Electronic, magnetic and transport properties of Fe intercalated 2H-TaS$_2$ studied by means of the KKR-CPA method

S. Mankovsky,* K. Chadova, D. Ködderitzsch, and H. Ebert

Department Chemie, Physikalische Chemie,
Universität München, Butenandstr. 5-13, 81377 München, Germany

W. Bensch
Inst. für Anorgan. Chemie, Universität Kiel,
Olshausenstr. 40, 24098 Kiel, Germany

(Dated: July 24, 2015)

The electronic, magnetic and transport properties of Fe intercalated 2H-TaS$_2$ have been investigated by means of the Korringa-Kohn-Rostoker (KKR) method. The non-stoichiometry and disorder in the system has been accounted for using the Coherent Potential Approximation (CPA) alloy theory. A pronounced influence of disorder on the spin magnetic moment has been found for the ferro-magnetically ordered material. The same applies for the spin-orbit induced orbital magnetic moment and magneto-crystalline anisotropy energy. The temperature-dependence of the resistivity of disordered 2H-Fe$_{0.28}$TaS$_2$ investigated on the basis of the Kubo-Středa formalism in combination with the alloy analogy model has been found in very satisfying agreement with experimental data. This also holds for the temperature dependent anomalous Hall resistivity $\rho_{xy}(T)$. The role of thermally induced lattice vibrations and spin fluctuations for the transport properties is discussed in detail.

PACS numbers: Valid PACS appear here

I. INTRODUCTION

Transition metal dichalcogenides are very attractive materials both from a fundamental point of view as well as concerning potential technological applications. They are formed by well separated trilayers of the type MX$_2$ (M: transition metal, X: S, Se, Te), that determine their quasi-2D structure leading to various interesting physical properties. These are for instance strongly anisotropic transport properties [1] or charge-density-wave (CDW) instabilities leading to the formation of CDW phases which can coexist at low temperature with superconductivity [2–4]. Many discussions in the literature concern the opto-electronic properties of the semiconducting dichalcogenides and their relation to the features of the energy gap as width and direct or indirect character [5, 6].

Most of the transition metal dichalcogenides are non-magnetic. However, they allow the intercalation of magnetic atoms or molecules between the X-M-X trilayers. This leads to an interesting class of magnetic materials having quasi-2D properties [7–10] which can be varied via the amount and type of intercalated atoms. This is demonstrated in the present theoretical work on Fe intercalated 2H-TaS$_2$, where the Fe atoms occupy the octahedral holes between prismatic MX$_2$ trilayers (see Fig. 1). In fact, Fe intercalated 2H-TaS$_2$ can be seen as a prototype material that has been investigated experimentally already some years ago as the closely related intercalated 2H-structured systems NbSe$_2$, TaSe$_2$, NbS$_2$, and TaS$_2$ with the magnetic 3d-metals Mn, Fe, Co and Ni as an intercalate [11–14]. As was shown, a common feature of these materials is the trend to create two-dimensional ordered 2 $\times$ 2 and $\sqrt{3} \times \sqrt{3}$ structures within the 3d-layer for the concentration $x = 1/4$ and 1/3, respectively, of the intercalate.

Depending on concentration and intercalation atom type, these materials exhibit for the ordered phase ferromagnetic (FM) [8] or anti-ferromagnetic (AFM) [11] magnetic order at low temperatures. The AFM order has been observed for the intercalated NbS$_2$ systems, e.g., Fe$_{1/3}$NbS$_2$, Co$_{1/3}$NbS$_2$, and Ni$_{1/3}$NbS$_2$, while in the case of TaS$_2$ based alloys intercalated by 3d-metals FM order has been found for Cr$_{1/3}$TaS$_2$ ($T_C = 116$ K), Mn$_{1/3}$TaS$_2$ ($T_C = 70$ K), and Fe$_{1/3}$TaS$_2$ ($T_C = 35$ K). In the case of non-stoichiometric, disordered systems the Curie temperature depends in addition on the concentration of the 3d element [9, 10]. A strong dependence of $T_C$ on the Fe concentration was found in particular for Fe$_x$TaS$_2$ [9] with $T_C = 90, 163, 90$, and 55 K for $x = 0.2, 0.26, 0.28, 0.34$, respectively. At $x = 0.45$ the system becomes AFM with a Néel temperature $T_N = 85$ K [10].

