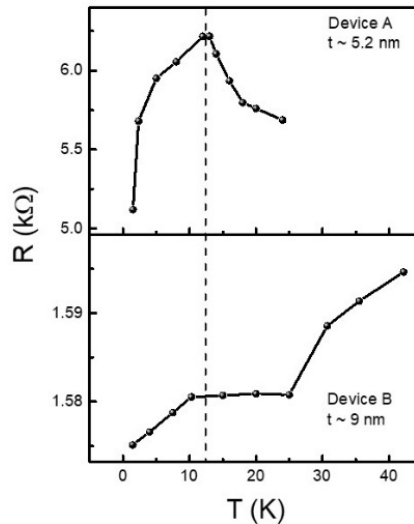


# Defect induced, layer-modulated magnetism in ultrathin metallic PtSe<sub>2</sub>

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Andras Kis

## 1. Temperature dependence of the ultra-thin PtSe<sub>2</sub>'s resistance

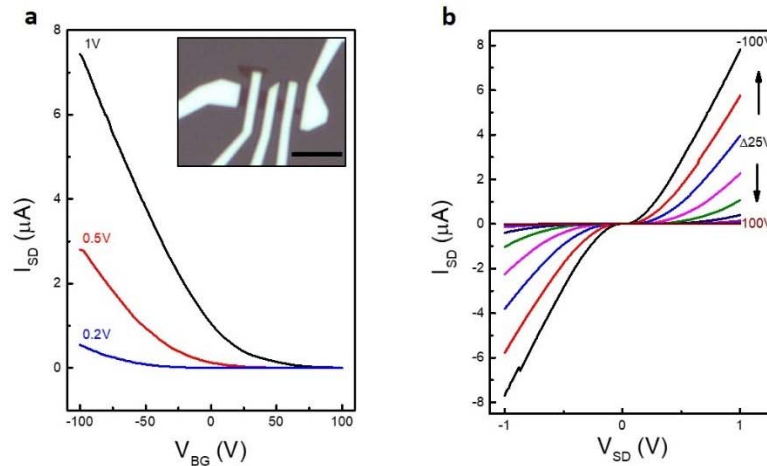
The bottom panel of Supplementary Fig. 1 shows the temperature dependence of the device resistance obtained from a  $\sim 9$  nm thick PtSe<sub>2</sub> (device B). The overall device resistance increases as the temperature is increased which provides an additional proof that our PtSe<sub>2</sub> crystal is metallic at this thickness range.<sup>1</sup> Similarly to the temperature dependence of the device resistance obtained from a 5.2 nm thick PtSe<sub>2</sub> (device A), we observe an anomaly in this sample which could be related to spin dependent scattering.



**Supplementary Fig. 1. Temperature dependence of the device resistance.** The total device resistance as a function of temperature obtained from  $\sim 5.2$  nm (device A, shown in Figure 2) and  $\sim 9$  nm thick PtSe<sub>2</sub> crystals. The black dotted line represents the position of the anomaly.

## 2. Charge transport characterization of device F (~ 2.2 nm thick PtSe<sub>2</sub>)

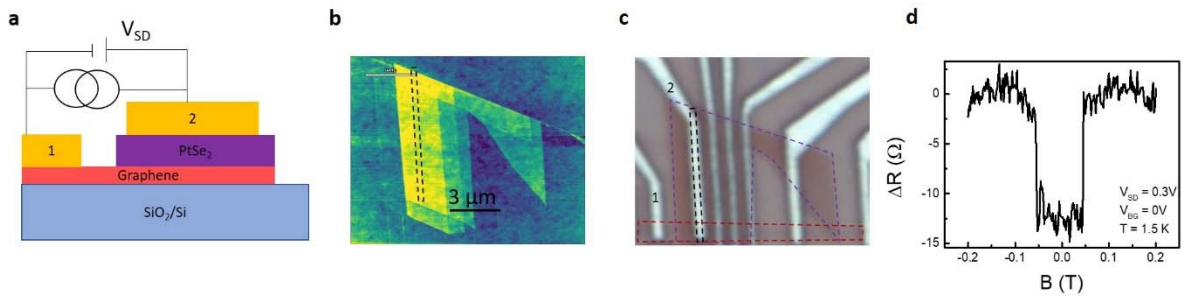
Supplementary Fig. 2 shows the charge transport characteristics of a ~ 2.2 nm thick PtSe<sub>2</sub> crystal (device F). In sharp contrast to the metallic response observed from relatively thicker samples as shown in Figure 1b and Figure S6, here we observe semiconducting behavior. The device shows p-type behavior with a hole mobility of ~ 32 cm<sup>2</sup>/Vs and an on/off ratio of ~ 5 × 10<sup>4</sup>. Observation of non-linear I<sub>SD</sub>-V<sub>SD</sub> relation suggests the presence of a Schottky barrier at the contacts. The obtained response is in a good agreement with recent findings.<sup>1,2</sup> We would like to note that it is difficult to probe magnetism in semiconducting flakes under lateral device measurement geometry since signal-to-noise ratio is unfortunately low. In this semiconducting device, we also performed magnetic field dependent measurements. However, here we could not probe the magnetization since noise in the device is much higher than the contribution we would expect from magnetism.



**Supplementary Fig. 2. Electrical transport characterization of device F. a**, V<sub>BG</sub> dependence of I<sub>SD</sub> measured at fixed biases of V<sub>SD</sub> = 0.2 V, 0.5 V and 1 V. Inset shows the optical image of the characterized device. Black solid line represents the scale bar (5 μm). **b**, V<sub>SD</sub> dependence of I<sub>SD</sub> measured at fixed V<sub>BG</sub> values. Charge transport measurements were performed at 1.5 K.

