Magnetic-field-induced FM-AFM metamagnetic transition and strong negative magnetoresistance in Mn$_{1/4}$NbS$_2$ under pressure.

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Transition metal dichalcogenides (TMDC) stand out with their high chemical stability and the possibility to incorporate a wide range of magnetic species between the layers. The behavior of conduction electrons in such materials intercalated by 3d-elements is closely related to their magnetic properties and can be sensitively controlled by external magnetic fields. Here, we study the magnetotransport properties of NbS$_2$ intercalated with Mn, Mn$_{1/4}$NbS$_2$, demonstrating a complex behavior of the magnetoresistance and of the ordinary and anomalous Hall resistivities. Application of pressure as tuning parameter leads to the drastic changes of the magnetotransport properties of Mn$_{1/4}$NbS$_2$ exhibiting large negative magnetoresistance up to 65% at 7.1 GPa. First-principles electronic structure calculations indicates pressure-induced transition from ferromagnetic to antiferromagnetic state. Theoretical calculations accounting for the finite temperature magnetic properties of Mn$_{1/4}$NbS$_2$ suggest a field-induced metamagnetic ferromagnetic-antiferromagnetic transition as an origin of the large negative magnetoresistance. These results inspire the development of materials for spintronic applications based on intercalated TMDC with a well controllable metamagnetic transition.

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I. INTRODUCTION

The transition metal dichalcogenides (TMDC) are in focus of various investigations since many years as they exhibit a broad spectrum of structure and composition dependent physical properties. Being non-magnetic itself, some of the known TMDC materials allow intercalation by magnetic 3d element$^{[1]}$, having a tendency to the formation of ordered compounds when the concentration of intercalating elements is close to 25% or 33%. This creates a family of TMDC-based magnetic compounds exhibiting rather peculiar magnetic and transport properties, which however have not been well investigated so far. Among the properties of the intercalated TMDC’s one can mention the high magnetic anisotropy$^{[2,3]}$ and anomalous Hall effect (AHE)$^{[4,5]}$ in Fe$_{1/4}$TaS$_2$ observed experimentally and discussed recently on the basis of the first-principles calculation$^{[5,6]}$. A large magnetoresistance (MR) has been found in disordered Fe$_2$TaS$_2$ single crystals, up to 60% at $x = 0.28$ and 140% at $x = 0.29$ reported recently that was attributed to the spin disorder and strong spin-orbit coupling in the system. A long-period helimagnetic (HM) structure along the hexagonal c-axis has been observed experimentally in Cr$_{1/3}$NbS$_2$, with the Cr magnetic moments aligned within the basal plane perpendicular to the c-axis$^{[7-9]}$. Stabilization of the HM structure in Cr$_{1/3}$NbS$_2$ has been confirmed theoretically by means of first principles calculations$^{[10]}$. Similar to Cr$_{1/3}$NbS$_2$ helimagnetic properties have been also predicted for Mn$_{1/3}$NbS$_2$ while for Fe$_{1/3}$NbS$_2$ stability of the magnetic structure referred to as an ordering of the third kind was demonstrated$^{[11]}$ in agreement with experimental results$^{[12-14]}$. The calculations demonstrate a transition to the AFM state also for Co$_{1/3}$NbS$_2$ and Ni$_{1/3}$NbS$_2$ reported recently. On the other hand, a suppression of the helimagnetic structure has been observed for Cr$_{1/3}$NbS$_2$ at $\sim 3 - 4$ GPa as a result of the structural transformations in the system$^{[15]}$.

In the present work we focus on the magnetic properties of Mn intercalated 2H-NbS$_2$ under pressure, with 25% intercalation concentration. In the first part we discuss the experimental results based on the magnetotransport measurements (magnetoresistance and Hall effect), as they are crucial for inferring information about the interactions between itinerant charge carriers and the magnetic degrees of freedom in a variety of magnetic materials. In order to interpret the details of the experimental measurements, theoretical results are discussed in the
second part, which are based on DFT calculations and Monte Carlo simulations.