Ordered Fe$_{1/4}$TaS$_2$ possesses a very pronounced out-of-plane magneto-crystalline anisotropy (MCA), i.e. the easy axis is along the c-axis. The extremely high anisotropy field $B_A$ of about 60 T [15, 16], that is by an order of magnitude higher than observed for Mn$_{1/4}$TaS$_2$ and Mn$_{1/4}$NbS$_2$ [7] (about 0.5 T), leads to an Ising-type behavior of the Fe magnetic moment.

* Sergiy.Mankovskyy@cup.uni-muenchen.de
The transport properties of magnetic intercalated transition metal dichalcogenides have been investigated by various authors. Examples for this are the electrical resistivity and anomalous Hall effect (AHE) [11] studied for alloys based on 2H-NbS$_2$. The magneto-transport and superconducting properties of disordered Fe intercalation compounds based on NbSe$_2$, TaSe$_2$ and TaS$_2$ have been investigated by Whitney et al. [17] for the dilute regime ($x < 0.1$). Recently, the results of magneto-transport measurements for Fe$_{1/4}$TaS$_2$ have been reported by Morosan et al. [18]. This material shows a strong anisotropy concerning the magnetization as well as the resistivity. Checkelsky et al. [15] focused on the temperature dependence of the resistivity of Fe$_{1/4}$TaS$_2$. These authors showed that the characteristics of the AHE for $T > 50$ K cannot be explained by the Karplus-Luttinger or Berry-phase mechanism. Instead it was concluded that it is governed by scattering processes connected with temperature induced phonons and magnons. These authors also discussed the unconventional behavior of the magnetoresistance as a function of temperature.

A very large magneto-resistance (MR) has been found recently for disordered Fe$_{0.25}$TaS$_2$ single crystal by Hardy et al. [19], which is nearly 100 times stronger than that observed for the ordered Fe$_{1/4}$TaS$_2$ compound. The authors point out the crucial role of spin disorder and strong spin-orbit coupling in the system, that can be exploited to create materials with large MR.

In the present work we will focus on TaS$_2$ intercalated with Fe as a prototype material for magnetic intercalated transition metal dichalcogenides. While several experimental studies on the magnetic and transport properties of this system can be found in the literature, only few theoretical investigations [20, 21] have been done so far with the focus on its electronic structure assuming an ordered state.

II. COMPUTATIONAL DETAILS

The present theoretical investigations on the magnetic and transport properties of Fe intercalated 2H-TaS$_2$ are based on first-principles electronic structure calculations which have been performed using the fully relativistic KKR Green function method.[22, 23] The combination with the coherent potential approximation (CPA) alloy theory allowed to deal with disorder on the Fe sub-lattice as well as the impact of finite temperatures on transport properties on the basis of the alloy analogy model (see below). The self-consistent calculations have been done in the framework of the local approximation to spin density functional theory (LSDA) using the parametrization for the exchange and correlation potential as given by Vosko functional theory (LSDA) using the parametrization for the framework of the local approximation to spin density theory. The self-consistent calculations have been done in the framework of the local approximation to spin density theory.

![Figure 1. The structure of the investigated Fe intercalated 2H-TaS$_2$ system showing the position occupied by the Fe atoms and empty spheres (ES) in between the S-Ta-S trilayers according to the Fe concentration.](image)

For the angular momentum expansion of the Green function a cutoff of $l_{\text{max}} = 3$ was applied. This is in particular important for the transport calculations that were based on the Kubo-Streda formalism [28] that among others gives access to the AHE. To deal with the temperature dependence of the transport properties a scheme has been used that is based on the alloy analogy model and that accounts for thermal lattice vibrations [30] as well as spin fluctuations.[31] Within this approach the spin fluctuations are represented by a temperature-dependent quasistatic spin configuration corresponding to the adiabatic approximation.[32] The spin configuration used as an input for the transport calculations may be determined for example by performing Monte Carlo simulations or deduced from the experimental temperature-dependent magnetization.[31] Here, the latter scheme has been applied using experimental data from Ref. 19.

