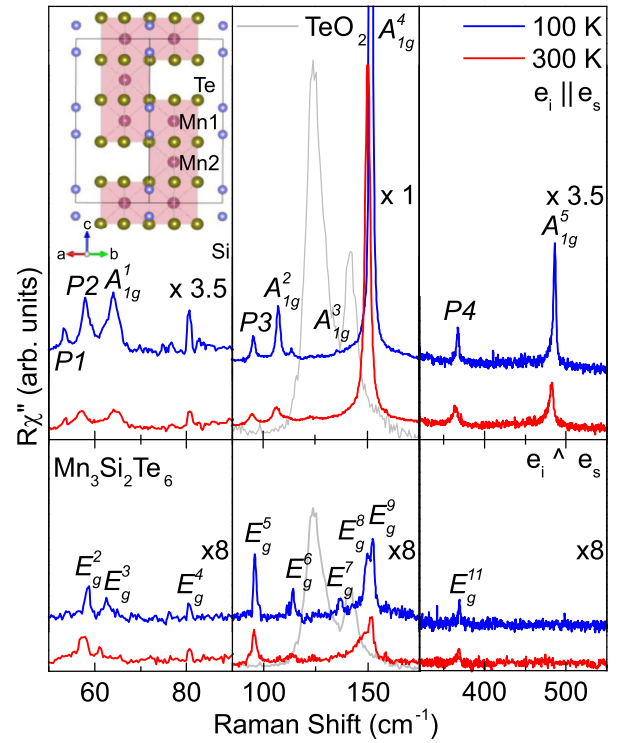


FIG. 1. Raman spectra of $\text{Mn}_3\text{Si}_2\text{Te}_6$ single crystal measured in two scattering geometries at $T = 100\text{ K}$ (blue solid line) and $T = 300\text{ K}$ (red solid lines) with incident light being directed along $[100]$. Peaks observed in both geometries are identified as E_g modes, whereas peaks observed only for the parallel polarization configuration are assigned as A_{1g} modes. Gray line: TeO_2 spectrum at 300 K , scaled for clarity. The crystal structure of $\text{Mn}_3\text{Si}_2\text{Te}_6$ viewed laterally along the c axis is presented in the inset.

Raman scattering events within the crystallographic ab plane, E_g symmetry modes can be observed in the Raman spectra measured in both parallel and crossed polarization configurations, whereas A_{1g} modes arise only for those in parallel polarization configuration.

As depicted in Fig. 1, nine phonon lines are observed in a parallel polarization configuration only, and identified as A_{1g} symmetry modes. According to the symmetry analysis only five A_{1g} symmetry modes are expected, resulting in four excess modes at 53.3 , 57.9 , 95.3 , and 366.7 cm^{-1} . These modes may arise from infrared/silent phonons activated by disorder and from the relaxation of the symmetry selection rules [24–27]. However, it is more likely they are overtones. Overtones, which are always observable in A symmetries, but can also be observed in other symmetries, can become observable in Raman spectra due to disorder and/or enhanced coupling of the phonons to other excitations such as in the case of spin-phonon coupling [28].

Aside from the discussed A_{1g} symmetry modes, our spectra host nine modes which obey the E_g selection rules. Therefore, nine out of the expected 11 E_g modes have been singled out and identified. The absence of two E_g modes might be attributed to their low intensity and/or the finite resolution of the spectrometer.

Calculated and experimental phonon energies are collected in Table II, and are found to be in good agreement with each

TABLE II. Phonon symmetries and phonon frequencies of $\text{Mn}_3\text{Si}_2\text{Te}_6$ phonons. The experimental values are determined at 100 K. All calculations have been performed at zero 0 K. The experimental uncertainty is 0.3 cm^{-1} .

