Extreme In-Plane Upper Critical Magnetic Fields of Heavily Doped Quasi 2D Transition Metal Dichalcogenides – Misfit (LaSe)1.14(NbSe2)n=1,2

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Extreme in-plane upper critical magnetic fields $B_{c2//ab}$ strongly violating the Pauli paramagnetic limit have been observed in the misfit layer $(LaSe)_{1.14}(NbSe_2)$ and $(LaSe)_{1.14}(NbSe_2)_2$ single crystals with T_c = 1.23 K and 5.7 K, respectively. The crystals show a 2D-3D transition at the temperatures slightly below T_c with an upturn in the temperature dependence of $B_{c2//ab}$, a temperature dependent huge superconducting anisotropy and a cusp-like behavior of the angular dependence of B_{c2}. As shown in our previous work a strong charge transfer occurs in $(LaSe)_{1.14}(NbSe_2)_2$ which makes this compound behaving as a stack of highly doped $NbSe_2$ monolayers, where the strong upper critical field can be attributed to the Ising coupling recently discovered in atomically thin transition metal dichalcogenides with strong spin-orbit coupling and lack of inversion symmetry. Surprisingly, while showing a very similar behavior $(LaSe)_{1.14}(NbSe_2)$ seems to imply a very different mechanism not related to Ising coupling since superconductivity rather appears in the LaSe layers while $NbSe_2$ layers behave like tunneling barriers. Despite their fundamental differences a common denominator in both misfits is a strong charge transfer from LaSe to $NbSe_2$ that makes them behaving as a stack of almost decoupled superconducting atomic layers.

Subject Areas: Condensed Matter Physics, Materials Science

I. INTRODUCTION

Transition metal dichalcogenides (TMDs) reveal remarkable electronic and mechanical properties with atomic-scale thickness, direct bandgap and strong spin-orbit coupling what makes them very interesting plaform for fundamental studies and for prospective applications in electronics, spintronics, optoelectronics, energy harvesting etc. [1]. They exhibit a rich physics with a competition between different ground states as charge or spin density waves states and superconductivity [2] which can be controled by electronic doping. The layered structure with strong in-plane bonding and weak, van der Waals coupling between the layers allows for preparation of fully two-dimensional (2D) devices. Recently, a new type of superconducting interaction – the Ising pairing – has been discovered in the atomically thin superconductors MoS_2 [3] and $NbSe_2$ [4]. The lack of crystal inversion symmetry in monolayer combined with strong spin-orbit coupling leads to an effective spin-orbit magnetic field which fixes the electron spins out of plane (Ising) with opposite signs for the opposite momenta at *K* and *K'* of the hexagonal Brillouin zone. The locking of spin and momentum in the superconducting pairing hinders the spin pair-breaking leading to anomalously high in-plane upper critical fields violating the Pauli limit. For instance in the $NbSe_2$ monolayer the Zeeman spin splitting is realized at fields where the superconducting condensation energy is overcome almost seven times [4]. It was also shown that upon increasing the number of $NbSe_2$ atomic layers with the onset of interlayer coupling and the restoring of inversion symmetry, the in-plane critical field becomes smaller compared to B_p [4] questioning the application of the Ising superconductivity in bulk materials.

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Here we show that non conventional superconductivity is at play in a family of bulk compounds made of the stacking of $NbSe_2$ layers and LaSe layers. Our transport and *ac* calorimetry measurements down to milikelvin temperatures and in magnetic fields up to 30 T show that in both misfit layer compounds - $(LaSe)_{1.14}(NbSe_2)$ and $(LaSe)_{1.14}(NbSe_2)_2$ - the in-plane critical field $B_{c2//ab}$ is overcoming the Pauli limiting B_P almost 10 and 5 times, respectively. The superconducting anisotropy $\gamma = B_{c2//ab} / B_{c2//c}$ is very high and temperature dependent. Moreover, the temperature dependence of $B_{c2//ab}$ displays an upturn close to T_c characteristic for a dimensional crossover in vortex matter from 3D to 2D upon lowering the temperature revealing in the quasi-2D regime where a cusp in the angular dependence of B_{c2} is found.

Let us first focus on the misfit TMDs compound $(LaSe)_{1.14}(NbSe_2)_2$ that is constituted of trilayers where a quasi-quadratic (Q) LaSe chalcogenide plane is sandwiched between two quasi-hexagonal (H) TMD $NbSe_2$ layers. This is an ideal platform to test 2D physics in a bulk compound as our experimental work as well as calculations [5] have demonstrated that despite being bulk single crystal $(LaSe)_{1.14}(NbSe_2)_2$ behaves as doped monolayer $NbSe_2$ with a rigid doping of 0.55–0.6 electrons per Nb atom. This doping level can be explained by an intuitive chemical model that assumes that each LaSe unit transfers 1 electron to the $NbSe_2$ layer. As there are 2 $NbSe_2$ units per 1.14 LaSe unit, one expects a charge transfer of 0.57 electron per $NbSe_2$ unit. This is precisely what our previous STM and ARPES measurements and DFT calculations show. Our work thus confirms that Ising superconducting coupling may be a possible scenario for the bulk compound $(LaSe)_{1.14}(NbSe_2)_2$. Notice that till now only monolayer-few-layer systems were exhibiting Ising superconductivity. Our wok suggest that bulk compound could exhibit it, too.

If we use the chemical model described above for the case of the $(LaSe)_{1.14}(NbSe_2)$ compound, where LaSe layers are simply alternating with $NbSe_2$ planes we find a charge transfer of 1.14 electron per $NbSe_2$ unit which is impossible since the undoped $NbSe_2$ unit can accept at most 1 electron. This indicates that the $NbSe_2$ layer should be totally filled in $(LaSe)_{1.14}(NbSe_2)$ while the metallicity/superconductivity should reside in LaSe layers, $NbSe_2$ layers behaving like tunneling barriers. Our preliminary DFT calculations are in favor of this mechanism and will be discussed in a separate article. Therefore, we expect that Ising scenario cannot explain the very high $B_{c2//c}$ of $(LaSe)_{1.14}(NbSe_2)$ because the symmetry of the LaSe layers is not compatible with any Ising spin-orbit coupling. The origin of the strong in-plane critical field in this compound is still unknown.

At first glance the superconducting misfit compounds $(LaSe)_{1.14}(NbSe_2)_{n=1,2}$ are expected to behave quite differently, one of them being an Ising superconductor while the other one does not benefit from any Ising spin-orbit coupling. However, they exhibit quite similar behavior in high magnetic fields. Thus the question arises, what explains their similarities? Is it due to the fact that both compounds can be described as a stack of weakly coupled superconducting 2D layers? A comprehensive study of the superconducting misfit $(LaSe)_{1.14}(NbSe_2)_{n=1,2}$ compounds would therefore be of great interest.

