Single crystal studies and electronic structure investigation of a room temperature semiconductor NaMnAs

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We report synthesis of single crystalline NaMnAs, confirm its antiferromagnetic order and characterise the sample by photoemission spectroscopy. The electronic structure was studied using optical transmittance, x-ray and ultraviolet spectroscopy and by theoretical modeling using local density approximation (LDA) extended to LDA+U when Heisenberg model parameters were determined. Optical transmittance measurement have confirmed the theoretical predictions that NaMnAs is a semiconductor. Also the Néel temperature was closer determined for the first time from temperature dependence of magnetization, in agreement with our Monte Carlo simulations.

I. INTRODUCTION

Antiferromagnets (AFMs) are increasingly coming into the spotlight for spintronics applications [1–4]. One of the motivations is robustness against stray magnetic fields for memory devices applications [5–7], thanks to compensation of magnetic moments. The aspect of linear spin waves dispersion close to the Γ point, as opposed to the quadratic trend in ferromagnets [8], has also been considered for possible magnonics technology [8–14].

While numerous AFM materials were discovered in previous century, for many of them, little is known beyond the bare fact that they are antiferromagnetic. One
of the most widely studied compounds in AFM spintronics\cite{15,16}, CuMnAs shows switching behavior in charge resistivity between binary\cite{17} or multi-level\cite{6} states, through the controlled application of electric current\cite{18,19} or optical\cite{20} pulses. Its tetragonal phase presents the additional benefits of above room temperature antiferromagnetic ordering\cite{21,22}, as well as lack of lattice strain in the deposition over a GaP substrate.

On the other hand, similarly to the other well-established example of Mn$_2$Au, CuMnAs presents no electronic band gap\cite{27}. This feature would be highly desirable for further spintunics and magnonics technologies, in which for instance lack of charge carriers have been predicted\cite{28} and observed\cite{29,30} to provide long range magnons diffusion length due to the depopulated Stoner continuum.

While the pursuit of better characterization of microscopic features and switching mechanisms in the most established AFMs continues, and typically resorts to high quality samples prepared by molecular beam epitaxy (MBE)\cite{31,32}, the search for other semiconducting AFMs has also carried on, taking advantage of the flexibility offered by bulk synthesis methods in exploring different compositions and lattice geometries.

Remaining within the AMnX family of alkaline metal / manganese-pnictide ternary compounds with a tetragonal non-symmorphic space group P4/nmm (Cu$_2$Sb-type structure), we recall the early work by Linowsky and Bronger (with $A = K$ and $X = P$, As)\cite{33} Schuster et al. (with $A = K$,Na and $X = Sb$, Bi, P)\cite{34}, Achenbach et al. (with $A = Li$, Na and $X = P$, As, Sb, Bi)\cite{35}, Bronger et al. ($X = Na,Li,K$ and $X = P$,As,Sb,Bi)\cite{36}. The later work showed that all these compound order antiferromagnetically well above the room temperature. These materials have recently been rediscovered as potential antiferromagnetic semiconductors\cite{31,35,36}. Here, we would like to focus on NaMnAs. Up to now only the crystal structure and magnetic structure by XRD and neutron diffraction, respectively, was reported on pulverised polycrystals\cite{2,6}. It has been shown that it orders antiferromagnetically with magnetic moments aligned along the $z$ axis and propagation vector $k = [000]$. The Néel temperature was estimated between 293 and 643 K; close to zero temperature, the Mn-magnetic moment was determined to be 4.0 $\mu_B$/Mn\cite{37}.

We report on the high quality single crystal growth of NaMnAs, confirm by optical transmission measurements its semiconducting nature and discuss various aspects of magnetic order both from experimental and theoretical point of view.

II. SAMPLE GROWTH AND CHARACTERIZATION

The NaMnAs single crystals were grown similar to Cu$_{1-x}$Mn$_{1+x}$As using the flux method\cite{43}. The single crystals were shiny flat rectangular plates ($2 \times 2 \times 0.1$ mm$^3$), which can be cleaved in the basal plane using a standard sticky tape. This suggests very weak bonds between the layers. A typical sample is shown in Fig. 2. The material is not stable on air. After few minutes it becomes dark so most of the manipulation has to be done under protective atmosphere (see Supplemental Material). It is rather typical for the flux method, that also other phases are grown; in this case MnAs crystals were formed during the synthesis. They form tiny needles which are often attached to the surface of NaMnAs crystals and are difficult to remove. This does not affect any spectroscopic measurements which are performed on impurity-free, cleaved surfaces. They influence however other bulk measurements such as magnetization (as discussed later).