Space group $P\bar{3}1c$			
n_0	Symm.	Expt. (cm^{-1})	Calc. (cm^{-1})
1	E_g^1		53.1
2	$P1$	53.3	
3	$P2$	57.9	
4	E_g^2	58.7	58.5
5	E_g^3	62.6	61.8
6	A_{1g}^1	64.2	62.3
7	E_g^4	80.4	82.7
8	$P3$	95.3	
9	E_g^5	95.9	90.3
10	A_{1g}^2	107.3	104.3
11	E_g^6	114.0	106.5
12	A_{1g}^3	135.4	134.2
13	E_g^7	136.6	136.1
14	E_g^8	149.8	143.4
15	A_{1g}^4	151.8	147.3
16	E_g^9	152.6	146.6
17	E_g^{10}		352.7
18	$P4$	366.7	
19	E_g^{11}	368.7	354.5
20	A_{1g}^5	486.7	475.8

other, with the discrepancy being below 8% for all observed modes.

Our data significantly differ from those presented in Ref. [14] where two Raman-active modes were reported, one at 118.4 cm^{-1} and the other at 136.9 cm^{-1} , assigned as E_g and A_{1g} , respectively. The E_g and A_{1g} modes in our spectra closest (in terms of energy) to those reported in Ref. [14] are the peaks at ~ 114.3 and 135.4 cm^{-1} (Table II). Although the discrepancy in phonon energy is not significant, the observed phonon linewidths strongly deviate from those presented in Ref. [14]. A possible explanation for the discrepancy is the presence of TeO_2 in samples presented in Ref. [14], as the peaks reported there match rather well with the Raman response of TeO_2 (Fig. 1). In order to avoid potential contamination in our study, measurements have been repeated on multiple crystals, and no oxide traces have been identified in the spectra.

B. Temperature dependence

Some of the modes represented in Fig. 1 exhibit an asymmetric line shape. Although the appearance of a mode asymmetry can be attributed to the presence of defects [29], this would have a significant impact also on the linewidths of other modes in the spectrum, which is not the case here. The asymmetry may arise from coupling between the phonon and other elementary excitations [30–32]. The line shape originating from such a coupling is given by the Fano

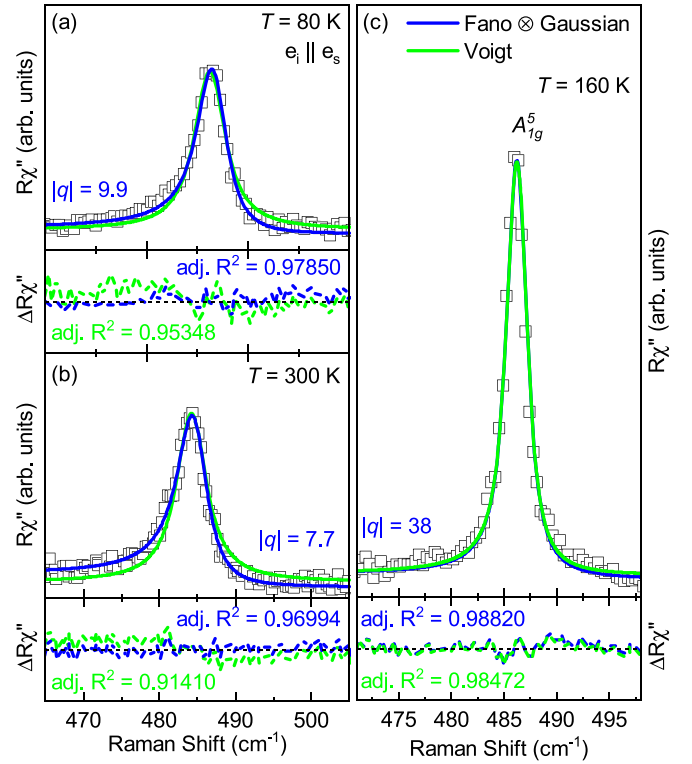


FIG. 2. Raman response as a function of the Raman shift. Quantitative analysis of the A_{1g}^5 mode at temperatures as indicated. (a) and (b) The blue solid lines represent the line shape obtained as a convolution of Fano profiles and Gaussian, whereas the green solid lines represent Voigt profiles. (c) Comparison between asymmetric (deep blue) and symmetric (light blue) line shapes obtained as a Fano-Gaussian convolution and a Voigt profile. Experimental data are represented by open squares.

profile [33–36]

$$I(\omega) = I_0 \frac{(q + \epsilon)^2}{1 + \epsilon^2},$$

where $\epsilon(\omega) = 2(\omega - \omega_0)/\Gamma$. Here, ω_0 is the phonon frequency in the absence of interaction, Γ is the full width at half maximum (FWHM), I_0 is the amplitude, and q is the Fano parameter. The Fano parameter and FWHM depend on the interaction strength between the phonon and the elementary excitation, and therefore can be used as its indicator. To include the finite spectral resolution of the experimental setup, the Fano profile is convoluted with a Gaussian function as demonstrated in Ref. [28].