### 3. Magnetoresistance measurements in device G (~ 2 nm thick PtSe<sub>2</sub>)

In our manuscript, we employ a local measurement geometry to probe the magnetism. Since the relative change in device resistance (due to magnetism) is small compared to the total device resistance, we have focused only on metallic samples. It is challenging to measure magneto-transport in crystals thinner than 2.5 nm (as they are very resistive) under such lateral measurement geometry due to low signal-to-noise ratio, as discussed above. Therefore, we prepared a new type of a device to prove that magnetization persists in a few-layer crystals as well. Here, we utilized graphene as a bottom electrode and we transferred ultra-thin PtSe<sub>2</sub> on top of graphene. Finally, we formed non-magnetic Pd contacts on graphene and on top of PtSe<sub>2</sub>. Measurement schematics and optical images of the device are shown in Supplementary Fig. 3a-c. The observation of anti-ferromagnetic response in this vertical device demonstrates that even ultra-thin PtSe<sub>2</sub> is magnetic.



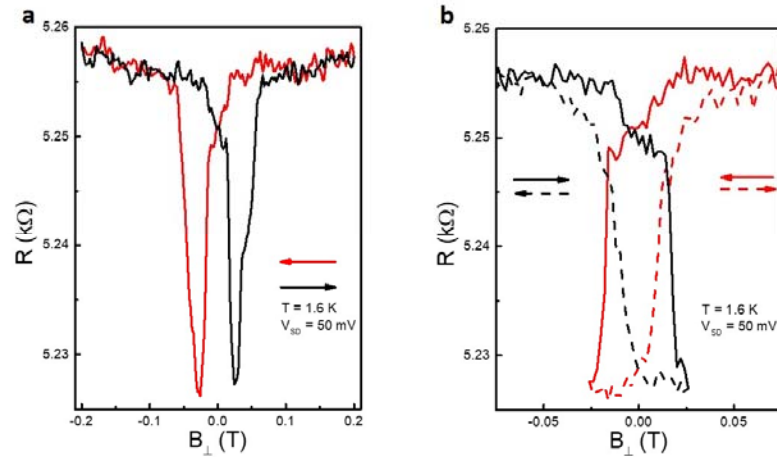
**Supplementary Fig. 3. PtSe<sub>2</sub>-based vertical device.** **a** Measurement configuration. **b** AFM picture of PtSe<sub>2</sub> used in device G. **c** Optical picture of a completed device. Red, purple and black dotted lines represent the position of bottom graphene contact, PtSe<sub>2</sub> and non-magnetic Pd electrode, respectively. **d** Magneto-transport response obtained in this device. Measurement temperature is 1.5 K.

Due to a complicated device structure (Si/SiO<sub>2</sub>/Graphene/PtSe<sub>2</sub>/top Pd metal contacts), we did not have enough space to place additional contacts in order to study the lateral transport

characteristic of this device. However, we expect this  $\sim 2$  nm thick crystal to be semiconducting. During this study, we measured electrical properties of 13 devices, two of them have thickness of  $\leq 2.5$  nm. These ultrathin devices exhibit semiconducting behavior. Our results are also in a good agreement with experimental works by A. Ciarrocchi et al.,<sup>1</sup> and X. Yu et al.,<sup>2</sup> that crystals thinner than 2.5 nm show semiconducting behavior. We finally would like to note that our  $\sim 2$  nm thick vertical PtSe<sub>2</sub>-based device shows antiferromagnetic behavior. It is clear that for insulating systems the RKKY model does not apply, as no Fermi surface can be conceived. For this thickness range, it is difficult for us to estimate the exchange coupling strength. We remark that the investigation of defect-induced magnetism in insulating PtSe<sub>2</sub> films does not fall within the scope of the present work, in which we specifically focus on metallic PtSe<sub>2</sub> samples.

#### **4. Additional magnetoresistance measurements in device A**

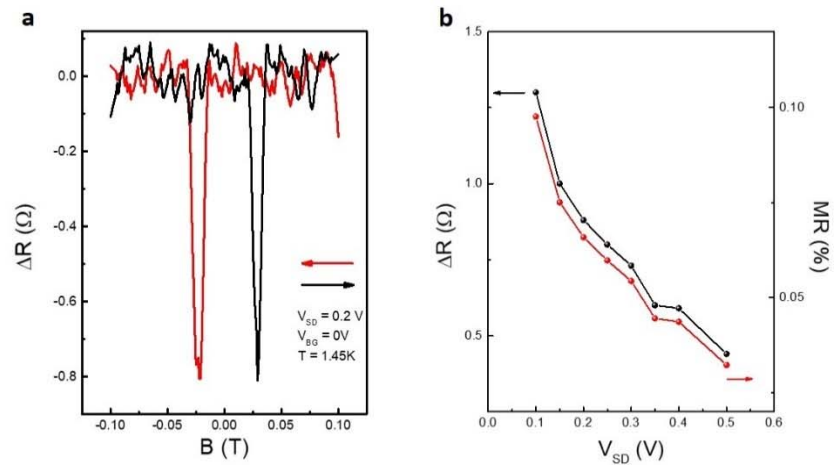
Supplementary Fig. 4 shows the dependence of the device resistance on the magnetic field sweep direction. As mentioned in the manuscript, we observe a dip in the resistance around 25 (-25) mT while the field is ramped from -0.2 T (0.2 T) to 0.2 T (-0.2 T) below a critical temperature of 13 K (Supplementary Fig. 4a). Next, we repeatedly sweep the field starting from -0.2 T (0.2 T) to 25 mT (-25 mT) where we previously observed the dip, then we sweep the field back to -0.2 T (0.2 T). As shown in Supplementary Fig. 4b, the device resistance stays in the same state until the negative (positive) field is applied which polarizes the magnet back to the initial state.