II. EXPERIMENT

The misfit TMDs [6] have a formula $(MX)_{1+x}(TX_2)_n$ (M=Sn, Sb, Pb, Bi, or Rare-Earth, X = Chalcogene, T = Transition metal, *x* misfit parameter, and n = 1, 2, 3) indicating alternating stacking of MX planes (having NaCl structure, quasi quadratic - Q) and TMD layers (CdI_2 or NbS_2 structure, quasi hexagonal - H). Due to different symmetries of the respective layers misfit results along the crystallographic *a* axis. We prepared the misfit layered system made of LaSe/$NbSe_2$ layers, namely $(LaSe)_{1.14}(NbSe_2)_2$, here denoted as 1Q2H, which has the highest transition temperature T_c = 5.3 K [7] among TMD misfits and $(LaSe)_{1.14}(NbSe_2)$, denoted as 1Q1H with T_c about 1.3 K [8]. The single crystals were prepared by the direct reaction of the elements La, Nb and Se in stoichiometric ratios as explained elsewhere [7]. The elements were ground in a mortar and then sealed in an evacuated silica tube. The tube was heated up in a furnace at 1050 °C during 15 days and then slowly cooled down to room temperature. The synthesis yielded large black crystals grown on the surface of a black powder. Energy dispersive X-ray spectroscopy and X-ray diffraction techniques were used to characterize the powder and some crystals. All these measurements confirmed the expected compositions and cell parameters of the 1Q1H and 1Q2H misfit compounds.

A standard lock-in technique was used to measure the magnetic field dependence of the sample resistance in a four-probe configuration at different fixed temperatures down to 100 mK and in magnetic fields up to 30 T in the Laboratoire National de Champs Magnétiques Intenses in Grenoble. The magnetoresistive transitions were also measured at different angles between the *ab* plane of the sample and the applied magnetic field keeping the current always orthogonal to the field. The angular resolution was better than 0.2 degree with the $\theta = 0^0$ orientation defined from the highest value of B_{c2}. The temperature dependence of the resistance at fixed magnetic fields up to 8 T was measured in a He-3 refrigerator in the Centre of Low Temperature Physics Košice. *ac* calorimeter installed in the same He-3 cryostat was used to measure the temperature and field sweeps of the specific heat of the same sample as for the resistive measurements. *ac* calorimetry [9,10] employs periodically modulated power on the sample and measures the resulting sinusoidal temperature response. In our case, heat is supplied to the sample at a frequency $\omega \sim$ several Hz by a light emitting diode via an optical fiber. The chromel-constantan thermocouple calibrated in the magnetic field is used to record the temperature oscillations. Although *ac* calorimetry is not capable of measuring the absolute values of the heat capacity, it is very sensitive to relative changes in minute samples and it enables continuous measurements.

III. SUPERCONDUCTING-TO-NORMAL STATE TRANSITIONS IN MAGNETIC FIELD. EXTREME IN-PLANE CRITICAL FIELDS

Figure 1a) shows the structure of the 1Q1H and 1Q2H crystals where quasi hexagonal $NbSe_2$ and quasi quadratic LaSe layers are stacked. In the case of 1Q1H one has an alternation of LaSe and $NbSe_2$ layers bound by iono-covalent bonding (left), notice that this is not a van der Waals material. The right of Fig. 1a) shows the structure of the 1Q2H compound, a central slab of LaSe/Q is

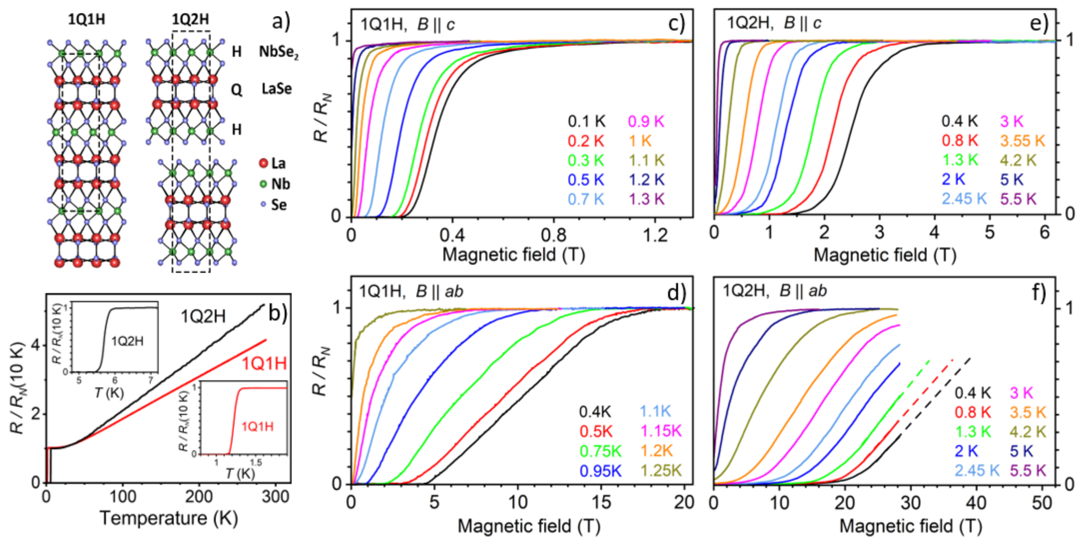

FIGURE 1. a) Left – crystal structure of $(LaSe)_{1.14}(NbSe_2)$ / 1Q1H, unit cell indicated by dashed rectangle comprises two LaSe and two $NbSe_2$ layers because of the 2*H*-$NbSe_2$ polytypism. Right – crystal structure of $(LaSe)_{1.14}(NbSe_2)_2$ / 1Q2H, unit cell comprises two trilayers $NbSe_2$ – LaSe - $NbSe_2$, becasuse of 2*H*-$NbSe_2$ polytype. Note that trilayer stacks are decoupled by van der Waals gap. b) Temperature dependence of resistivity normalized to residual value for 1Q2H and 1Q1H, respectively. Insets show superconducting transition in detail. c) and d) Resistive transitions as a function of magnetic field oriented perpendicular and parallel to the *ab* plane of the 1Q1H misfit compound at fixed temperatures, respectively. e) and f) resistive transitions for the misfit 1Q2H for *B* perpendicular and parallel with *ab* planes of the 1Q2H system, respectively. Dashed lines in f) extrapolate resistivity measurements up to fields where linear behaviour is expected.

sandwiched between two $NbSe_2$/H layers. The 1Q2H trilayer is bound by iono-covalent bonding while the crystal is made by van der Waals stacking of the trilayers.