The high-intensity peak at 486.7 cm^{-1} , identified as the A_{1g}^5 symmetry mode, does not overlap with any other mode. The quantitative analysis of this peak is performed using both the symmetric Voigt profile and the Fano-Gaussian convolution mentioned above. The comparison between the two models and the experimental data at 80 and 300 K are presented in Figs. 2(a) and 2(b), respectively. The asymmetric line shapes provide a satisfactory description of the measured phonon line shape, suggesting the presence of an additional scattering mechanism in $\text{Mn}_3\text{Si}_2\text{Te}_6$.

The spectral region of the A_{1g}^5 Raman-active mode in the temperature range of interest is presented in Fig. 3(a). The

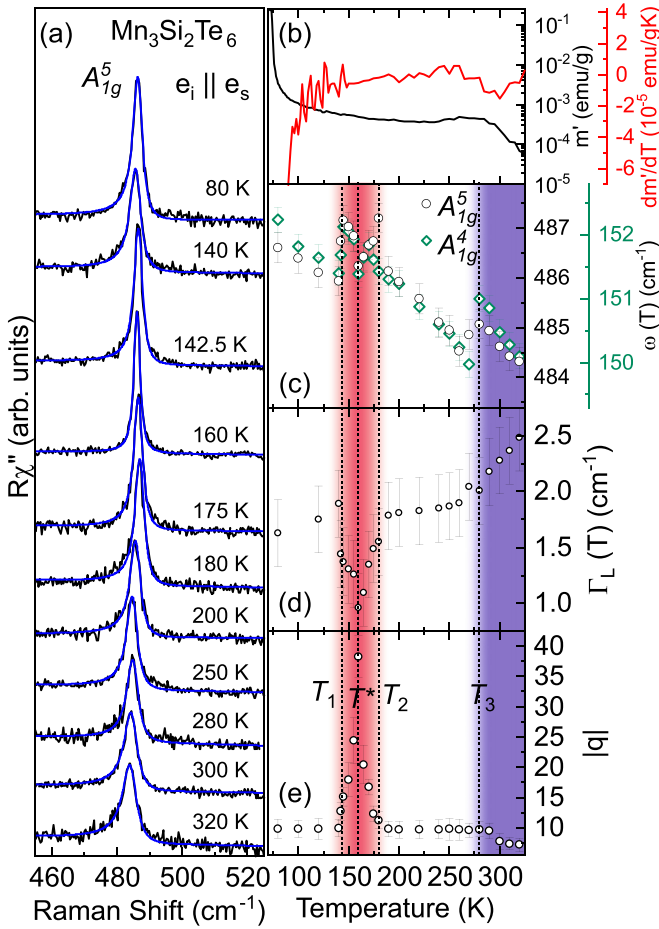


FIG. 3. (a) The spectral region of the A_{1g}^5 Raman-active mode of $Mn_3Si_2Te_6$ at indicated temperatures measured in the parallel polarization configuration. Green solid lines represent line shapes obtained as a convolution of the Fano line shape and Gaussian, calculated to fit the experimental data. (b) Temperature dependence of ac susceptibility real part $m'(T)$ and its temperature derivative plotted as a function of temperature with $\mathbf{H} \parallel \mathbf{ab}$. Temperature dependence of (c) the energy of the A_{1g}^4 and A_{1g}^5 as well as (d) the linewidth, and (e) the Fano parameter $|q|$ of the A_{1g}^5 mode.

blue solid lines represent fits to the experimental data obtained using the Fano-Gaussian line shape. The temperature dependence of the phonon energy, linewidth, and the Fano parameter $|q|$ of the A_{1g}^5 mode are depicted in Figs. 3(c)–3(e), respectively. By increasing the temperature above 80 K, the A_{1g}^5 mode broadens and softens up to $T_1 = 142.5$ K, where it abruptly narrows and shifts to higher energies followed by further softening and narrowing up to $T^* = 160$ K. Additional heating leads to a broadening and hardening before the drop in phonon energy at $\sim T_2 = 190$ K. In the region T_2 the mode softens and broadens with an additional jump in phonon energy at $T_3 = 285$ K. A similar trend is also observed for the A_{1g}^4 mode, as evidenced in Fig. 3(b).