II. TECHNICAL DETAILS

A. Experimental details

1. Sample preparation

A mixture of 1 g in total of the elements (Mn, 99.95 %, Alfa Aesar; Nb, 99.9 % chempur; S, 99.9995 %, Alfa Aesar) with nominal stoichiometry Mn$_{0.265}$NbS$_2$ were ground and loaded into an argon flushed silica ampoule. CBr$_4$ ($\sim 25$ mg, 98 %, Fluka) was added as transport agent. Due to the volatility of CBr$_4$, the lower end of the filled ampoule was cooled with liquid nitrogen prior to evacuation ($p \leq 1 \times 10^{-4}$ mbar), after which the ampoule was sealed. The ampoule was placed in the natural gradient of a single tube furnace in inverse position for the pre reaction and cleaning transport. After heating to 450°C during 6 h, the temperature was maintained there for 10 h before it was raised to 900°C. After two days the ampoule was placed in a gradient 900°C $\rightarrow \sim 800$°C and within 14 d crystals of several mm diameter in the basal plane grew. The ampoule was post-annealed by slow cooling from 800°C to room temperature within 24 h to allow for a good order of the Mn-ions which become disordered above $\sim 400$°C.$^{21,22}$ After opening the ampoule the crystals were washed with water, a dilute solution of Na$_2$S$_2$O$_3$ (97 %, Grüssing), water and acetone. The crystals have dimensions up to several mm in diameter and 1 mm in height and show a metallic silver luster. They were stored in an evacuated desiccator until usage.

2. Characterisation

EDX-spectra were acquired on a Philips XL30 ESEM equipped with an EDAX EDX-detector operated at 20 kV acceleration voltage. At least two crystals from each batch were analysed, on each crystal the composition was measured on three spots with an integration time of 120 s each.

The series of 00l-reflections were measured on a Panalytical X’Pert Pro-MPD (Cu-K$_\alpha$ radiation, 1/16° divergence mask, Göbel mirror, primary soller slit (0.04 rad) on the incident beam path, parallel plate collimator and PIXcel 1D detector on the diffracted beam path). The instrumental broadening was derived from a measurement of LaB$_6$ (NIST SRM 660c) via fitting the profile to a Thompson-Cox-Hastings Pseudo-Voigt profile with a Pawley-fit.

All fittings of the lattice parameters were carried out using Topas-Academic Version 6.$^{23}$ via Pawley-fits.

3. Ambient pressure experiments

The magnetization was measured with a MPMS3 (SQUID-VSM, Quantum Design) on a single crystal ($m = 1.859$ mg; flat platelet showing hexagon faces) with the magnetic field applied along the [1000] (in-plane (IP)) or along the [0001] (out-of-plane (OP)) direction, respectively. $M(B)$ isotherms at selected temperatures were recorded after cooling in zero field from $T = 200$ K, temperature sweeps were taken during cooling in low fields. The heat capacity was determined on the same crystal with the HC option in a PPMS-9 (Quantum Design) at zero field and with $B = 9$ T applied along [0001] (OP).

Transverse magnetoresistance (TMR) and Hall resistance $\rho_H$ data as function of magnetic field along [0001] (OP) were measured in a conventional four-wire and a five-wire (with external potentiometer) configuration, respectively. The electrical transport option of a PPMS-9 was used to take data in magnetic field sweeps at selected constant temperatures. Symmetrization of the TMR and antisymmetrization of the Hall data with respect to applied field was performed.

4. High pressure experiments

For high-pressure experiments, a diamond anvil cell manufactured from the nonmagnetic alloy MP35N and equipped with Boehler-Almax design diamond anvils with 500-µm culets was used. The tungsten gasket was insulated with a cubic BN/epoxy mixture. A single crystal sample of suitable size (120 $\mu$m $\times$ 120 $\mu$m $\times$ 10 $\mu$m) was cut and placed into the central hole of the gasket filled with NaCl as a pressure-transmitting medium along with a ruby chip for pressure calibration. The electrical leads were fabricated from 5 $\mu$m thick Pt foil and attached to the sample in a van der Pauw configuration. Electrical resistivity was measured at different pressures in temperature range 1.8-300 K in magnetic field up to 9 T with Physical Property Measurement System (PPMS-9, Quantum Design).

High pressure Raman spectra were recorded at room temperature using a customary confocal micro-Raman spectrometer with a HeNe-laser as the excitation source and a single-grating spectrograph with 1 cm$^{-1}$ resolution. Pressure was measured with accuracy of $\sim 0.1$ GPa using the ruby luminescence method.
B. Computational details

The first-principles electronic structure calculations have been performed using the spin-polarized relativistic KKR (SPR-KKR) Green function method.\(^\text{25,29}\) For the angular momentum expansion of the Green function a cutoff of \(l_{\text{max}} = 3\) was applied. All calculations have been performed within the framework of the local spin density approximation (LSDA) to density functional theory (DFT) as well as beyond the level of LSDA by accounting for correlation effects by means of the LDA+U scheme.\(^\text{27,29}\) The LSDA calculations used a parametrization for the exchange and correlation potential as given by Vosko et al.\(^\text{29}\). In the LDA+U calculations the so-called atomic limit expression was used for double-counting correction in the LDA+U functional, with the parameters \(U = 3\) eV and \(J = 0.7\) eV.