A. Composition and crystal quality

The composition and the crystal structure of selected single crystals have been determined by energy-dispersive x-ray spectroscopy (EDS) and by single-crystal x-ray diffraction (XRD), respectively. EDS was performed using Scanning Electron Microscope (SEM) equipped with an energy dispersive x-ray detector Bruker AXS which utilizes ESPRIT software package (a non-standard method with precision up to 1 %). The as-grown samples were mounted on a SEM stub using carbon tape, freshly cleaved, and quickly installed into the SEM. The surfaces appear very flat and homogeneous with the stoichiometry: $Na_{0.96(0.02)}Mn_{1.07(0.02)}As_{0.97(0.02)}$, reproducible across several growth-batches. High resolution XRD using Rigaku Smartlab 45/200 in parallel beam mode was performed on an as grown single crystal with the (00l) planes parallel to the sample holder. The sample was preserved by kapton tape during the measurement. From the refined XRD peaks positions, a Cohen-Wagner plot provides the lattice parameters: $a = b = 4.213 \pm 0.002$ and $c = 7.0955 \pm 0.0005$ (Å). The higher precision of the $c$-parameter is due to the higher number of measured (00l) diffraction peaks. Also the free $z$-component of the $2c$ atomic position was refined being 0.6675 and 0.2166 for Na and As atoms, respectively. The standard single crystal diffraction collecting the full diffraction pattern was preformed as well, however, the crystals exhibit large degree of mosaicity, preventing proper crystal structure refinement (See Supplemental Material at ).

Fig. 1 shows a symmetric 29/ω scan of the (00l) diffraction peaks. The peak width is limited by the resolution of the diffractometer, and it suggests excellent homogeneity of the crystals. Additionally, scans across the (205) and (206) directions were performed in order to determine the $a$ lattice parameter.
FIG. 1. Symmetric 2θ/ω scan of the (001) NaMnAs single crystals (a), and Qz scan across the (205) and (206) directions, a and (b), respectively. Open circles represent the calculated diffraction intensities, using the crystal structure from Ref. [37]. In the calculation we assumed an ideal kinematically diffracting crystal lattice.

FIG. 2. Optical microscope image of typical NaMnAs single crystal. The sample thickness in the order of 100 µm. The c-axis is pointing perpendicular to the plane while a-axes are parallel with the long edges of the sample.

FIG. 3. Unit cell of NaMnAs with magnetic moment directions refined by Bronger et al. [37].

B. X-ray photoemission spectroscopy

The sample was investigated by x-ray photoemission spectroscopy (XPS) after a fresh cleave under UHV conditions. Sodium, arsenic and manganese shallow core levels (CLs) were probed using monochromatised Al Kα radiation (ℏω = 1486.7 eV), revealing depth-sensitive information about the sample composition and its homogeneity as discussed in the Supplemental Material. In addition, details in the spectral lineshape of Mn CLs allows an insight into the Mn 3d shell configuration. The Mn 2p CL in Fig. 4 shows a complex spectral shape, which can be reproduced using six fitted Voigt profiles (referred to as P1–P6) and a ranged Shirley background. Energy positions, widths, and intensities of the Voigt profiles are summarised in Tab. 1. The double-peak structure (P1 and P2 separated by 1.1 eV in our case) of the 2p3/2 CL is a typical multiplet splitting effect in Mn observed for example in bulk Mn-oxides with Mn^{2+} or Mn^{3+} and even Mn^{4+} states due to strong crystal field effects. [44]
TABLE I. Peak energy positions, FWHM values, and total intensities of Voigt peaks $P_1 - P_6$ in Fig.4. For $P_1 - P_3$ and $P_5 - P_6$ natural linewidths of 0.3 eV and 0.9 eV were assumed, respectively.