As explained above the LaSe has been supposed to be a massive electron donor of $NbSe_2$ layer(s) [11]. Quasiparticle interference (QPIs) spectroscopy and angle-resolved photoemission spectroscopy (ARPES) supported by the density functional theory (DFT) calculations evidence a Fermi surface equivalent to that of the monolayer $NbSe_2$ with a rigid band shift of +0.3 eV, i.e. a transfer of 0.6 electron per niobium atom [5]. In the case of 1Q1H, 1.14 LaSe dopes just one $NbSe_2$, and thus one expects a complete filling of the $NbSe_2$ bands, the metallicity residing in the LaSe which are filled with the 0.14 (=1.14-1.0) remaining electrons.

Figure 1 b) displays the temperature dependence of the resistance *R* of the both 1Q1H and 1Q2H samples indicating a good metallic conductivity with the residual resistivity ratio RRR = 4.3 and 5.5, resp. Both samples reveal a sharp transition to the superconducting state with T_c= 1.23 K and the width of the transition between 0.1 and 0.9R_n being ΔT_c= 0.1 K for 1Q1H and T_c= 5.7 K and ΔT_c= 0.2 K for the 1Q2H compound.

The resistive transitions from the superconducting to normal state in applied magnetic field oriented parallel to the *c* axis (upper figures) and parallel to the *ab* plane (lower figures) are presented in Fig. 1 c – f) for both compounds. The measured resistances were normalized to the high field values. The transitions are shifted to higher fields and broadened with decreasing temperature. After the main increase of the resistance at the transition there is a field range where the resistance is only slightly increasing before it reaches the constant normal-state value. This effect is more remarkable for the perpendicular field orientation (parallel with the *c* axis) indicating important role of superconducting fluctuations. The 1Q1H sample shows the superconducting transitions at the fields parallel to the *c* axis below 0.5 T down to 100 mK. On the other hand, for the fields parallel to the *ab* plane the onset of the normal state starts at 5 T but the full normal state is achieved only above 18 T at 400 mK. In the case of 1Q2H the transitions at fields parallel to *c* direction are below 3 T while for the in-plane fields the transition starts at 20 T and goes far beyond the 28 T limit of the Bitter magnet in Grenoble pointing at some 50 T at 400 mK. We determined the upper critical magnetic field at 90 percent of the transition to the normal state (0.9R_n) to better estimate a huge extent of the superconducting state in these low T_c samples but the determination of B_{c2} at the midpoint of the transition yields qualitatively the same conclusions (See Supplemental Material [12]).

To evaluate the temperature dependence of B_{c2} in more detail we made the measurements of temperature dependence of the resistance at fixed magnetic field in a superconducting coil. The measurements were performed on the 1Q1H sample from the same batch as before in the Bitter coil and a very good agreement between these two measurements is found and no degradation of the samples observed. Moreover, on the same piece of the sample we performed specific heat measurements by a very sensitive *ac* calorimetry [9]. In Fig. 2 a) the superconducting transitions are displayed for the indicated fields parallel to the *c* axis while in Fig. 2 b) for fields parallel with the *ab* plane. One can see that the superconducting anomaly in specific heat characteristic for the second order phase transition onsets close to the temperature where the resistance sharply drops to zero. For the in-field measurements in both field orientations the transitions get broadened but a very good coincidence is found between the superconducting onsets and midpoints of the respective resistive transition and the specific heat anomaly. This strongly suggests that both physical quantities are well characterizing the bulk superconductivity in the system. Remarkably, even if the specific heat anomaly is well pronounced, the amplitude of the anomaly is quite rapidly suppressed upon increasing magnetic field, reminiscent of the situation in high-T_c cuprate superconductors [13,14], where broadening of the transition in a magnetic field was attributed to a weakening of the coupling between the CuO_2 planes that limits the superconducting order to two dimensions, thereby enhancing fluctuations.

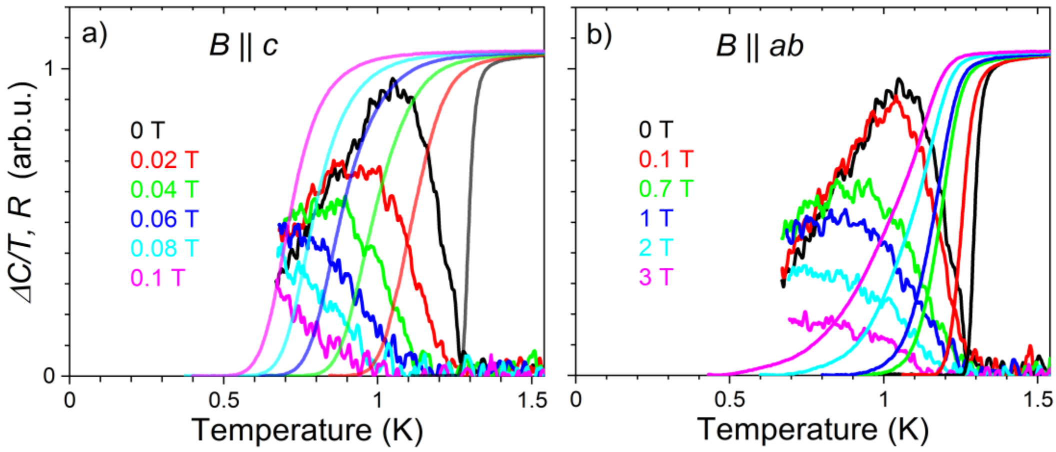

FIGURE 2. Superconducting transitions of $(LaSe)_{1.14}(NbSe_2)$ obtained by resistive and heat capacity measurements. a) the superconducting transitions are displayed for the indicated fields parallel to the *c* axis while in b) for the fields parallel with the *ab* plane.

Figure 3 presents the main result of the paper showing the temperature dependence of upper critical fields for both principal field orientations. Figure 3a) shows the in-plane B_{c2} values of 1Q1H obtained at 0.9 R_n of $R(B)$ – solid red points and R(T) characteristics – open red points. The black asterisks are obtained at the onset of the specific heat anomaly in Fig. 2b). Below T_c the resulting $B_{c2//ab}(T)$ dependence shows a pronounced upturn and changes a curvature from positive to negative one. At lower temperatures $B_{c2//ab}(T)$ can be well approximated by a square root temperature dependence (dashed line). The experimental value $B_{c2//ab}$(0.4 K) = 15 T and extrapolated $B_{c2//ab}$(0 K) is close to 19 T. The upper limit of the in-plane upper critical fields is obtained from the interlayer transport, namely from the conductance $\sigma_c(B)=1/R_c(B)$ (see Supplemental Material [12]) with $B_{c2//ab}$(0 K) above 20 T (gray points and dashed line - approximated square-root temperature dependence). Thus, for fields parallel to the *ab* plane of 1Q1H all the measurements, namely the specific heat, intralayer (in-plane) resistivity and interlayer resistivity provide very consistent results pointing to extremely high upper critical field exceeding B_p=2.2 T (green dashed line in Fig. 3 a)) by a factor about 9 to 10. By the blue points the temperature dependence of $B_{c2//c}(T)$ is shown obtained from $R(B)$ in Fig. 1c) and by the pink asterisks – from specific heat in Fig. 2a). $B_{c2//c}$ values are multiplied by factor 10 for clarity. The temperature dependence shows a positive curvature below T_c changing to a negative one below T_c/2 with extrapolated $B_{c2//c}$(0 K) close to 0.5 T. Then, the superconducting anisotropy $\gamma = B_{c2//ab}/B_{c2//c}$ at low temperatures achieves about 40.