In order to investigate the equilibrium magnetic structure as well as finite temperature magnetic properties of the compounds under consideration, Monte Carlo simulations have been performed, which are based on the Heisenberg model with the exchange coupling parameters \(J_{ij}\) calculated from first principles.\(^\text{30}\)

The temperature-dependent behavior of electronic resistivity of the systems under consideration was investigated on the basis of the Kubo-Streda formalism in combination with the alloy analogy model. It allows to account for thermal lattice vibrations as well as spin fluctuations,\(^\text{12}\) treating them within the adiabatic approximation.\(^\text{13}\)

The properties corresponding to ambient pressure have been calculated using the structure parameters obtained in experiment. The Mn intercalated TMDC system under investigation, Mn\(_{1/4}\)NbS\(_2\), exhibits a \(2 \times 2\) superstructure in the Mn layers arranged within the so-called van der Waals gap, leading to a well-defined ordered compound crystallizing in the space group P6\(_3\)/mmc (SG194), with \(a = 6.67\) Å, \(c = 12.49\) Å. This implies an occupation of the \((2a)\) Wyckoff positions by Mn atoms, and occupation of the \((2b)\) and \((6b)\) (with \(x = 0.5\)) positions by Nb atoms, and \((4f)\)-\((z = 0.121)\) and \((12k)\)-positions (\(x = 5/6, z = 0.37\)) – by S atoms.

In the investigations of the pressure dependent properties, the pressure dependent structure parameters of Mn\(_{1/4}\)NbS\(_2\) have not been measured. Therefore, auxiliary calculations have been performed using the VASP package in order to determine the relationship between the applied pressure and lattice parameters. In these calculations using the GGA density functional for the exchange and correlation potential the PBE-parametrization scheme has been used as given by Perdew et al.\(^\text{30}\). As the van der Waals interactions may be important to describe correctly the pressure dependent behaviour of TMDC-based systems,\(^\text{26}\) these interactions have been taken into account using the DFT-D3 method for the dispersion corrections as given by Grimme et al.\(^\text{26}\). The Monkhorst-Pack \((8 \times 8 \times 8)\) \(k\)-point grid was used for the integration over the Brillouin zone. A plane wave basis set up to a cutoff energy of 440 eV was used for the wave function representation.

III. RESULTS

A. Experiment

The details of sample preparation are described in section I A. The elemental composition was determined by means of EDX to be Mn\(_{0.25}\)NbS\(_2\) within the limits of experimental accuracy. The Mn ions are known to form a superstructure of \(2a \times 2a\) with respect to the 2H-NbS\(_2\) host lattice. In fact, the composition determined is very close to the ideal value for this type of superstructure. To check this, X-ray diffraction was carried out on a thin piece cut from a crystal, which was oriented with reflections of the [001] zone axis being under diffraction condition. The corresponding diffraction pattern is presented in Fig. 1(a). There are only reflections of type \(hk0\) and \(h0k\) visible which have a very narrow full width at half maximum (FWHM), indicating large coherently diffracting domains. This holds true both for the host structure (110 reflection) as well as for the domains of the superstructure (100 reflection). To further ensure the crystal quality the series of 001-reflections was measured (see Fig. 1(b)). Also here a very low FWHM can be observed, indicating a large domain size along the c-axis. The rocking curves measured on the 001-reflections are of a very low average FWHM (0.06°, an example is shown in the inset of Fig. 1(b)), underscoring the high quality of the crystals.

From the XRD data presented here we can conclude that only the \(2a \times 2a\) type superstructure is formed by the Mn-ions with long range order. This is evidenced by the presence of only one set of 001-reflections and in particular by the diffraction pattern of the [001] zone axis, where only reflections belonging to this type of superstructure are present. The lattice parameters are \(a = b = 6.6715(4)\) Å and \(c = 12.493163(3)\) Å, in very good agreement with reports from literature\(^\text{12,39}\).\(^\text{39}\) These measurements showed reproducible results on several crystals from the same batch. In summary, the samples can be described as nearly perfect Mn\(_{1/4}\)NbS\(_2\).