This intriguing temperature dependence is also manifested in the asymmetry, i.e., the Fano parameter $|q|$ [Fig. 3(d)] of the A_{1g}^5 peak. At the lowest experimental temperature, 80 K, the A_{1g}^5 mode exhibits strong asymmetry with a Fano parameter $|q| = 9.9$. Upon heating the sample to $\sim T_1$ a Fano parameter

remains nearly constant before the significant increase in the temperature range between T_1 and T^* resulting in a symmetric line shape [$|q| = 38$, Fig. 3(c)]. A further temperature increase leads to a strong decrease of $|q|$ up to T_2 , where the asymmetry is restored ($|q| = 9.9$), remaining almost constant up to T_3 . At higher temperatures, the line shape becomes more asymmetric, reaching $|q| \sim 8$ at the highest experimentally accessible temperature $T = 320$ K.

While the ferrimagnetic order in $Mn_3Si_2Te_6$ is established only at $T_c = 78$ K [12,14], the asymmetry of the mode can be observed at all experimental temperatures. Based on the research done on $Mn_3Si_2Te_6$ and related materials, the most probable scenario is the one in which the observed asymmetry can be traced to an enhanced spin-phonon interaction related to short-range correlations, that can survive up to temperatures well above T_c [24,37–39]. We may speculate, according to the results presented in Ref. [15], that these short-range correlations are likely in terms of the antiferromagnetic exchange interaction between the three nearest Mn-Mn pairs (as depicted in Fig. 1) in the paramagnetic background. However, this alone cannot explain sudden changes in the properties of the A_{1g}^5 phonon mode. Rather, the existence of competing short-range magnetic phases may be responsible for the observed behavior of the phonon modes. The first phonon mode anomaly at $T_3 = 285$ K corresponds to the anomaly in $m'(T)_{ab}$ [Fig. 3(b)] and can be seen as the outlet of additional short-range order in the paramagnetic domains [40] and possibly change of their nature of previously established ones. The onset in temperature with the magnetization anomaly near 330 K [14,41] is likely the consequence of local disorder. At T_2 , $Mn_3Si_2Te_6$ becomes locally magnetically frustrated, resulting in the change in magnetostriction and a rapid decrease of the spin-phonon interaction that is manifested in the strong evolution of the phonon self-energy (Fig. 3). At this temperature both the magnetoresistance and nonlinearity of Hall resistance become observable [41]. In this scenario, by further lowering the temperature, at T_1 a new short-range magnetic order and the strong spin-phonon interaction are established. The new magnetic order is most likely antiferromagnetic [15]. In order to fully understand the complex evolution of the short-range magnetic correlation in $Mn_3Si_2Te_6$ that is manifested through the anomalous temperature development of the A_{1g}^5 mode, further investigations are required.

IV. CONCLUSION

The lattice dynamic in single-crystalline $Mn_3Si_2Te_6$ using Raman spectroscopy is analyzed. Five A_{1g} modes and nine E_g modes are observed and assigned according to the $P\bar{3}1c$ symmetry group. Four additional peaks to the ones assigned to the $P\bar{3}1c$ symmetry group, obeying A_{1g} selection rules, are attributed to overtones. There is a pronounced asymmetry of the A_{1g}^5 phonon mode at 100 and 300 K. The unconventional temperature evolution of the A_{1g}^5 Raman mode reveals three successive, possibly magnetic, phase transitions that may significantly impact the strength of the spin-phonon interaction in $Mn_3Si_2Te_6$. These are likely caused by the competition between the various magnetic states, close in energy. This paper provides comprehensive insight into the lattice properties, their temperature dependence, and shows arguments

for the existence of competing short-range magnetic phases in $\text{Mn}_3\text{Si}_2\text{Te}_6$.

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