III. RESULTS

A. Electronic structure

At low temperatures, pure 2H-TaS$_2$ exhibits a charge density wave (CDW) instability [33] driven by the Fermi surface nesting mechanism, bringing the system into the CDW state below $T_{\text{CDW}} = 80$ K [3]. Intercalation with Fe obviously strongly modifies the Fermi surface due to Fe-related electronic states resulting in a shift of the Fermi energy and a smearing of the electronic bands due to the disorder within the Fe layers. This suppresses the CDW instability and the intercalated system shows conventional metallic behavior.

These findings are reflected by the results of calculations on the electronic structure. Fig. 2 shows the corresponding spin-integrated Bloch spectral function (BSF) $A(\vec{k}, E)$ calculated for 2H-TaS$_2$, disordered Fe$_{0.25}$TaS$_2$, disordered Fe$_{0.25}$TaS$_2$. The parameters specifying the structure of Fe intercalated 2H-TaS$_2$ as shown in Fig. 1 have been taken from the experiment [10, 18].
as well as ordered Fe_{1/4}TaS_{2}. To avoid the use of an ex-

tremely fine mesh of \vec{k}- and E-points these calculations were done using a small imaginary part of the energy E in the case of the ordered compounds TaS_{2} and Fe_{1/4}TaS_{2}. The resulting BSF for TaS_{2} corresponds essentially to the dispersion relation \( E(\vec{k}) \) given by Blaha [34] with the differences primarily to be ascribed to the impact of the spin-orbit coupling that is accounted for within the present fully relativistic calculations. Intercalation of Fe leads for the disordered case, apart from the exchange splitting, primarily to a broadening of the bands as can be seen from Fig. 2 b). For ordered Fe_{1/4}TaS_{2}, on the other hand, the band structure gets much more complex due to the increase of the size of the unit by a factor of 4 and the occurrence of new Fe-related states (see Fig. 2 c).

The various features in the BSF in Fig. 2 are also reflected by the component and spin-resolved density of states (DOS) shown in Fig. 3 for Fe (a), Ta (b) and S (c) in pure TaS_{2}, disordered Fe_{0.25}TaS_{2} as well as ordered Fe_{1/4}TaS_{2}. The rather broad Fe energy bands (Fig. 3 a) indicate a significant hybridization with the electronic states of the host atoms, especially with the neighboring S atoms. This can also be concluded from the partial DOS of S, shown in Fig. 3 (c). Obviously, disorder in the Fe sub-lattice leads for Fe itself to quite pronounced changes when compared to the ordered case; apart from a broadening and resulting smearing of the spectral features in the Fe DOS one notices a substantial redistribution of spectral weight together with an apparent change in the exchange splitting. For the S and Ta sublattices, on the other side, disorder leads first of all to a smearing of the DOS curve. Interestingly the impact of disorder for Ta is at least as pronounced as for the S, being next-nearest neighbor to Fe (see Fig. 1).
B. Magnetic moments

Calculations of the magnetic moments for ferromagnetic disordered 2H-Fe₇TaS₂ have been done first using the GGA approach for the treatment of exchange and correlation. As this led to results that were too low when compared to experiment (see below) the LDA+U method was used instead with the corresponding parameters given in section II. As can be seen from Fig. 4 this led for disordered 2H-Fe₇TaS₂ to a spin magnetic moment that increases nearly monotonously from about 2.42 to 3.05 μₜₜ when the Fe concentration x increases from 0.05 to 0.5. On the other hand, the relatively large

spin-orbit induced orbital moment decreases from about 0.82 to 0.29 μₜₜ. In the case of ordered 2H-Fe₁/₄TaS₂ quite pronounced changes compared to the disordered state are found; upon ordering the spin moment increases from 2.76 to 3.64 μₜₜ while the orbital moment decreases from 0.48 to 0.16 μₜₜ. For the GGA calculations the corresponding changes are 1.93 to 3.1 μₜₜ for the spin moment and 0.12 to 0.11 μₜₜ for the orbital moment, respectively. The increase of the spin magnetic with ordering is quite common and can often be associated with the DOS of the ordered state that is more structured and less broad than for the disordered state (see Fig. 3). For the same reason one has usually also an increase of the orbital magnetic moment. On the other hand, the orbital magnetic moment depends much more on the details of the electronic structure in the vicinity of the Fermi energy than the spin magnetic moment. This together with the relatively small width of the Fe sub-band seems to be the reason for the observed pronounced decrease for the orbital moment upon ordering.