**Supplementary Fig. 4. Magnetoresistance measurements in device A.** **a**, Magnetoresistance of PtSe<sub>2</sub> as a function of out-of-plane magnetic field. Red (black) arrow represents the sweep direction. **b**, Observation of a minor loop in PtSe<sub>2</sub>. In this measurement configuration, the device resistance is first measured while the B field is swept from 200 mT to -26 mT (solid red line). Then, the sweep direction is reversed, and the field is swept from -26 mT to 200 mT (dashed red line). The same protocol is applied for the opposite sweep directions as well (Solid and dashed black lines).

## 5. Additional magnetoresistance measurements in device H

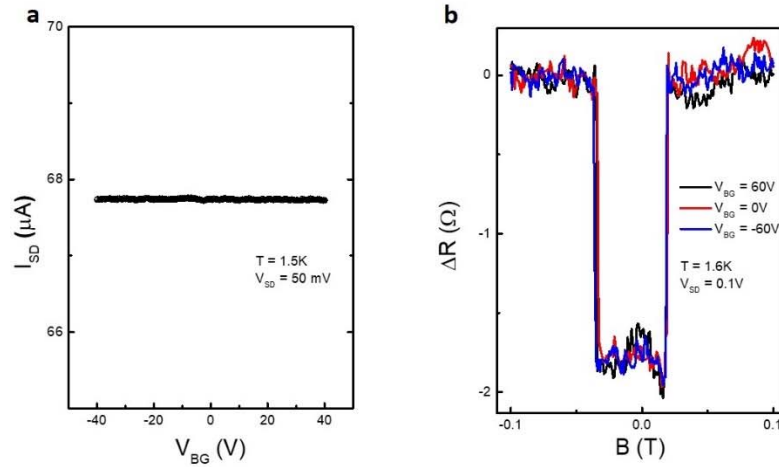
Similarly to the ferromagnetic response observed in Figure 2, we characterized three additional devices which show similar coercive field values, bias and gate dependencies. Supplementary Fig. 5a shows the change in device resistance under backward and forward magnetic field sweep directions at fixed bias of  $V_{SD} = 0.2$  V for device H. Differently, this device was studied at the higher bias regime as well (Supplementary Fig. 5b). Here, we detect a further reduction in the calculated magneto-resistance percentage as the bias is increased, in good agreement with the tendency observed in Figure 2b.



**Supplementary Fig. 5. Bias dependent magnetoresistance measurements in device H. a,** The change in the device resistance under the forward and backward field sweep directions at fixed  $V_{SD} = 0.2$  V and  $V_{BG} = 0$  V. **b,**  $V_{SD}$  dependence of the calculated magneto-resistance percentage. Measurements were taken at  $V_{BG} = 0$  V and  $T = 1.45$  K.

## 6. Gate voltage dependent measurements in device B

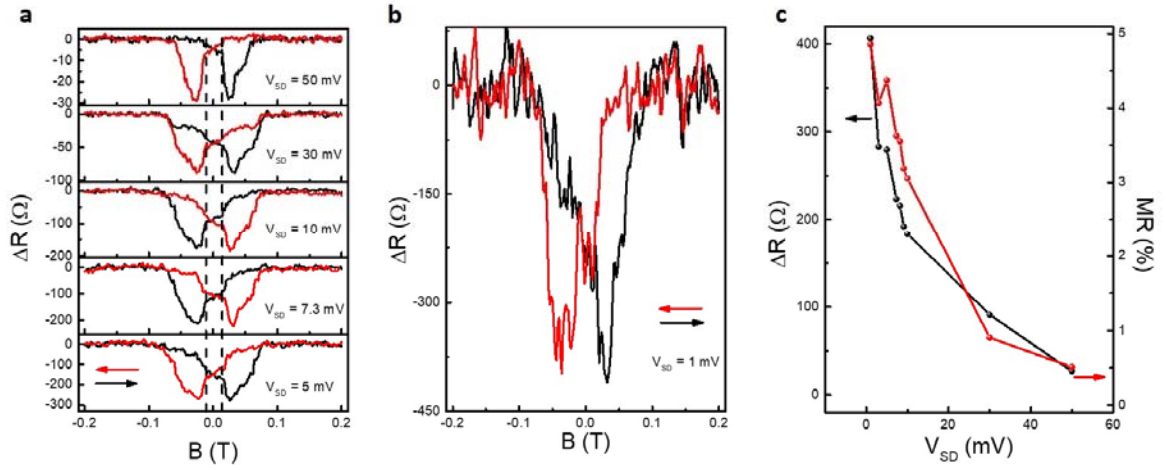
Supplementary Fig. 6a shows the gate voltage dependence of the bias current at fixed bias voltage of  $V_{SD} = 50$  mV. Observation of nearly gate-independent response shows the metallic characteristic of this ultra-thin PtSe<sub>2</sub>. Similarly to the device conductance, the change in the device resistance under magnetic field,  $\Delta R$ , is also insensitive to  $V_{BG}$  as shown in Supplementary Fig. 6b. Two-plateau response is observed at  $V_{BG} = 0, 60, -60$  V with identical switching field values.



**Supplementary Fig. 6. Gate-voltage dependent magnetoresistance measurements in device B.** **a**,  $V_{BG}$  dependence of  $I_{SD}$  measured at fixed bias of  $V_{SD} = 50$  mV. **b**, Dependence of change in device resistance on the magnetic field at fixed bias of  $V_{SD} = 0.1$  V. Measurements were taken at  $V_{BG} = 0, 60$  and  $-60$  V and  $T = 1.6$  K.