In Fig. 3 b) the upper critical magnetic fields for 1Q2H are presented, constructed in a similar way as for 1Q1H. Here, $B_{c2//ab}$ established at 0.9 R_n (red points) from the resistive transitions are accessible only down to 3 K where $B_{c2//ab}$ = 27.3 T. Then, we also present the transitions taken at 0.7 R_n by the smaller light red points. One can see that below T_c = 5.7 K $B_{c2//ab}(T)$ has a positive curvature changing to a negative one below 4 K. The low temperature $B_{c2//ab}(T)$ could be approximated by the square root temperature

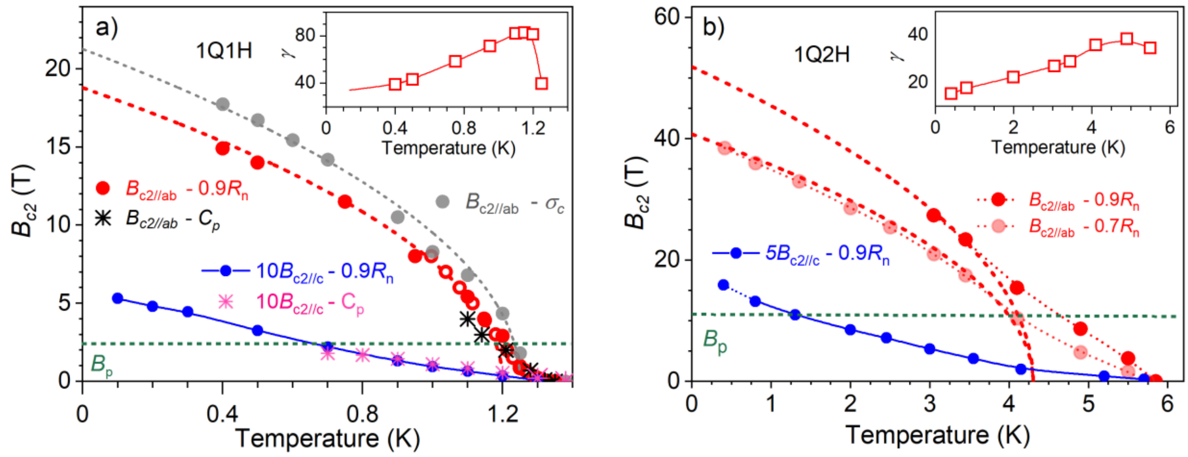

FIGURE 3. Upper critical magnetic fields of a) $(LaSe)_{1.14}(NbSe_2)$ / 1Q1H and b) $(LaSe)_{1.14}(NbSe_2)_2$ / 1Q2H misfit compounds, Red and blue points show B_{c2} for fields applied parallel and perpendicular to ab planes, respectively as determined at the 90% of the resistive transition. In a) solid red points are from field sweeps and open red points from temperature sweeps of the resistance. Gray points are determined from the interlayer transport, namely from the conductance $\sigma_c(B)=1/R_c(B)$ (see Supplemental Material [12]). Stars denote values obtained from the onset of the heat capacity anomaly. Light red points in b) are taken at 0.7 R_n. For better readability $B_{c2//c}$ values are multiplied by 10 and 5 for 1Q1H and 1Q2H, respectively. Green dashed lines show Pauli paramagnetic limiting field for respective compounds. In the case of 1Q2H $B_{c2//ab}$ for fields larger than 30 T are determined at 70% of the resistive transitions. Dashed lines are approximations by a square root temperature dependence. Solid lines are guides for the eye. The temperature dependence of the superconducting anisotropy $\gamma = B_{c2//ab}/B_{c2//c}$ for both compounds are shown in the insets.

dependence providing $B_{c2//ab}$(0 K) equal to 40 and 53 T at 0.7 and 0.9 R_n, respectively. This is 4 to 5 times higher than the Pauli limit B_p=10.5 T indicated by the green dashed line. The $B_{c2//c}(T)$ shown by the blue points (values multiplied by 5 for clarity) reveals a positive curvature all the way down to the lowest temperature of 400 mK. The superconducting anisotropy $\gamma = B_{c2//ab}/B_{c2//c}$ at low temperatures is approximately 15.

IV. TWO-DIMENSIONAL SUPERCONDUCTIVITY, DIMENSIONAL CROSSOVER

Lawrence and Doniach [15] described the behavior of layered superconductors in a magnetic field based on a model system of stacked two-dimensional superconducting layers coupled together by Josephson tunneling between adjacent planes. In contrast to the isotropic case where the magnetic flux penetration occurs in the form of vortices of circular symmetry, in an anisotropic superconductor the vortex cores will be flattened in the interlayer *c* direction for magnetic fields parallel to the layered structure (*ab* planes) with $\xi_c < \xi_{ab}$ for the vortex core radii ξ_c and ξ_{ab}, respectively, perpendicular and parallel to the planes. If ξ_c is bigger than the distance between the adjacent superconducting layers the system is anisotropic but still three-dimensional with the upper critical magnetic fields for fields perpendicular and parallel to the layers determined by a product of the corresponding coherence lengths: $B_{c2//c} = \Phi_0/(2\pi\xi_{ab}^2)$ and $B_{c2//ab} = \Phi_0/(2\pi\xi_{ab}\xi_c)$, respectively, where Φ_0 is the flux quantum. In some cases including the high-T_c cuprates the critical fields can be very high and in extremely anisotropic superconductors ξ_c could shrink with decreasing temperature below the value of the interlayer distance *D*. Then, the vortices are confined between the superconducting layers for fields applied parallel to the layers leading to a dimensional crossover. According to the simplest Lawrence-Doniach model the upper critical $B_{c2//ab}$ parallel to the *ab* planes is predicted to diverge at the dimensional transition at a temperature T^*, where $\xi_c(T^*) \approx D$. The real finite value of the upper critical field $B_{c2//ab}$ is caused by the finite superconducting layer thickness, Pauli paramagnetism and spin-orbit scattering. Klemm, Luther and Beasley (KLB theory) [16] have extended the Lawrence-Doniach model to include these effects. They show that the divergence is removed but the dimensional crossover to a two-dimensional superconductivity is still characterized by a strong upward curvature of $B_{c2//ab}(T)$. Experiments on the intercalated layered compounds based on 2*H*-TaS_2 [17] revealed a strong upward curvature of the temperature dependence of the parallel upper critical fields accompanied by the temperature dependent critical field anisotropy $\gamma = B_{c2//ab}/B_{c2//c}$ reaching maximum values of about 60 at the dimensional crossover and strong in-plane upper critical fields achieving up to 3 B_p on account of the strong spin-orbit scattering rate due to collisions at the interfaces between TaS_2 layers with the heavy Ta atom (*Z*=73) and the light organic layers of intercalants.