The magnetic moment of Mn\(_{1/4}\)NbS\(_2\) as function of the magnetic field \(M(H) (\mu_B\text{f.u.})\) is shown in Fig. 2 for different temperatures. All \(M(H)\) curves do not exhibit detectable signature of a field hysteresis. The shape of the magnetization curves shown in Fig. 2 evidence that Mn\(_{1/4}\)NbS\(_2\) is a soft easy-plane ferromagnet. For both orientations of the magnetic field, in-plane (IP) and out-of-plane (OP), a saturation magnetization at \(T = 2.0\) K of \(1.05\mu_B\text{f.u.}\) is attained, indicating a local magnetic moment \(M_{\text{Mn}} = 4.2\mu_B\) per Mn ion. The observed behavior and the derived characteristic values are in fair agreement with a previous investigation by Onuki et al.\(^\text{10}\). Magnetization data measured while cooling or warming in low magnetic fields indicate a ferromagnetic (FM) or-
rdering at $T_C = 104(2)$ K. The same critical temperature is obtained from the heat capacity measurements (SM, Fig. 1).

The electrical resistivity $\rho(T)$ of Mn$_{1/4}$NbS$_2$ (see Fig. 3) measured at different pressures exhibits well-defined metallic-like behaviour typical for magnetically ordered systems. For all pressures it decreases upon sample cooling from room temperature, changing the slope at the critical temperature $T_c$ corresponding to a transition to a magnetically ordered state. At ambient pressure this corresponds to a Curie temperature $T_C \approx 104$ K as Mn$_{1/4}$NbS$_2$ exhibits FM order at lower temperatures. A pressure increase up to 10 GPa results in a continuous decrease of the critical temperature down to $\sim 75$ K at 10 GPa. However, it increases abruptly to $\sim 135$ K at 13.5 GPa, while a further pressure increase results in a decrease of the critical temperature reaching 40 K at a pressure of 22.2 GPa; the highest pressure attained in this study.

The sudden increase of the critical temperature at 13.5 GPa can indicate a change of the crystal structure of Mn$_{1/4}$NbS$_2$ above 10 GPa. To monitor the possible structural phase transition, the investigation of the Raman spectra changes for Mn$_{1/4}$NbS$_2$ under pressure have been performed, as is shown in Fig. 4(a). The Raman spectra at ambient pressure are qualitatively similar to that of the related isostructural compound Fe$_{0.239}$NbS$_2$. All Raman resonances observed at ambient pressure are persistent in the Raman spectra up to the pressures beyond 20 GPa (Fig. 4(a)) while the frequency of these peaks shown in Fig. 4(b) shows a normal increase with pressure without any discontinuities indicating no structural phase transition in this pressure.

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**FIG. 1.** Observed and calculated diffraction patterns for a sample of Mn$_{0.25}$NbS$_2$ for the set of h0l-reflections (a) and 00l-reflections (b). In the inset of (b) a representative rocking curve of the 002 reflection is presented.

**FIG. 2.** Magnetic moment $M(\mu_B/\text{f.u.})$ of Mn$_{1/4}$NbS$_2$ as a function of the magnetic field oriented along [0001] (a) and along [1000] directions. The inset in (a) displays the magnetic moment as a function of temperature, obtained during cooling in low fields of 50 (squares) and 100 mT (diamonds) for both the IP and OP field directions.

**FIG. 3.** Electrical resistivity obtained experimentally for Mn$_{1/4}$NbS$_2$ at zero magnetic field, plotted as a function of temperature for different pressure values.
regime. These observations allow to make conclusions about possible changes of the low-temperature magnetic structure of Mn$_{1/4}$NbS$_2$ above 10 GPa. However, we will focus below on the pressure effect in the region up to \( \sim 10 \) GPa, while the results obtained at higher pressure need more detailed investigations.