## 7. Source-drain bias dependent magnetoresistance measurements in device A

Supplementary Fig. 7a shows the dependence of the device resistance on the field at fixed biases of  $V_{SD} = 5, 7.3, 10, 30$  and  $50$  mV. As the bias is reduced, the magnitude of the change in device resistance increases. The highest value of  $\sim 400$  ohm is observed for the lowest bias of  $V_{SD} = 1$  mV (Supplementary Fig. 7b). Supplementary Fig. 7c shows the dependence of the calculated magnetoresistance change on the applied bias voltage.

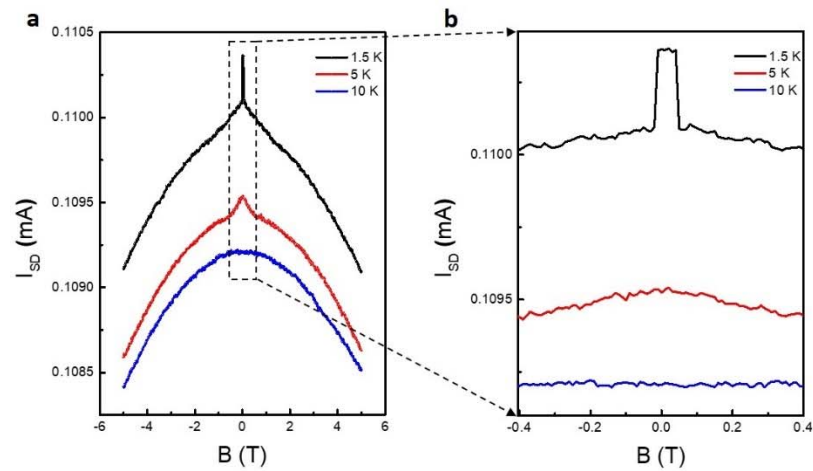


**Supplementary Fig. 7.  $V_{SD}$  dependent magnetoresistance measurements in device A. a,** The change in the device resistance for forward and backward field sweep directions at fixed bias values. Dotted lines represent the appearance of systematic kinks in the magneto-transport measurements which could be related with the switching of different layers at different field values. **b,** Field dependence of the change in device resistance measured at fixed bias value of  $V_{SD} = 1$  mV. **c,** Bias dependence of the calculated magneto-resistance percentage. Measurements were taken at  $V_{BG} = 0$  V and  $T = 1.5$  K.

## 8. Additional magnetoresistance measurements in device I under large field values

Supplementary Fig. 8 shows the out-of-plane magnetic field dependence of the device current measured at a fixed bias of  $V_{SD} = 0.1$  V. Here, the field is swept from -5 T to 5 T. In addition to the weak antilocalization effect (expected from PtSe<sub>2</sub> due to its high spin orbit coupling strength), we observe an anomaly near  $B = 0$  T, similar to Figure 3 (*device B*). As discussed in the manuscript, this anomaly is related with the antiferromagnetic ordering. The signal disappears above a critical temperature ( $\sim 5$  K for this device).

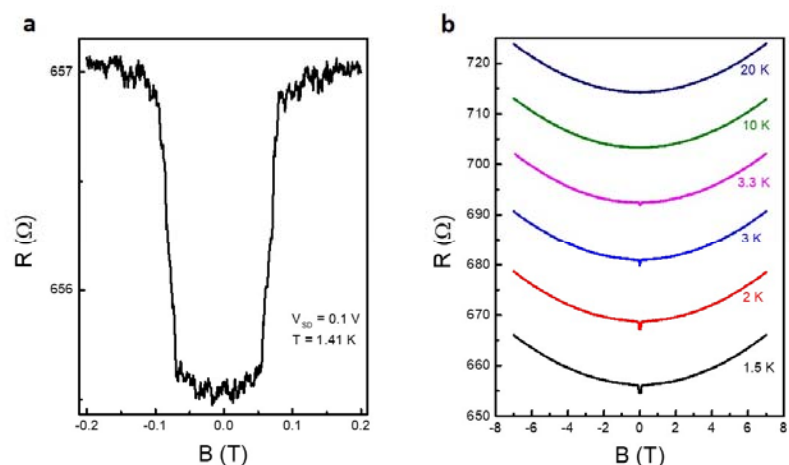




**Supplementary Fig. 8. Magnetic field dependence of the bias current.** **a**, Dependence of the bias current on magnetic field at fixed bias of  $V_{SD} = 0.1$  V. The rectangle shape box shows the zoomed-out region of the data shown in **b**. Measurements were taken at  $T = 1.5, 5$  and  $10$  K.