In our previous work [8] we have found that the $(LaSe)_{1.14}(NbSe_2)$ misfit layer compound behaves as a stack of intrinsic Josephson junctions making it a 1-Kelvin analogue to the high-T_c $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor [18]. To be so, the interlayer superconducting coherence length ξ_c should be shorter than the distance between superconducting atomic layers. In this limit one can see $(LaSe)_{1.14}(NbSe_2)$ misfit as slabs of superconducting LaSe rock-salt layers separated by insulating $NbSe_2$ layers behaving as Josephson tunnel junctions. The short ξ_c imposes such a high in-plane upper critical magnetic field $B_{c2//ab} \propto 1/\xi_c$ for orbital pair breaking that Cooper pairs rather break at the Pauli or Clogston-Chandrasekhar limit B_p[T] = $1.84T_c$[K] ≈ 2.2 T [19,20] where the Zeeman spin splitting overcomes the superconducting condensation energy. But preliminary experiments on 1Q1H [21] have shown that $B_{c2//ab}$ violates the conventional Pauli limit by an enormous factor of 10, almost as high as for the superconductors URhGe and UCoGe [22] where the ferromagnetic order hinders the Pauli pair breaking mechanism. These findings suggested the presence of an unconventional superconducting state in the $(LaSe)_{1.14}(NbSe_2)$ misfit layer, however without a proposed microscopic mechanism to explain the enormous upper critical field.

In the case of $(LaSe)_{1.14}(NbSe_2)$ and $(LaSe)_{1.14}(NbSe_2)_2$ a dimensional crossover is evidenced by an upturn of $B_{c2//ab}(T)$ and also the temperature dependent anisotropy factor γ (see insets in Fig. 3). From $B_{c2//c}$ data we can estimate the size of the coherence length ξ_{ab}. For 1Q1H with ξ_{ab}(1.2 K) ≈ 97 nm taking into account the anisotropy factor of about 82 one obtains ξ_c (1.2 K) = 1.2 nm which is close to the thickness of a stack of one H and one Q layers, which is ca. 1.2 nm [23]. Similarly for 1Q2H at 5 K we obtain ξ_{ab} ≈ 40 nm and with γ ≈ 40 we get ξ_c ≈ 1 nm. Again this is close to the distance of about 1.2 nm separating two $NbSe_2$ layers across a LaSe layer in this compound [7]. Then, the conditions for dimensional transition are fulfilled.

Deutscher and Entin-Wohlman [24] have shown that a layered superconductor consisting of alternating insulating layer of thickness s and superconducting layer of thickness d shows a dimensional crossover with an upturn in $B_{c2//ab}(T)$ depending on a ratio between s and d. While condition for a dimensional crossover $\xi_c < D = s + d$ is the same as in the Lawrence-Doniach model, the upturn is more pronounced for $s > d$. This is demonstrated in Fig. 3 where the upturn is more pronounced in 1Q1H with D consisting of one superconducting and one insulating layer but in 1Q2H the effect is weaker because D consists of two superconducting $NbSe_2$ layers (d) and one insulating LaSe layer (s).

2D superconductivity can also be addressed via studying the angular dependence of the upper critical field $B_{c2}(\theta)$, where θ is the angle between the applied field and the ab plane of the sample. Within the anisotropic 3D Ginzburg-Landau (GL) model $B_{c2}(\theta)$ can be described by a simple ellipsoidal formula with a rounded maximum around $\theta = 0$ (magnetic field parallel to the layers) $\left(\frac{B_{c2}(\Theta)\sin\Theta}{B_{c2||c}}\right)^2 + \left(\frac{B_{c2}(\Theta)\cos\Theta}{B_{c2||ab}}\right)^2 = 1$. In 2D regime the superconducting layers are decoupled and can be treated as isolated thin films. For this case Tinkham [25] proposed the equation $\left|\frac{B_{c2}(\Theta)\sin\Theta}{B_{c2||c}}\right| + \left(\frac{B_{c2}(\Theta)\cos\Theta}{B_{c2||ab}}\right)^2 = 1$, with a finite slopes at $\theta = 0$ making a cusp. This effect was also observed

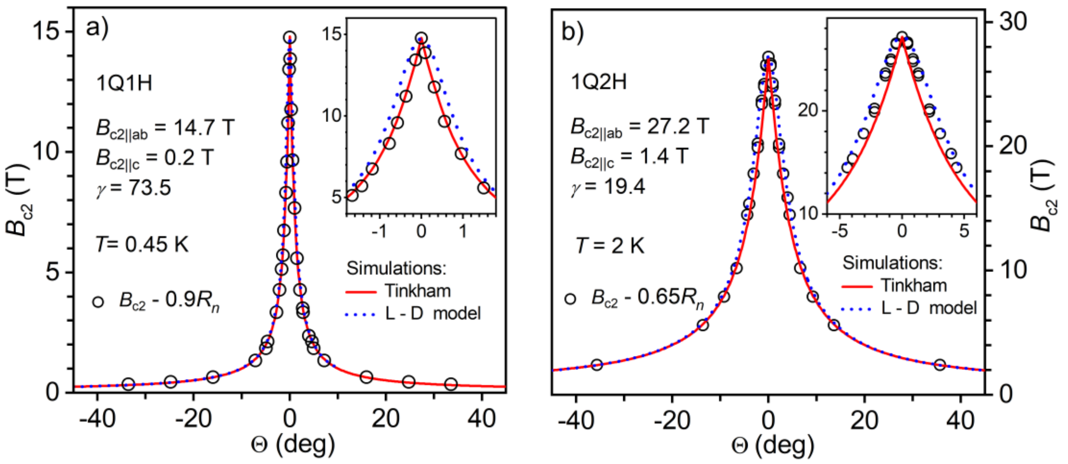

Figure 4. a) shows angular dependence $B_{c2}(\theta)$ of the 1Q1H sample taken at 0.45 K. b) shows angular dependence $B_{c2}(\theta)$ of the 1Q2H sample taken at 2 K. Both cases of $B_{c2}(\theta)$ dependences are compared with the anisotropic 3D GL model and 2D model of Tinkham. Insets display small angles to better distinguish between these two models.

in superconducting superlattices below the 2D-3D transition [26]. The situation remains unclear in the natural layered single crystals. In the case of the extremely anisotropic $Bi_{2.2}Sr_{1.8}CaCu_2O_{8+\delta}$ high-T_c cuprate the angular dependence of the resistively determined B_{c2} shows the cusp-like form of the Tinkham thin-film formula [27].