|       | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ |
|-------|-------|-------|-------|-------|-------|-------|
| Energy [eV] | 639.33 | 640.38 | 641.70 | 643.46 | 650.73 | 651.42 |
| FWHM [eV] | 0.75 | 1.41 | 0.97 | 4.05 | 1.06 | 1.60 |
| Area [a.u.] | 169 | 260 | 37 | 114 | 65 | 89 |

However, such a double-peak structure has also been observed for single Mn atoms embedded in Bi$_2$Te$_3$, where peaks can be reproduced in a MnX$_6$ (e.g. X = Br) cluster model with Mn in a 2+ state. Splitting effects in the 2p$_{1/2}$ CL (P5 and P6) are similar but broadened due to super-Coster-Kronig decay processes, which limits the information on the Mn chemical state. Finally, the smaller spectral feature P3 located at 1.3 eV higher binding energy (BE) compared to P2 may belong to a $J = 1, 2, 3, 4$ series of bound states between 2p$_{3/2}$ hole and 3d valence electrons.

In the following we will discuss possible charge-transfer (CT) effects, which have been identified e.g. in MnO spectra. Despite the convincingly present feature P4 (we were unable to obtain good fits when P4 is removed), we believe that a CT peak is absent. This feature found in Fig. 5 of Ref. 48 is located at significantly higher energies than P4 in our measurements. On the other hand, shake-up satellite of the 2p$_{1/2}$ CL was reported at lower energies 49. The absence of the CT peak bears witness against ionic character of binding in our samples, consistent with ab initio predictions discussed later. We therefore conclude that the object of our study has grown in the desired composition (without significant amounts of other phases such as MnAs or manganese oxides) and relegate a more detailed analysis of the XPS for later investigations.

C. Ultraviolet photoemission spectroscopy

The same device (as in the case of XPS) with a different photon excitation energy ($h\omega = 21.2$ eV, He I line) was used to obtain UPS data shown in Fig.5 covering BEs in the range [$2$ eV, -0.5 eV] measured in normal emission at a photon energy of 21.2 eV. The reference point $E = 0$ eV corresponds to the Fermi level of the PES analyzer. In semiconductors the position of the Fermi energy ($E_F$) with respect to the valence band maximum (VBM) is sensitive to defect states and possible surface band bending effects. Kraut et al. 50 described procedures to quantify defect induced shifts in $E_F$ and band bending in the semiconductor GaAs by referencing shallow CLs such as $E_{Ga\,3d}$ to the VBM value $E_{VBM}$. Thereby values $E_{VBM}$ are estimated using the leading edge method, which approximates the density of states (DOS) by a tangential line at the maximum steepness of the VB edge.

In our case the tangential line of the dominant intensity suggests a VBM at $E = 0.19$ eV. Looking more closely to the UPS intensity at lower BEs (see inset in Fig.5), it is evident that the intensity stretches all the way to $E = 0$ and then disappears, suggesting a well-defined sample Fermi edge and that the Fermi level is intersecting the upper VB states. Therefore, we conclude that our sample is a p-type semiconductor.

FIG. 4. XPS of the Mn 2p core level. Peaks and the fitting procedure are discussed in the text, the broad peak P4 is the shake-up feature.

FIG. 5. UPS data covering the VBM region measured with a photon energy $h\omega = 21.2$ eV. The position of the VBM at 0.19 eV is estimated by the leading edge method (see text). In the inset the signal intensity around $E = 0$ (analyzer Fermi edge) is shown in detail.
III. MAGNETIZATION MEASUREMENTS

In order to determine the Néel temperature $T_N$ on NaMnAs single crystals, we have performed high temperature magnetization measurements using VSM Oven option (Quantum Design PPMS). A set of about 15 single crystals, with total mass of 16 mg was placed in the sample holder and fixed by copper foil with magnetic field oriented in the basal plane (see Supplemental Material). The temperature dependence of magnetization was measured in the range 300-880 K and magnetic field of 1 T.