The LDA+U-based results differ quite substantially from that of Ko et al. [21] who used the GGA+U scheme with the values for U and J as given in section II and spin-orbit coupling treated as a perturbation. This approach led for the spin and orbital magnetic moment to the values 2.95 and 1.0 μₜₜ, respectively. These results imply that in particular the orbital magnetic moment depend quite sensitively on the treatment of exchange and correlation as well as spin orbit coupling.

Experimental work on ordered 2H-Fe₁/₄TaS₂ led to a total magnetic moment per Fe atom of 3.9 μₜₜ and a Curie temperature of $T_C = 160$ K. [18] This is in close agreement with more recent work by Checkelsky et al. [15] ($T_C = 160$ K) as well as Choi et al. [16]. The later authors did measurements on ordered samples obtained as grown (AG) and by slow cooling (SC) leading to a total moment of 4.0 μₜₜ and a Curie temperature of $T_C = 156$ and 159 K, respectively. Additional measurements on quenched (Q) disordered samples led to a substantially lower Curie temperature of $T_C = 104$ K.

On the basis of XMCD measurements at the L₂,₃-edges of Fe the ratio of the spin ($m_{spin}$) to the orbital ($m_{orb}$) moment has been estimated to be $m_{orb}/m_{spin} = 0.33$ [21]. Assuming an ionic configuration for Fe with a spin moment of 4.0 μₜₜ an orbital moment of 1.33 μₜₜ was suggested. Using instead the value 4.0 μₜₜ for the total moment as given above an orbital moment of 1.0 μₜₜ results from the analysis of the XMCD measurements.

When comparing the experimental results with the theoretical ones given in Fig. 4 one finds that the spin magnetic moment calculated for the 2H-Fe₁/₄TaS₂ compound is in a good agreement with the experimental data while the orbital one seems to be too low. This might be to a large extent due to the pronounced dependence of the orbital magnetic moment on the computational details that was discussed above.

C. Magneto-crystalline anisotropy

The magneto-crystalline anisotropy energy $\Delta E_{MCA}$ defined as the difference in energy for the in-plane and out-of-plane orientation of the magnetization has been calculated by means of the so-called torque method [35]. $\Delta E_{MCA}(x)$ determined this way for disordered Fe₇TaS₂ as a function of the Fe concentration x and expressed with respect to the formula unit (see below) increases monotonously with x. To compare with experimental data $\Delta E_{MCA}(x)$ was converted into an anisotropy field $B_A = \Delta E_{MCA}/M_{f.u.}$, where the magnetic moment per formula unit ($M_{f.u.}$) is given by that per Fe atom via $M_{f.u.} = xM_{Fe}$. Using this representation for the magneto-crystalline anisotropy $B_A(x)$ decreases monotonously with x as can be seen in Fig. 5. For $x = 0.25$ calculations have been done in addition assuming an ordered compound Fe₁/₄TaS₂. As often found, ordering increases the anisotropy field in a quite pronounced way. Astonishingly, this consequence of ordering for $\Delta E_{MCA}(x)$ is reversed when compared to the situation for the orbital magnetic moment. Comparison of the theoretical result for $B_A$ with the experimental value for $x = 1/4$ confirms the large anisotropy field found in
experiment. Nevertheless, the theoretical value for the ordered as well as for the disordered state are well above the experimental value. This indicates again that a certain amount of disorder may be present in the sample investigated.