In Fig. 4 a) we present $B_{c2}(\theta)$ of the 1Q1H sample taken at 0.45 K. This particular 1Q1H sample has lower perpendicular critical fields $B_{c2//c}$ than that in Fig. 1 c), probably due to smaller disorder but it has a very similar $B_{c2//ab}$. $B_{c2}(\theta)$ data are compared with both models: the anisotropic 3D GL and 2D model of Tinkham. For such a high anisotropy (γ=73.5) the difference is minor but the inset showing small angles is better compatible with 2D model indicating the two-dimensional character of the vortex matter. Figure 4 b) shows the angular dependence

$B_{c2}(\theta)$ for 1Q2H sample taken at 2 K. Even the inset displaying small angles is not capable to distinguish the two models since the experimental data lies exactly in between. It is noteworthy that these experiments are rather challenging and $B_{c2}(\theta)$ with cusp-like behavior could be observed only on very tiny samples with a clear plane parallel geometry, while in samples with a slightly wavy surfaces the angular dependence always revealed the round maximum, probably due to angle averaging.

The major finding of the paper as presented in Fig. 3 is in strong violation of conventional Pauli limit. In 1Q1H B_p = 2.2 T is exceeded by enormous factor of 9 to 10 while in 1Q2H B_p = 10.5 T is outperformed by factor of about 5. Such a strong enhancement of in-plane critical field cannot be explained by the KLB theory taking into account of spin-orbit scattering [16]. It would require unrealistically short spin-orbit scattering times given the atomic numbers $Z = 57$ and 41 for La and Nb, as compared to Ta with $Z = 73$ [17] as the spin-orbit scattering has been shown to follow the Abrikosov-Gor'kov value ~ Z^4 [28]. Thus, different spin-orbit effects must be at play in case of $(LaSe)_{1.14}(NbSe_2)$ and $(LaSe)_{1.14}(NbSe_2)_2$. This is indeed in agreement with the fact that $(LaSe)_{1.14}(NbSe_2)_2$ is probably an Ising superconductor while this is not the case of $(LaSe)_{1.14}(NbSe_2)$.

In atomically thin TMDs a lack of crystal inversion symmetry and strong spin-orbit coupling has been shown to lead to the Zeeman protected so called Ising superconductivity with $B_{c2//ab}$ exceeding B_p by an order of magnitude, e.g. in MoS_2, $NbSe_2$, TaS_2 [3,4,29]. In the bulk the effective Zeeman field is supposed to be weakened by interlayer coupling and by restoration of centrosymmetry of the systems. More recently, even in atomically thin 2D systems with inversion symmetry preserved, where the aforementioned Ising superconductivity cannot exist, a large $B_{c2//ab}$ strongly exceeding B_p has been detected in $PdTe_2$ [30] and few-layer stanene [31]. A new mechanism (called Ising II) of superconducting pairing between carriers residing in bands with different orbital indices near the Γ point is proposed where the bands are spin split without inversion symmetry breaking. Yet another possibility to strongly enhance the in-plane $B_{c2//ab}$ in atomic layer superconductors – pairing with the Rashba spin orbit coupling - was suggested in the case of crystalline atomic layer of In on Si surface [32].

Our recent paper [5] shows that a single crystal of 1Q2H - $(LaSe)_{1.14}(NbSe_2)_2$ is electronically equivalent to a $NbSe_2$ single atomic layer with a rigid doping of 0.55–0.6 electrons per Nb atom or ≈ 6×10^{14} cm^{-2}. An electronic charge transfer occurs from LaSe to $NbSe_2$ layers. Importantly, also the spin split Fermi surfaces around K and K' points in the Brillouin zone of $(LaSe)_{1.14}(NbSe_2)_2$ have been observed in the quasiparticle interferences data measured by scanning tunneling microscope (STM) in agreement with DFT calculations again very similar to the case of monolayer of $NbSe_2$. This is strongly indicating that Ising pairing is responsible for very high in-plane $B_{c2//ab}$ critical fields despite the fact that it is a fully bulk single crystal.

In the case of 1Q1H - $(LaSe)_{1.14}(NbSe_2)$ compound even much larger charge transfer is expected as the electronic donor LaSe is supplying not two $NbSe_2$ layers but just one. Our preliminary ARPES measurements show a tendency towards further filling of the $NbSe_2$ bands on the surface while DFT calculations point to totally filled $NbSe_2$ bands in the bulk of the sample [33]. On the other hand, the $NbSe_2$ surface layer of the 1Q1H crystal is different – it gets only half doping compared to the $NbSe_2$ layers located in the bulk which obtain doping from both the top and bottom LaSe layers. Then, the electronic structure of this surface layer should be very similar to 1Q2H which has rigidly shifted bands of monolayer $NbSe_2$. Naively, one might speculate that the superconductivity of 1Q1H originates from the top-most layer of $NbSe_2$ and naturally explain its low T_c, extreme anisotropy, 2D behavior with cusp-like dependence of $B_{c2}(\theta)$ and extreme $B_{c2//ab}$ due to Ising coupling. However, the specific heat measurements evidence that these effects are characteristic for the bulk of the sample. Thus, the real mechanism of extremely high in-plane critical field in 1Q1H remains to be explored and will be addressed in the forthcoming paper [33]. Very recently, another misfit layer compound, $(SnSe)_{1.16}(NbSe_2)_2$ with T_c=5.3 K and $B_{c2//ab}$ = 1.59 B_p has been reported [34]. In *4Hb*-TaS_2 [35], where *1T*-TaS_2 (Mott insulator) and *1H*-TaS_2 (superconductor) are stacked, strong Ising spin-orbit coupling is present and $B_{c2//ab}$ overrides B_p almost 4 times, still the exact mechanism remains unknown. In Pd-based quasi-one-dimensional bulk chalcogenides contaning Nb [36] 2D superconductivity is found with $B_{c2//ab}$ four times higher than B_p but its band structure calculations are contradicting the Ising scenario. Thus, extreme upper critical magnetic fields in bulk materials indicating unconventional superconductivity remain challenging and ask for further studies.