## 9. Additional magnetoresistance measurements in device J under large field values

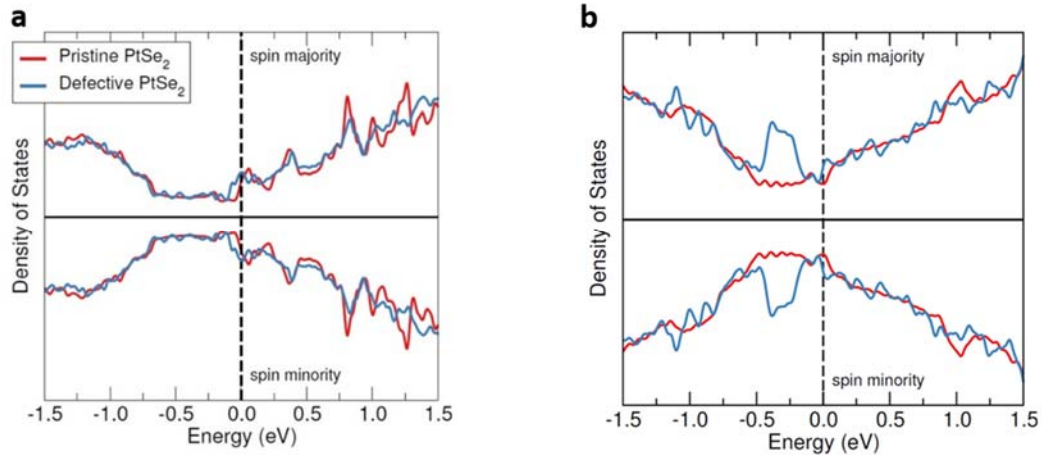
Similarly to the magnetic response shown in Supplementary Fig. 8 and Figure 3 for device I and device B, here we demonstrate two-plateau response obtained from device J (Supplementary Fig. 9). Switching fields are comparable. The signal in this  $\sim 9$  nm thick device disappears above 3.3 K.



**Supplementary Fig. 9. Magnetic field and temperature dependence of the total device resistance.** **a**, Dependence of the device resistance on the magnetic field at fixed bias of  $V_{SD} = 0.1$  V. **b**, Temperature dependence of the signal shown in **a**, but at higher magnetic field range. The field was swept from -7 T to 7 T while the device resistance was being recorded. Measurements were taken at  $T = 1.5, 2, 3, 3.3, 10,$  and 20 K.

## 10. Additional first-principles calculations of vacancy defects

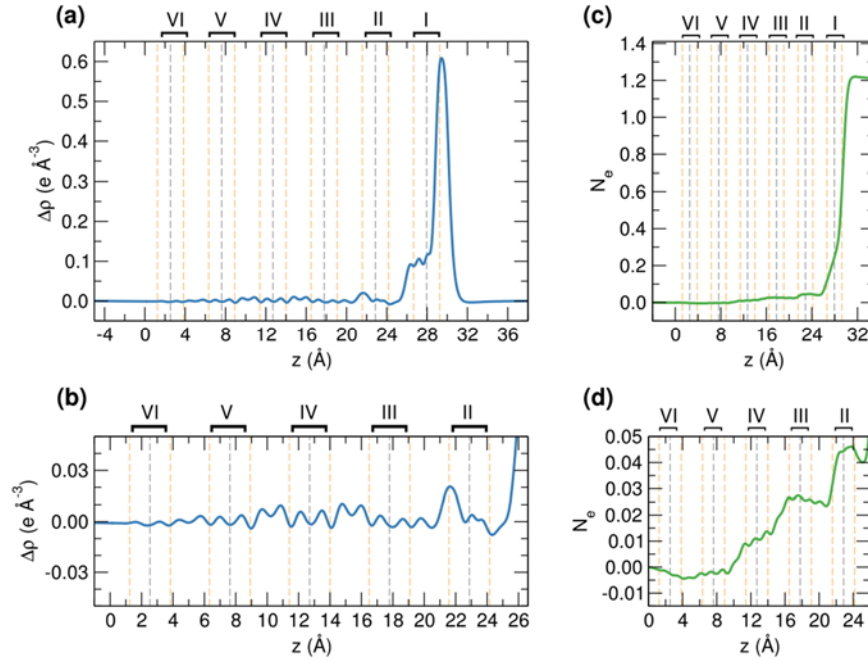
We complete our first-principles investigation of vacancy defects in PtSe<sub>2</sub> by considering the Se vacancy defect. Though widely observed in PtSe<sub>2</sub>, we find that this type of defect does not induce magnetism, as confirmed by inspecting the spin density of the system and as illustrated by the electronic density of states shown in Supplementary Fig. 10a. Overall, we find that the presence of Se vacancies has a minor effect on the electronic structure of PtSe<sub>2</sub>.



**Supplementary Fig. 10. Density of states with and without Se vacancy.** Electronic density of states of (a) multilayer PtSe<sub>2</sub> with (blue) and without (red) a Se vacancy and (b) bulk PtSe<sub>2</sub> with and without a Pt vacancy. Fermi level is set to zero (vertical dashed line).

Next, we consider Pt vacancies in bulk PtSe<sub>2</sub>. Surprisingly, our calculations show that Pt vacancy defects in bulk PtSe<sub>2</sub> are *non-magnetic*, hence there is a pronounced difference between the electronic and magnetic properties of Pt vacancies in bulk and surface locations. This observation points to a *non-uniform* (or *surface*) character of magnetization in thin films of PtSe<sub>2</sub>. The surface character of magnetism in PtSe<sub>2</sub> is supported by the fact no magnetism is experimentally observed in bulk samples of PtSe<sub>2</sub>, as discussed below (Supplementary Section 12). In the surface magnetism scenario, the interplay between the ferro- and antiferromagnetic configurations of thin films can be explained by the thickness dependent effective magnetic exchange coupling between the surface-localized magnetic moments. As discussed in the main text within the framework of the RKKY model, one can consider PtSe<sub>2</sub> thin films as a magnetic bilayer system. Making a rigorous correspondence between the proposed RKKY picture and the results of first-principles calculations goes beyond the scope of this work. Nevertheless, the calculated spin density across the 6-layer slab with Pt vacancy

in layer I clearly supports the RKKY interaction scenario (Supplementary Fig. 11). The large magnetic moment of 1.2 Bohr magneton in layer I induces a decaying spin polarization across the slab that changes its sign upon reaching layer VI, especially clearly visible in the plots of the integrated spin density (panels (c) and (d) of Supplementary Fig. 11).