![FIG. 4. Pressure evolution of Raman spectra (a) and pressure dependence of the frequencies of the observed Raman peaks (b) (a) (b)](image)

The transverse MR, which is defined as MR(%) = \((\rho(T, H) - \rho(T, 0))/\rho(T, 0)\cdot 100\)%, and the Hall resistance \(\rho_H(H)\) measured at ambient pressure are presented in Fig. as a function of applied field \(H\). The MR for the FM state at \(T < 10\) K is positive in the magnetic field regime \(\mu_0 H \approx 1.5\) to 3.5 T. This behavior is obviously connected to the slow turning of the magnetic moments out-of-plane with increasing field, before reaching magnetic saturation. However, the MR effect is getting negative at higher magnetic field with the maximum at the saturation point. The MR is negative for all magnetic fields when the temperature increases approach \(T_C\), showing a maximum at the Curie temperature. The positive slope for the Hall resistivity (see Fig. (b)) indicates a dominating hole-type conductivity in Mn$_{1/4}$NbS$_2$ at ambient pressure. While linear at high temperatures, the Hall resistivity \(\rho_H(H)\) below \(T_C\) has a contribution due to the anomalous Hall effect vanishing in the magnetically disordered state.

The magnetoresistance and Hall resistivity measured in the DAC at the lowest applied pressure 0.25 GPa (SM, Fig. 2 (b)) demonstrate qualitatively a similar behaviour compared to ambient pressure. However, application of a higher pressure has a significant impact on the shape of the Hall resistance \(\rho_H(H)\) and magnetoresistance \(MR(H)\). The low-temperature magnetotransport data (Fig. as well as Figs. 2 (b), (d), (f), (h) in SM) indicate the pressure-induced change of the MR that can be associated with the modification of magnetic properties of Mn$_{1/4}$NbS$_2$. The positive MR observed at ambient pressure is continuously suppressed while the absolute value of the negative MR at the highest fields continuously increases (Fig. (a)). For \(p = 5.5\) GPa, MR is negative for all applied magnetic fields, for all temperature regimes (SM, Fig. 2 (d)). Approaching the pressure \(7.1\) GPa, MR in the high filed regime increases up to 65% (Fig. (a)). At \(p = 10\) GPa, MR drastically drops to 3.2% at 9 T although it remains negative with nearly parabolic dependence. Above 10 GPa, MR suddenly decreases to the very low positive values (only about 0.1% at 9 T at 13.5 GPa).

Hall resistivity curves \(\rho_H(H)\) at pressures up to 5.5 GPa at the low temperature (Fig. (b)); SM, Fig. 2 (a), (c), (e), (g)) are qualitatively similar to that for ambient pressure demonstrating two regimes. Two regimes in the Hall resistivity curves are still persistent at further pressure increase as can be seen from the \(\rho_H(H)\) curve at 7.1 GPa (Fig. (b)). At \(p = 10\) GPa, Hall resistivity \(\rho_H(H)\) is sublinear, while above 10 GPa \(\rho_H(H)\) is linear at all temperatures (above and below the critical temperature derived from the temperature dependence of resistivity) with a negative slope revealing dominating electron conductivity in Mn$_{1/4}$NbS$_2$ and \(\rho_H(H)\) indicating the suppression of ferromagnetic order. For the magnetically ordered state \((T < T_c)\) of Mn$_{1/4}$NbS$_2$, when the temperature increases, one can clearly see the contribution due to the extraordinary Hall effect vanishing in the magnet-
icularly disordered state (SM, Fig. 2 (a), (c), (e) and (g)). As it follows from the results for different pressure values $\rho_{AHE}$ changes the sign twice upon pressure increase.

![Graph](image)

**FIG. 6.** Pressure and temperature dependent transverse magnetoresistance (a) and Hall resistivity (b) at $T = 2K$ for Mn$_{1/4}$NbS$_2$ plotted as function of external magnetic field.

### B. Theory

To allow a detailed interpretation of the experimental results, theoretical investigations based on first-principles electronic structure calculations have been performed by using the SPR-KKR band structure method. The DFT calculations based on local density approximation (LSDA) for FM Mn$_{1/4}$NbS$_2$ at ambient pressure lead to an underestimation of the Mn spin magnetic moment ($3.3\mu_B$ vs. experimental 4.2$\mu_B$ per atom), and to a suppression of the Mn spin magnetic moment at high pressure. Therefore, the calculations have been extended treating correlation effects beyond LSDA, using the LSDA+U approach with the Hubbard $U$ parameter for Mn of $U = 3$ eV. This leads to an increase of the spin magnetic moment of Mn at ambient pressure up to $3.8\mu_B$ as well as to a stabilization of the finite Mn spin magnetic moment on the Mn atom when the pressure increases up to 11 GPa.