V. CONCLUSIONS

It has been shown that two superconducting misfit layer compounds - $(LaSe)_{1.14}(NbSe_2)$ and $(LaSe)_{1.14}(NbSe_2)_2$ with T_c=1.23 K and 5.7 K reveal extremely high in-plane upper critical field reaching about 20 T and 50 T, respectively, which is 10 and 5 times more than the respective Pauli paramagnetic limits. Both compounds also show a 2D-3D dimensional crossover below T_c with an upturn in $B_{c2//ab}$ temperature dependence, a very high and temperature dependent superconducting anisotropy and a cusp in the angular dependence of B_{c2} for fields parallel to the layers. In 1Q2H $(LaSe)_{1.14}(NbSe_2)_2$ which is composed of weakly, van der Waals coupled $NbSe_2$ - LaSe - $NbSe_2$ trilayers the Ising spin-orbit coupling is most probably responsible for a very strong in-plane upper critical field. In the 1Q1H $(LaSe)_{1.14}(NbSe_2)$, with iono-covalent bonding between LaSe and $NbSe_2$ slabs, the real mechanism standing behind the huge $B_{c2//ab}$, which is ten times bigger than the Pauli paramagnetic limit, remains to be explored.

ACKNOWLEDGEMENTS

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Supplemental Material for

„ Extreme In-Plane Upper Critical Magnetic Fields of Heavily Doped quasi 2D Transition Metal Dichalcogenides – Misfit $(LaSe)_{1.14}(NbSe_2)_{n=1,2}$"

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Upper critical magnetic field in $(LaSe)_{1.14}(NbSe_2)$ and $(LaSe)_{1.14}(NbSe_2)_2$ determined at midpoint of the resistive transitions

Figure S1 a) presents the upper critical magnetic fields of the 1Q1H $(LaSe)_{1.14}(NbSe_2)$ misfit compound as determined at the midpoint of the resistive transition 0.5 R_n of $R(B)$ from Fig. 1 c) and d) of the main text. The major features shown in Fig. 3a) of the main text are well reproduced, here: it is an upturn of $B_{c2//ab}$, a negative derivative dB_{c2}/dT at lower temperatures, obviously lower absolute values of $B_{c2//ab}$ pointing to about $B_{c2//ab}$ = 13 T at zero temperatures but this is still almost six times bigger than the Pauli limit B_P = 2.2 T indicated by the green dashed line. Also, the temperature dependence of perpendicular field $B_{c2//c}$ of Fig. S1 a) is qualitatively similar to what is presented in Fig. 1 of the main text with a change of curvature from positive to negative one upon decrease of temperature but proportionally lower $B_{c2//c}$(0 K) = 0.35 T. The temperature dependent superconducting anisotropy $\gamma = B_{c2//ab}/B_{c2//c}$ is shown in the inset.

In the case of the 1Q2H $(LaSe)_{1.14}(NbSe_2)_2$ compound the resulting temperature dependence of B_{c2} obtained from the midpoint of the resistive transitions shown in Fig. 1 e) and f) in the main text is shown in Fig. S1 b). $B_{c2//ab}$ (T) shows an upturn at about 4 K and $B_{c2//ab}$ reaches some 36 T at zero temperature violating B_P = 10.5 T (indicated by the green dashed line) almost 3.5 times. The transversal field $B_{c2//c}$ as a function of temperature shows a positive curvature at all temperatures again in accordance with the result in Fig. 3 b) of the main text. The temperature dependence of the superconducting anisotropy $\gamma = B_{c2//ab}/B_{c2//c}$ is shown in the inset in a qualitative accord with the data in Fig. 3 of the main text.

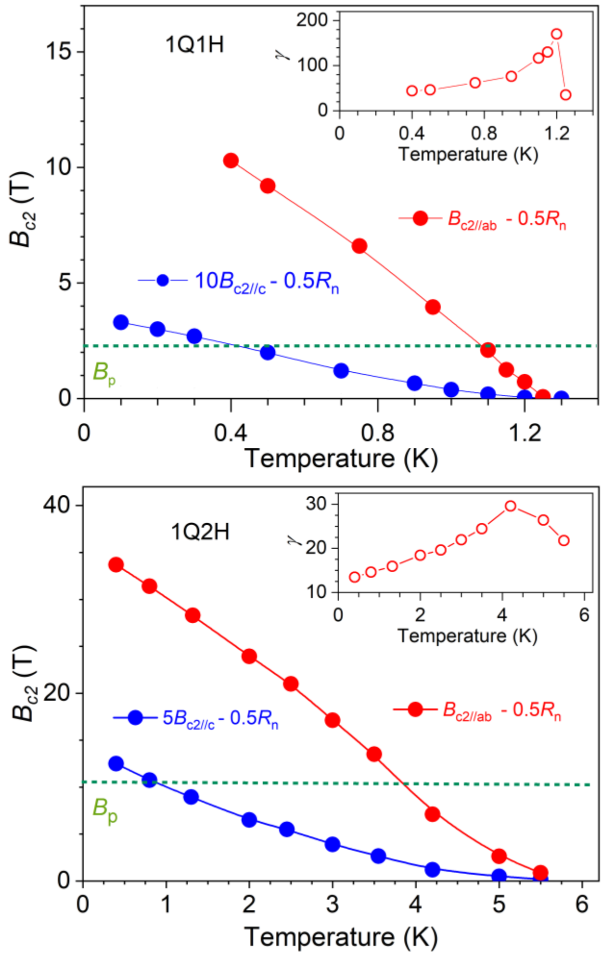

FIGURE S1. a) Upper critical magnetic fields of $(LaSe)_{1.14}(NbSe_2)$ / 1Q1H and b) $LaSe)_{1.14}(NbSe_2)_2$ / 1Q2H misfit compounds determined at midpoint of the resistive transition 0.5 R_n. Red points – in-plane $B_{c2//ab}$, blue points - $B_{c2//c}$. Solid lines are guides for the eye. Green dashed line is the Pauli limiting field B_P. The temperature dependence of the superconducting anisotropy $\gamma = B_{c2//ab} / B_{c2//c}$ for both compounds are shown in the insets.

Determination of the in-plane upper critical magnetic field $B_{c2//ab}$ from the interlayer transport measurement