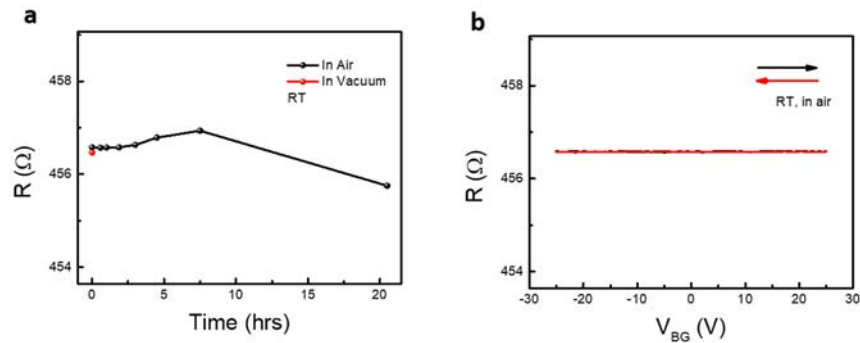
**Supplementary Fig. 11. Spin polarization as a function of thickness.** **a** Spin density  $\Delta\rho(z)$  as a function of out-of-plane position  $z$  (and averaged in  $xy$  plane) across the 6-layer slab with a magnetic Pt vacancy defect in layer I. **b** Details of induced spin density  $\Delta\rho(z)$  in layers II-VI. **c,d** Spin density integrated from 0 to  $z$  as a function  $z$ . Panel **d** clearly demonstrates the opposite sign spin polarization in layer VI.

## 11. Role of exposure to air on electronic and magnetic properties of PtSe<sub>2</sub>

In order to address the role of air exposure on the electronic and magnetic properties of our samples, we have performed additional experiments and calculations.

As a first step, we evaluate the basic electronic properties of one representative device under controlled conditions. To this end, the device was annealed at 250 °C under high vacuum

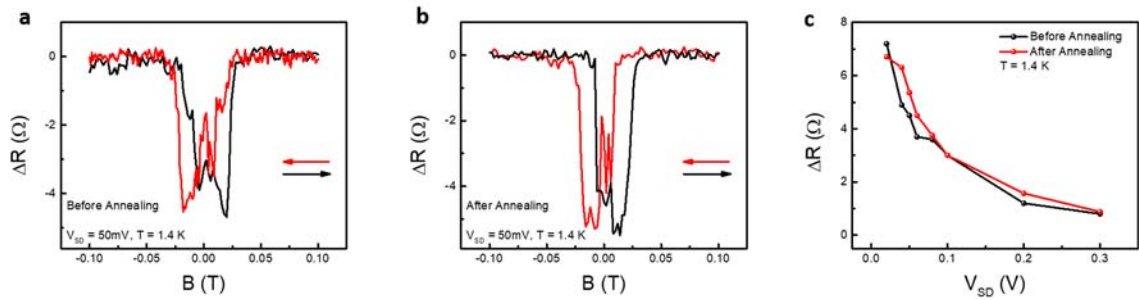
conditions to remove potential adsorbates. We note that such high-temperature annealing does not lead to any degradation of the crystal (See Supplementary Fig. 12). This approach was previously adopted to remove contaminants such as O<sub>2</sub> and H<sub>2</sub> from two-dimensional MoS<sub>2</sub><sup>3</sup> and graphene<sup>4</sup>, without creating additional defects. After measuring the device resistance under vacuum conditions, we exposed it to air and measured the evolution of its resistance in time. If significant contaminants-induced charge transfer had occurred, the device resistance would have shown rapid changes as well as hysteresis in transport measurements.<sup>5</sup> On the other hand, as shown in Supplementary Fig. 12, the transport characteristics of our metallic PtSe<sub>2</sub> sample are fully preserved upon air exposure, thereby indicating the electronic properties of the device are not affected.



**Supplementary Fig. 12. Role of air exposure on electronic properties of PtSe<sub>2</sub>** (a) Transport characteristics of a ~ metallic PtSe<sub>2</sub> device measured under vacuum and air conditions. The device is first measured under vacuum ( $\sim 2 \times 10^{-4}$  Torr) and then directly exposed to air and measured as a function of time. (b) Back gate voltage dependence of device resistance under backward (red arrow) and forward (black arrow) gate sweeps.

Secondly, we address the magnetic properties of one of our device under controlled conditions. We firstly measure our device at 1.4 K without any annealing treatment. As shown in Supplementary Fig. 13a, we observe a ferromagnetic response. Then, we anneal our device at 250 °C under vacuum conditions to desorb possible adsorbates. As shown in Supplementary

Fig. 13b, we similarly observe a ferromagnetic response. Note that the shape of switching curves, magnitude of  $\Delta R$  and coercive fields are almost identical for these two measurements.  $V_{SD}$  dependence of  $\Delta R$  is also almost identical before and after the annealing treatment (Supplementary Fig. 13c). These observations suggest that magnetic properties are also preserved after removing the possible adsorbates.