The pressure-volume dependence, $p - V$, determined for ordered Mn$_{1/4}$NbS$_2$ using the VASP package (see SM, Fig. 3), shows a linear $p - V$ dependence up to a pressure of $\sim 9$ GPa. At higher pressures one can expect an instability of the original crystalline or magnetic phase. This is in line with the experimental results that show significant changes of the MR when the pressure increases above 10 GPa. On the other hand, the experimental Raman spectra do not exhibit any evidence for a structural phase transition in this pressure regime. As it follows from the electronic structure calculations within the LSDA+U approach, a pressure increase up to $p = 8$ GPa leads to a decrease of the Mn spin magnetic moment from $m = 3.8\mu_B$ at ambient pressure down to $m = 3.2\mu_B$ at $p = 8$ GPa and to $2.2\mu_B$ at 10.5 GPa. Thus, one may speculate about a possible pressure induced transition to the low-spin magnetic state. However, more detailed investigations on the properties of Mn$_{1/4}$NbS$_2$, both theoretical and experimental, are required for this pressure regime, while we will focus here on the low-pressure phase exhibiting linear $p - V$ dependence shown in Fig. 3 (SM).

The properties of the Hall resistivity are determined by the features of the electronic structure. To demonstrate this, Fig. 7 shows the calculated Bloch spectral functions (BSF) $A(\vec{k}, E)$ ((a) and (b)), and $A(\vec{k}_||, E_F)$ ((c) and (d)) representing the electronic band structure and Fermi surface projection onto the (001) plane for the two pressures $p = 0$ and 8 GPa, respectively. A positive slope of the Hall resistivity $\rho_H(B)$ found experimentally at ambient and small pressures implies a dominating hole type character of the electric carriers in line with the hole-like pockets around the K-point of the BZ (see Fig. 7(a)) created by the unoccupied top of the minority-spin bands (red symbols). This is also seen in the Fermi surface cut shown in Fig. 7(c) (right panel) representing the Fermi surface created by the minority-spin states, as well as the hole-like pockets created by the majority-spin states (a) blue symbols) along the $\Gamma - M$ and $K - M$ symmetry directions. When the pressure increases above 3.5 GPa, the minority-spin pockets at the K point disappear as the corresponding energy bands (red) move down in energy, as can be seen in Fig. 7(b) for $p = 8.0$ GPa. At this pressure, the shape of the Fermi surface has essentially electron-like features (see Fig. 7(d)), leading to the electron-like character for the ordinary Hall effect, although the hole-like pockets created by the majority-spin states around K point still survive also at this pressure.

The MR is a characteristic of the change of the electrical resistivity $\rho(T, B)$ in the presence of an external magnetic field $B$. The corresponding resistivities $\rho(T, B)$ are calculated for the mono-domain system, as a function of the temperature. Therefore, in the case of PM-ordered Mn$_{1/4}$NbS$_2$, these results should be compared with the experimental data for an applied magnetic field strong enough to ensure magnetization saturation in the system.

The temperature dependent electrical resistivity of magnetically ordered metallic systems is determined by thermally induced lattice vibrations and spin fluctuations. Because of a weak dependence of the lattice vi-
brations on the magnetic field, their contribution to the MR can be neglected and we will focus on the transverse spin fluctuations that are strongly affected by the temperature and dependent on the magnetic structure in the system. Monte Carlo (MC) simulations give access to the $M(T, B)$ dependencies for Mn$_{1/4}$NbS$_2$ characterizing the amplitude of the transverse spin fluctuations and as a result the amplitude of the electron scattering on thermal spin fluctuations. These simulations use the exchange coupling parameters obtained within first-principles calculations performed for the FM reference state. A positive first- and second-neighbor exchange coupling parameters $J_{ij}$ at low pressure (see Fig. 3(a)) guarantee the FM ground state of the system. The $M(T, B)$ dependence obtained within MC simulations for Mn$_{1/4}$NbS$_2$ at ambient pressure is shown in Fig. 8 (b) for $B = 0$ T and $4$ T, respectively. The resistivities as a function of the temperature calculated on the basis of $M(T, 0)$ and $M(T, B = 4$ T) lead to the negative magnetoresistance $MR(T)$ plotted in Fig. 3(b). In this case the MR is governed by the mechanism rather common for FM metal, alignment of the spin magnetic moments along the magnetic field reduces the electron scattering and decreases the resistivity $\rho(T, B = 4$ T) with respect to $\rho(T, 0)$, leading to a negative magnetoresistance in the FM ordered system. The impact of the field on the magnetization has a maximum around the Curie temperature, leading to a maximum of the MR in this temperature region. This is in good agreement with the experimental findings as it is shown in Fig. 9 (a).