D. Electrical resistivity

The temperature-dependent longitudinal electrical resistivities, $\rho_{xx}(T)$ and $\rho_{yy}(T)$, and $\rho_{zz}(T)$, calculated for ferromagnetic disordered 2H-Fe$_{0.28}$TaS$_2$ using the scheme described in section II are shown in Fig. 6 (a). For the in-plane longitudinal electrical resistivity $\rho_{xx}(T)$ results are given in addition that account only for the lattice vibrations ($vib$) and spin fluctuations ($fluct$), respectively. For $T = 0$ K all individual $\rho_{xx}(T)$ curves represent the residual resistivity due to the random disorder in the Fe sub-lattice. Keeping the magnetic spin configuration fixed and dealing only with the impact of thermal lattice vibrations on the resistivity a pronounced and monotonous increase with temperature is observed for the corresponding curve $\rho_{xx}^{vib}(T)$ (up triangles). Considering on the other hand $\rho_{xx}^{fluct}(T)$ (down triangles) that accounts for the spin fluctuations only one finds a rather weak increase with temperature. Accounting for both temperature dependent scattering mechanisms simultaneously one finds for the resulting curve $\rho_{xx}^{tot}(T)$ (full squares) only minor changes compared to $\rho_{xx}^{vib}(T)$. As found before for ferromagnetic bcc-Fe [31], this finding clearly shows that $\rho_{xx}^{vib}(T)$ and $\rho_{xx}^{fluct}(T)$ are not additive, i.e. the Matthiesen rule is violated. Comparing the calculated $\rho_{xx}(T)$ curve with the available experimental data [9, 20] one can see that the experimental and theoretical residual resistivities agree rather well. The fact that the theoretical values are somewhat higher may indicate that the assumption of fully random disorder on the Fe sub-lattice for the calculations is not fully justified; i.e. there might be some order present in the experimentally investigated samples.

The various curves in Fig. 6 (a) clearly show that the thermal lattice vibrations are primarily responsible for the temperature dependence of $\rho_{xx}(T)$ including the change of its slope close to the Curie temperature. For that reason this peculiar behavior cannot be ascribed to the temperature induced magnetic disorder as it was assumed before.[9, 20] Obviously, the temperature dependence of $\rho_{xx}(T)$ has primarily to be ascribed to the increasing smearing of the energy bands with temperature due to electron scattering caused by lattice vibrations. For low temperature, this results in a rather fast increase of the resistivity due to a corresponding increasing cross section for the inter-band scattering. For higher temperatures, a saturation of the number of channels for the inter-band scattering seems to occur leading finally to a rather weak increase of $\rho_{xx}(T)$ with temperature.

As can be seen in Fig. 6 (a), the calculated out-of-plane resistivity $\rho_{zz}(T)$ for $T = 0$ K is larger than its in-plane counterpart $\rho_{xx}(T)$ reflecting the 2D-character of the system. The finding that this difference is relatively weak is due to the disorder in the Fe sub-lattice that causes in both cases a large residual resistivity. With increas-
ing temperature this difference diminishes monotonously being nearly absent for the highest temperature considered here \((T = 125 \text{ K})\). This behavior of the resistivity has been observed and discussed before for example for the compounds \(\text{Nb}_3\text{Sn}\) and \(\text{Nb}_3\text{Sb}\)\([36–38]\). The fact that the \(\rho_{zz}(T)\) curve is not shifted rigidly against that for \(\rho_{xx}(T)\) clearly shows once more that the contributions to the resistivity due to chemical and thermal disorder are not simply additive. This non-additive behavior together with the fact that the temperature dependence for \(\rho_{xx}(T)\) as well as for \(\rho_{zz}(T)\) is obviously dominated by the thermal lattice vibrations leads obviously to the decreasing anisotropy of the resistivity with increasing temperature seen in Fig. 6 (a).