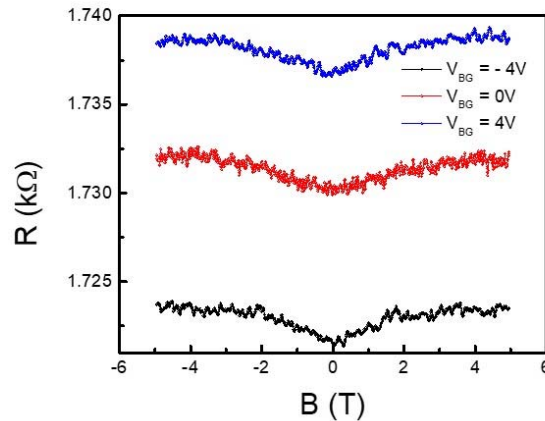
**Supplementary Fig. 13. Role of air exposure on magnetic properties of PtSe<sub>2</sub>.** The resistance change under magnetic field acquired at fixed bias of  $V_{SD} = 50$  mV at 1.4 K in an as fabricated device, without any annealing treatment. (b) The resistance change under magnetic field acquired at a fixed bias of  $V_{SD} = 50$  mV at 1.4 K after 250 C annealing. (c) Source-drain bias ( $V_{SD}$ ) dependences of the change in the device resistance before and after the annealing treatment.

Hence, we conclude from our additional experiments that the electronic and magnetic properties of our samples are preserved upon air exposure. It is worth noticing in this context that recent first-principles calculations<sup>6</sup> found that the dissociation of contaminants (e.g. H<sub>2</sub>O) on PtSe<sub>2</sub> requires an energy barrier larger than 1.5 eV. This indicates that chemisorption is very unlikely to occur even at relatively high temperatures.

## 12. Thickness dependent magnetoresistance in PtSe<sub>2</sub>

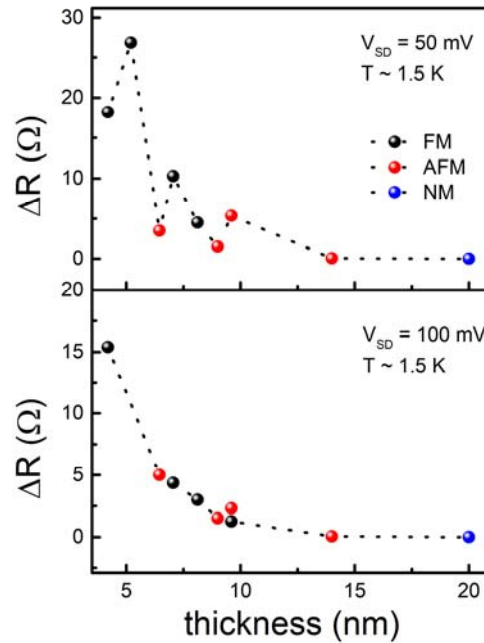
Bulk PtSe<sub>2</sub> do not show any sign of magnetism. Supplementary Fig. 14 shows the magneto-transport measurements from a bulk sample, where the magnetism-related signals shown in

manuscript are missing. Similarly, magneto-transport studies on thick PtSe<sub>2</sub> crystals (60 and 150 nm thick bulk crystals) measured by other groups also do not show any sign of magnetism.<sup>7</sup> They observe a similar B field dependence to our data, as shown in Supplementary Fig. 14. This further suggests that the magnetism we describe in our manuscript occurs only in ultra-thin samples where defects play a critical contribution.



**Supplementary Fig. 14. Magneto-transport in ~ 20 nm thick PtSe<sub>2</sub>.** Magnetic field dependence of resistance in bulk PtSe<sub>2</sub>. Measurement temperature is 1.5 K.

Our thickness dependent measurements, in good agreement with the surface magnetism scenario suggested by our DFT calculations, show that as the thickness of the crystal is increased, the MR decreases. Supplementary Fig. 15 summarizes devices with their thickness, MR magnitude and magnetic behavior. Please see the details of the protocol we followed below.



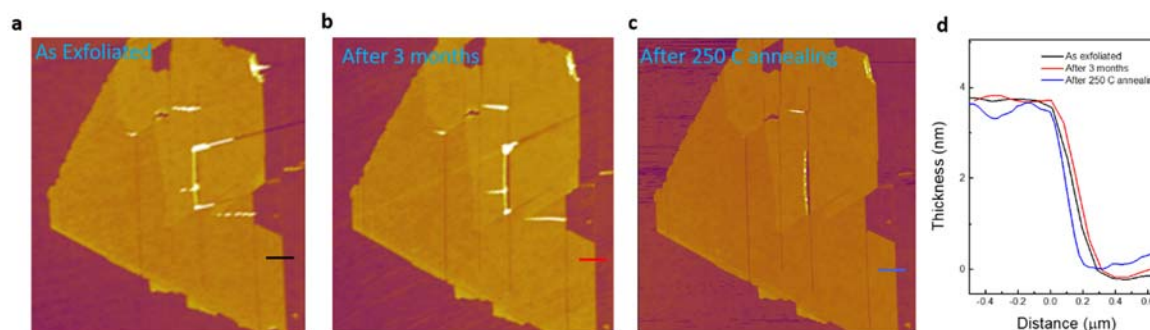
**Supplementary Fig. 15. Thickness dependent MR.** Thickness dependence of MR curves for studied samples at fixed  $V_{SD}$  of 50 mV and 100 mV. Black (red) dots represent devices showing characteristic FM (AFM) response. The blue dot indicates the absence of magnetism in thicker crystals. Error bars in crystal thicknesses have not been included due to the fact that AFM measurements have been performed under different scanning conditions.

As shown in Fig. 2b & Fig. 3b and discussed in manuscript, the measured MR strongly depends on the applied bias. Therefore, we focused on plotting the thickness dependence of MR at fixed biases ( $V_{SD} = 50$  mV and 100 mV). Since we had this insight on strong bias dependence of MR signal after several devices have already been characterized, the first batch of characterized samples was not studied in detail as a function of bias. Therefore, not all measured devices are included in this plot, but only those measured at 50 mV and 100 mV biases. Nevertheless, this summary has three main messages: 1-) MR magnitude decreases as crystal thickness increases, 2-) there is the presence of layer dependent magnetism and 3-) magnetism disappears at thicker crystals.