When the pressure increases, the calculated exchange coupling parameters $J_{ij}$ exhibit significant changes, as shown in Fig. 3(a). The first-neighbor interaction parameters corresponding to an interaction between the Mn ions located in neighboring Mn layers in Mn$_{1/4}$NbS$_2$ become negative when the pressure is approaching $p = 8$ GPa. This should lead to an antiferromagnetic alignment of the magnetic moments of these layers if no other interactions are taken into account. The second-neighbor parameters characterizing the Mn-Mn interactions within the layers are positive, stabilizing the FM order within the layers, although they decrease with increasing pressure. The total energy calculations for $p = 8$ GPa give the difference $E_{FM} - E_{AFM} = 36$ meV per formula unit, indicating stability of the AFM state. The dependence of the exchange coupling parameters on the magnetic configuration can be crucial to describe metamagnetic phase transitions properly as it was found for instance discussing the AFM-FM transition in FeRh. Therefore, the calculations of $J_{ij}$ for Mn$_{1/4}$NbS$_2$ at $p = 8$ GPa have been performed for the AFM reference state with the layer-by-layer antiferromagnetic alignment of the magnetic moments. The resulting Mn-Mn exchange coupling parameters presented in Fig. 3(a) by closed triangles, stabilize the AFM state in the system. This is shown by MC simulations taking into account the exchange interactions only within a sphere with radius $R = 2a$, with $a$ the lattice parameter (see Fig. 3(c), closed circles). The external magnetic field pushes the magnetic moments towards the FM alignment (see open circles in Fig. 3(c)). This leads to a modification of the Mn-Mn exchange interaction parameters (Fig. 3(a), open triangles) and to a stabilization of the FM state. Note that in the case of ambient pressure, the exchange parameters calculated both for the FM as well as for the AFM reference state indicate stability of the FM state (Fig. 3(c), diamonds). Thus, one can expect a field-induced AFM-FM transition at $p = 8$ GPa. MC simulations for the pressure $p = 9$ GPa demonstrate the stability of the layer-by-layer AFM state (see Fig. 3(d)) for which the field induced metamagnetic transition is not possible anymore (see Fig. 3(d), open circles).

To discuss the behaviour of the magnetoresistance $MR(T)$ of Mn$_{1/4}$NbS$_2$ at $p = 8$ GPa, the change of the resistivity during the AFM-to-FM transition was calculated as a difference of the electrical resistivities for the AFM (i.e., without magnetic field) and for the FM (with magnetic field) states of the system. The AFM state was approximated by the layer-by-layer antiferromagnetic structure, i.e., with two sublattices having antiparallel alignment of the magnetic moments. For the sake of simplicity, the temperature dependent magnetization for each sublattice, $M(T)$, was taken the same as for the FM state calculated for $p = 8$ GPa (open diamonds in Fig. 3(c)). The resulting MR is shown in Fig. 3(b) by circles as a function of the temperature. A crucial result following from these calculations is the maximum of the MR at low temperature due to weak thermal disorder in the system. When the temperature increases the MR decreases and vanishes at the critical temperature due to a transition to the paramagnetic state. A similar behavior of the MR has been obtained experimentally, as it is shown in Fig. 3(a) by circles.

Finally, it is worth to discuss briefly also the pressure dependent behavior of the non-conventional contribution to the Hall resistivity for Mn$_{1/4}$NbS$_2$. As it was shown above, the high-field $\rho_{xy}(B)$ extrapolated to the $B = 0$ T limit gives the AH resistivity (AHR) assuming FM order in the system, which exhibits a non-monotonous behaviour changing sign twice upon the pressure increase up to 10 GPa (see SM, Fig. 2 (a), (c), (e)). However, no indication for a sign change of the AHR has been found in calculations for the FM state of the system.