Figure S2 shows the resistive transitions $R(B)$ as a function of the magnetic field oriented parallel with the ab plane of the 1Q1H $(LaSe)_{1.14}(NbSe_2)$ misfit compound at fixed temperatures. While in the part a) the measurements with the current and voltage electrodes put on the same top surface *ab* plane reproduce the intralayer resistance R_{ab} what is already presented in Fig. 1 d) of the main text, in Fig. S2 b) we display interlayer measurements of R_c taken at configuration where one voltage and one current contact are put on the top *ab*-surface plane and the other pair of contact electrodes are on the bottom *ab*-surface plane of the sample. At all indicated temperatures upon increased magnetic field B the zero-resistant state is followed by the onset of finite resistance increasing to a peak, then decreasing to an almost constant background with a slightly positive magnetoresistance in the normal state. All the data have been normalized to the value at 20 T. At decreasing temperature the peak is broadened, its amplitude suppressed and position shifted to higher fields. The peak position is always found close to the field where the intralayer resistance R_{ab} drops to zero. Figure S2 c) displays the interlayer magnetotransport data recalculated in the conductance, $\sigma_c = 1/R_c$. One can see that before reaching the normal state a linear dependence of the applied field is present, which is stressed by the dashed lines. The intersections of the dashed lines with the normal state background have been taken for determination of the upper limit of the in-plane upper critical magnetic field $B_{c2//ab}$. This is presented in the Fig. 3 a) of the main text. In our previous work [8] we have found that the highly anisotropic $(LaSe)_{1.14}(NbSe_2)$ misfit layer compound behaves as a stack of intrinsic Josephson junctions. Peak in the interlayer resistance R_c preceding a full transition to the superconducting state, there measured at fields parallel to the *c* axis of the crystal, has been interpreted as due to the interplay between the quasiparticle and Josephson tunneling across the atomic layers creating intrinsic Josephson junctions. At small fields first, Josephson coupling between superconducting planes is suppressed, finite resistance/conductance appears with a maximum/minimum. At increasing field the number of the vortices is increased proportionally to the field strength, cores of the vortices are normal areas with quasiparticles allowing for quasiparticle tunneling between decoupled yet superconducting layers allowing for decrease of resistance and increase of conductance until the full normal state is achieved.

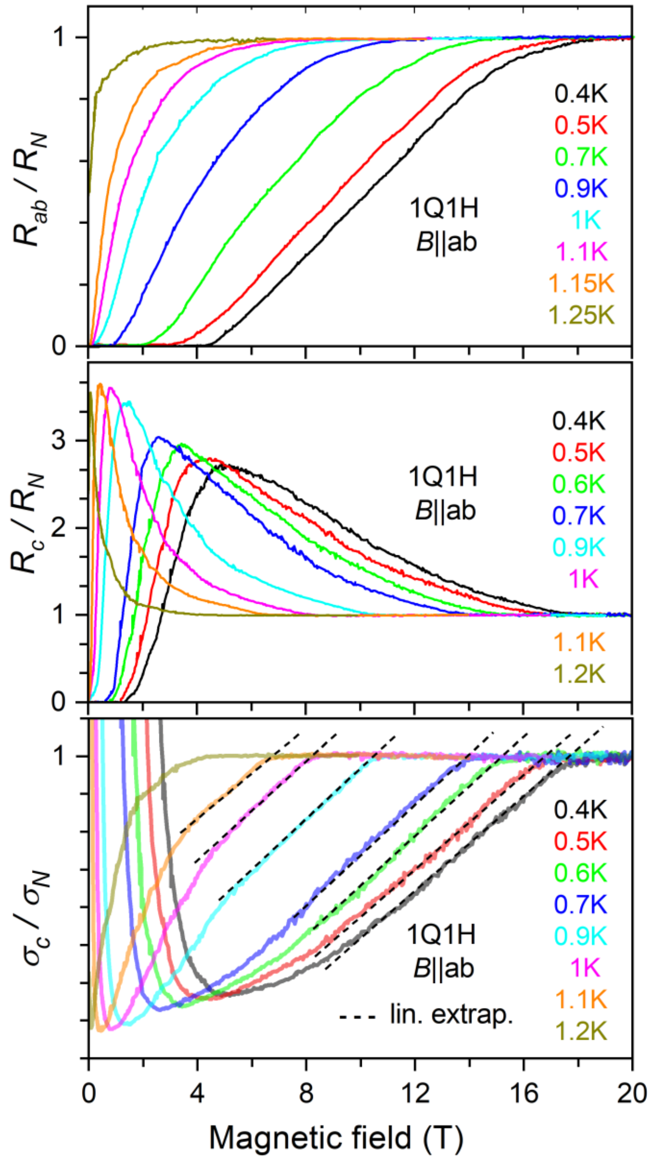

FIGURE S2. a) In-plane resistive transitions R_{ab} as a function of magnetic field oriented parallel to the *ab* plane of the $(LaSe)_{1.14}(NbSe_2)$ / 1Q1H misfit compound at fixed temperatures (same as in Fig. 1 d) of the main text). b) Interlayer measurements of R_c taken at configuration where one voltage and one current contact are put on the top *ab*-surface plane and the other pair of contact electrodes are on the bottom *ab*-surface plane of the sample. c) displays the interlayer magnetotransport data recalculated in the conductance, $\sigma_c = 1/R_c$. Dashed line is linear extrapolation. All resistances are normalized to the high field value.

Angular dependence of B_{c2}

Figure S3 displays the experimental data of the resistance of the 1Q2H $(LaSe)_{1.14}(NbSe_2)_2$ misfit compound as a function of applied magnetic field oriented at different angles θ with respect to the *ab* plane of the crystal with $\theta = 0$ for magnetic field parallel to the *ab* plane. The data has been used to construct the angular dependence of the upper critical magnetic field B_{c2} presented in Fig. 4 b) of the main text.

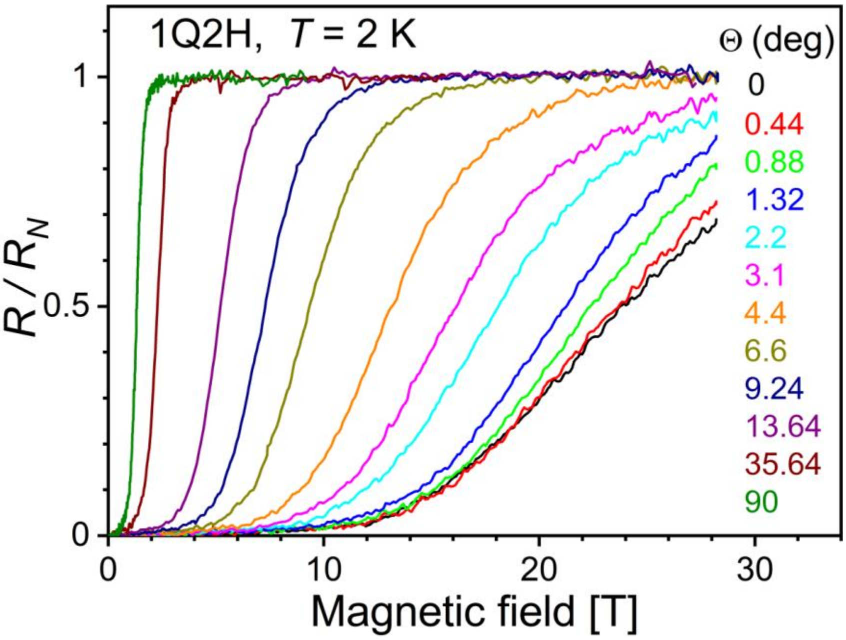

FIGURE S3. Resistive transitions R as a function of magnetic field oriented at different angle θ with respect to the *ab* plane of the sample. The data is taken to determine the angular dependence of $B_{c2}(\theta)$ in Fig. 4 b) of the main text.