### 13. Air Stability of PtSe<sub>2</sub>

Air-stability of PtSe<sub>2</sub> was previously investigated by Y. Zhao et al. through surface and Raman characterization techniques.<sup>6</sup> Here, we perform complementary experiments to demonstrate the air-stability of PtSe<sub>2</sub> after a variety of treatments. Our AFM scans demonstrate that ultra-thin PtSe<sub>2</sub> (~3.9 nm) does not show any signs of degradation even 3 months after its exfoliation. To further demonstrate its stability, we annealed our crystal at 250 °C. The sample remains pristine even after such annealing step, as shown in Supplementary Fig. 16. We note that well-known crystals such as CrI<sub>3</sub><sup>8</sup> and black phosphorus<sup>9,10</sup> do not exhibit such long-term stability. In this regards, we suggest that metallic PtSe<sub>2</sub> stands out from many atomically-thin crystals.

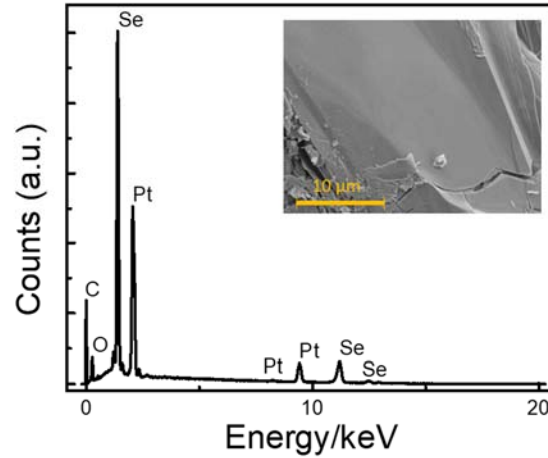


**Supplementary Fig. 16. Environmental sensitivity of PtSe<sub>2</sub>.** (a) AFM image taken approximately 1 hour after exfoliation. (b) AFM image of the same flake 3 months after its exfoliation. The flake was stored in the glove-box but no special care was taken: the flake was exposed to air while transferring it between different equipment. (c) The same flake after 250 °C annealing for 1 hour under vacuum conditions ( $\sim 1 \times 10^{-6}$  Torr). Height scale bar is  $\pm 10$  nm. Following the solid lines, we measure a height of  $\sim 3.9$  nm after each process.

### 14. EDX spectrum of PtSe<sub>2</sub>

For determining the elemental analysis of PtSe<sub>2</sub> crystal, we characterize its energy-dispersive x-ray (EDX) spectra. Supplementary Fig. 17 shows the EDX spectrum of PtSe<sub>2</sub> deposited on a carbon tape. The spectra show signals of carbon, oxygen, platinum and selenide. We believe that the detected carbon signal is due to the carbon substrate. It is absent if the crystal is

transferred onto an SiO<sub>2</sub> substrate. There is no element detected apart from oxygen, platinum and selenium which rules out the possibility of any intercalation process during growth. The presence of oxygen was also detected in a previous study.<sup>11</sup>

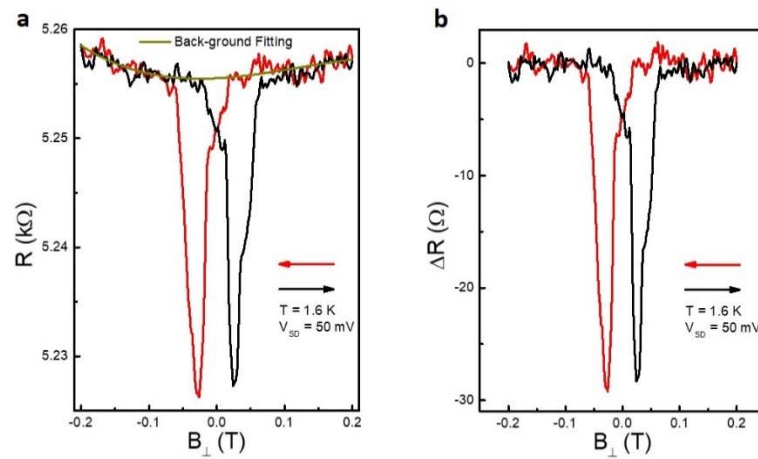


**Supplementary Fig. 17. EDX spectrum of PtSe<sub>2</sub>.** EDX analysis of PtSe<sub>2</sub>. Inset shows the SEM image of the crystal.

### **15. Calculation of $\Delta R$**

In this section, we discuss how the change in device resistance  $\Delta R$  is calculated. Figure S18a shows the dependence of the device resistance on the magnetic field sweep directions. Resistance values for both backward and forward sweep directions are nearly identical above coercive fields of  $\sim 25$  mT. By using a polynomial function, we perform the fitting for the magnetic field dependence of the device resistance by excluding the data between  $-25 \text{ mT} < B < 25 \text{ mT}$  range. After this, we subtract the background fitting line from the measurement curves to calculate the change in device resistance due to the MR effect (Supplementary Fig. 18).

Similar background resistance subtraction has been also employed for spin valve curves to extract the spin-dependent contribution to the resistance.



**Supplementary Fig. 18. Subtracting the background signal.** **a**, Magnetoresistance of PtSe<sub>2</sub> as a function of the out-of-plane magnetic field. Red and black arrows represent the sweep direction. Solid yellow line represents the polynomial fitting as described above. **b**, The change in the device resistance upon application of forward and backward sweep directions, after background subtraction.

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