On the other hand, in the intermediate pressure regime, before the layer-by-layer AFM state is stabilized, a non-collinear AFM structure is expected as a results of competition between the FM and AFM interatomic exchange interactions. Moreover, in this case the Dzyaloshinskii-Moriya interactions (DMI) should have a crucial role for the formation of a chiral magnetic texture, despite its magnitude ($\sim 0.2$ meV) is smaller by an order of magnitude when compared to the competing isotropic exchange interactions. As a result, an additional topological contribution to the Hall resistivity occurs in the presence of an external magnetic field, $\rho_{xy}^{THE}$ (topological
Hall effect (THE)\(^{10}\)

\[
\rho_{xy} = \rho_{xy}^{OHE} + \rho_{xy}^{AHE} + \rho_{xy}^{THE}
\]  

(1)

with \(\rho_{xy}^{AHE} \sim M_z\) and \(\rho_{xy}^{THE} \sim \vec{B}_{eff}\), where \(M_z\) is the magnetization component along the \(z\) direction and \(\vec{B}_{eff}\) is the emergent magnetic field having topological origin and being nonzero in the magnetic textures characterized by finite scalar chirality. Note also that a competition of \(\rho_{xy}\) with \(\rho_{eff}\) can lead also to the formation of more complicated topologically nontrivial magnetic textures (e.g. skyrmions) as it was predicted recently for Fe\(_{1/4}\)TaS\(_2\).\(^{15}\) Both extraordinary contributions to the Hall resistivity increase in the system with the in-plane magnetic anisotropy due to increase of the external magnetic field.

IV. SUMMARY

To summarize, we present the results of experimental and theoretical investigations on the pressure dependent magnetic and transport properties of Mn\(_{1/4}\)NbS\(_2\). A strong increase of the magnetoresistance up to \(\sim 60\%\) at low temperature has been observed experimentally for the pressure \(p = 7.1\ \text{GPa}\). To get insight into the driving mechanism behind this phenomenon, theoretical investigations have been performed based on first-principles electronic structure calculations combined with Monte Carlo simulations. As a result, the field-induced metamagnetic AFM-FM transition was suggested as a mechanism responsible for the high magnetoresistance at \(p = 7.1\ \text{GPa}\), which is larger than \(\sim 50\%\) as was observed for FeRh\(^{47}\). This suggests a new family of materials with controllable metamagnetic transition from AFM to FM ordering that is very promising for various future applications, i.e. materials based on intercalated TMDCs, for which however tuning of the interatomic exchange parameters due to composition variation instead of pressure may be more appropriate. In particular, one can expect a transition from the FM to the AFM state upon substitution of Mn by Fe, coming towards AFM-ordered Fe\(_{1/4}\)NbS\(_2\).\(^{15}\) The pressure induced modification of the Hall resistivity including ordinary and extraordinary (anomalous and topological) contributions is discussed on the basis of calculated electronic structure and exchange coupling parameters and their modifications induced by increasing pressure. Mutual analysis of the experimental and theoretical results allows to make a suggestion about the field-controlled formation of chiral magnetic structure in the intermediate pressure regime characterized by strong competition of the FM and AFM interatomic exchange interactions in Mn\(_{1/4}\)NbS\(_2\).

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FIG. 7. Bloch spectral function for Mn$_{1/4}$NbS$_2$ under pressure for $p = 0$ and 8.0 GPa, (a) and (b), respectively. Blue symbols display majority-spin states and red symbols - minority-spin states. (c) and (d) represent the Bloch spectral function $A(k_x, k_y, E_F)$ at the Fermi level for Mn$_{1/4}$NbS$_2$ under pressure for $p = 0$ and 8.0 GPa, respectively. Left panel corresponds to majority-spin states, right to minority spin states.
FIG. 8. (a) Pressure dependent exchange interactions for Mn$_{1/4}$NbS$_2$; Open symbols represent the results calculated for the FM reference states, closed symbols the AFM reference state. The MC results for the temperature dependent magnetization $M(T)$ of Mn$_{1/4}$NbS$_2$ for different pressure: $M(T)$ calculated for $B = 0$ (closed circles) and 4.0 T (open circles) at $p = 0.0$ (b), $p = 8.0$ (c) and $p = 9.0$ GPa (d).
FIG. 9. (a) The temperature dependent magnetoresistance of Mn$_{1/4}$NbS$_2$: (a) Experimental results for the magnetic field $B = 7.5$ T and the two pressures 0 and 7.1 GPa; (b) theoretical results for the magnetic field $B = 4$ T used in the case of $p = 0$ and 5 GPa. The results for $p = 8$ GPa are obtained using the resistivities for the FM and AFM states, $\text{MR} = (\rho(T, \text{FM}) - \rho(T, \text{AFM}))/\rho(T, \text{AFM})$. 