The temperature-dependent transverse electrical resistivity \(\rho_{xy}(T)\) for disordered 2H-\(\text{Fe}_x\text{TaS}_2\) is shown in Fig. 6 (b). For \(T = 0 \text{ K}\) the various theoretical curves are determined only by the chemical disorder on the Fe sub-lattice and for that reason all coincide. The value \(\rho_{xy}(0)\) may be decomposed into its intrinsic or coherent and extrinsic or incoherent contribution \([29, 39]\). The later part represents in particular all so-called skew scattering contributions. Keeping the spin configuration fixed to that for \(T = 0 \text{ K}\) (corresponding to a collinear ferromagnetic ordering) and accounting for the lattice vibrations only the resulting \(\rho_{xy}^{\text{vib}}(T)\) rises with temperature \(T\) and shows a broad maximum around 40 K. For higher temperatures \(\rho_{xy}^{\text{vib}}(T)\) decreases with \(T\) as was found before for example in the case of pure Ni in the regime below the Curie temperature.\([30]\) On the other hand, if the lattice structure is kept undistorted and spin fluctuations are accounted for \(\rho_{xy}^{\text{fluct}}(T)\) monotonously decreases with \(T\) until the Curie temperature is reached and \(\rho_{xy}^{\text{fluct}}(T)\) vanishes as the thermally averaged z-component of the magnetization \((M_z)_T\) vanishes. If both scattering mechanism are accounted for one finds again that these do not act in a simple additive way. Nevertheless, from the behavior of the individual curves \(\rho_{xy}^{\text{vib}}(T)\) and \(\rho_{xy}^{\text{fluct}}(T)\) one may expect the behavior of the transverse resistivity \(\rho_{xy}(T)\) that account for the lattice vibrations and spin fluctuations simultaneously. When comparing these results with the corresponding experimental data, a reasonable agreement is found. In particular concerning the presence of a maximum for \(\rho_{xy}(T)\) with temperature. The individual curves \(\rho_{xy}^{\text{vib}}(T)\) and \(\rho_{xy}^{\text{fluct}}(T)\) clearly demonstrate the importance of extrinsic contributions to \(\rho_{xy}(T)\) supporting the conclusions of Checkelsky et al. \([15]\) concerning their role for \(\text{Fe}_x\text{TaS}_2\) mentioned in the introduction.

IV. SUMMARY

Using the KKR-CPA band structure method for disordered systems the electronic structure as well as magnetic and transport properties of ferromagnetic ordered and disordered 2H-\(\text{Fe}_x\text{TaS}_2\) have been investigated. By means of the fully relativistic of the KKR-CPA the spin-orbit induced orbital magnetic moment and magneto-crystalline anisotropy energy could be calculated in particular. The various magnetic properties were found in reasonable agreement with available experimental data with clear indications for the strong impact of the degree of order on the Fe sub-lattice of the system. In addition, a prominent role of correlation effects was found that were ascribed to relatively narrow with of the Fe-related bands. The temperature-dependence of the longitudinal resistivity as well as transverse anomalous Hall resistivity was studied using the alloy analogy model within the framework of the Kubo-Streda formalism. The results obtained for disordered 2H-\(\text{Fe}_{0.28}\text{TaS}_2\) were found in very satisfying agreement with experimental data. Additional calculations accounting for thermally induced lattice vibrations and spin fluctuations individually clearly showed that their contribution to the resistivity is not additive and that the temperature-dependence of the longitudinal resistivity is nearly exclusively determined by the lattice vibrations.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (DFG) via the priority programs SPP 1415 and SPP 1538 is thankfully acknowledged.

[1] R. Friend and A. Yoffe, Advances in Physics 36, 1 (1987), http://dx.doi.org/10.1080/0001873750011021951.
[2] J. Wilson, F. D. Salvo, and S. Mahajan, Advances in Physics 24, 117 (1975), http://dx.doi.org/10.1080/00018737500110391.
[3] R. L. Withers and J. A. Wilson, J. Phys. C: Solid State Phys. 19, 4809 (1986).
[4] A. H. Castro Neto, Phys. Rev. Lett. 86, 4382 (2001).
[5] J. Wilson and A. Yoffe, Advances in Physics 18, 193 (1969), http://dx.doi.org/10.1080/0001873630901130.
[6] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nat Nano 7, 699 (2012).
[7] S. S. P. Parkin and R. H. Friend, Philosophical Magazine Part B 41, 65 (1980), http://dx.doi.org/10.1080/13642818008245370.
[8] S. S. P. Parkin and R. H. Friend, Philosophical Magazine Part B 41, 95 (1980), http://dx.doi.org/10.1080/13642818008245371.
[9] M. Eibschutz, S. Mahajan, J. F. DiSalvo, G. W. Hull, and J. V. Waszczak, Journal of Applied Physics 52, 2098 (1981).
[10] H. Narita, H. Ikuta, H. Hinode, T. Uchida, T. Ohtani, and M. Wakihiara, Journal of Solid State Chemistry 108, 148 (1994).