![FIG. 6. Susceptibility measurements (temperature dependent magnetisation at $B = 1$ T). The shift of maximum in the inset, upon thermal cycling, is likely an artefact of the signal-enhancement method.](image)

We have observed, that the overall magnetic signal increases and slowly saturates upon repeating the heating cycles (Fig. 6). This is probably due to the fact, that in vacuum and high temperatures conditions, the sample surface becomes Na deficient and larger amount of MnAs phase is grown, increasing the paramagnetic signal. This hypothesis is supported by XRD measurements of as grown and annealed piece of crystal (see Supplemental Material), where new MnAs peaks appeared after annealing the crystal at similar conditions. MnAs in its hexagonal form order ferromagnetically at around 315 K with magnetic-filed dependent temperature hysteresis [51–53].

Magnetization isotherm plots (see Fig. 7) at 400, and 600 K show linear behavior without hysteresis, while the isotherm at 350 K shows a weak paramagnetic contribution and a weak up-turn at high magnetic fields. At lower temperatures (not shown) a hysteresis can be seen connected to the presence of FM impurity of MnAs.

![FIG. 7. Magnetization isotherm of NaMnAs single crystals with magnetic field oriented in basal plane.](image)

Considering the presence of MnAs impurities, the magnetization measurement should be considered as partially qualitative. The value of $T_N$ fits, however, in the expected range between 295 a 643 K reported by Bronger et al. [37].

IV. MAGNETIC ORDER

Results of the previous Section confirm NaMnAs as an antiferromagnetic material. Contrary to the simple case of ferromagnets, this however still allows for many types of magnetic order described by the set of Mn magnetic moments $\{S_{Mn}\vec{m}_i\}$ where we assume $|\vec{m}_i| = 1$ and equal magnitude of all Mn moments $S_{Mn}$. From theoretical point of view, the ground state follows from energy minimisation of

$$E = -\frac{1}{2} \sum_{ij} J_{ij} \vec{m}_i \cdot \vec{m}_j$$

once we neglect higher order terms (as discussed in Appendix). While we relegate a quantitative discussion of the Heisenberg parameters $J_{ij}$ to Sec. VLB, we now qualitatively describe the implications of this form of energy on the ordering of classical magnetic moments $\vec{m}_i$ arranged on lattice shown in Fig. 3. To begin with, let us assume that non-zero $J_{ij}$ occur only for nearest neighbours in the basal plane (intralayer coupling $J_0$) and along the c-axis (interlayer coupling $J_c$). In terms of signs, there are then four options, one leading to ferromagnetic order (when both $J_0$, $J_c$ are positive) and the three remaining options forcing three different types of AFM order. For $J_0 > 0$ and $J_c < 0$, each Mn layer is ferromagnetically ordered and such AFM structure has never been identified across AMnX compounds (where A is an alkali metal and X is As or Sb) as the early neutron scattering measurements by Bronger et al. [37] revealed. The remaining two options with $J_0 < 0$ lead to a checkerboard pattern of moments, interleaved along the $+$ or $-$ out-of-plane direction with propagation vector either $\vec{k} = (000)$ or $(00 \frac{1}{2})$. Bronger et al. also determined...
\( S_{\text{Mn}} = 3.45 \) at room temperature in NaMnAs; it was not clear however, at which temperature the magnetic order collapses (the only piece of information to this end was that at 643 K, magnetic signal in neutron scattering data has already vanished).

While for \( A = \text{Li or K} \) the Mn planes are however further coupled with Heisenberg exchange parameters favoring anti-parallel couplings along the (001) axis, effectively resulting in a twice as big magnetic unit cell, in NaMnAs the manganese layers are only weakly coupled to favor a parallel ordering: in other words, \( J_c > 0 \) should apply this case. Such simplified qualitative consideration can become inappropriate when \( J_{ij} \) in Eq. (1) do not decay fast enough with the distance between sites \( i \) and \( j \) but in case of NaMnAs, as we show in Sec. VI.B, the effective magnetic interactions are rather short-ranged.

We conclude this short Section by several remarks on theoretical studies in this class of materials. Zhou et al. [38] compared the ground state energy within density functional theory (DFT) framework and the energetically most favourable magnetic order is the one shown in Fig. [3]. We confirm this also for DFT+U (as used previously [31] for LiMnAs and KMnAs; see also Sec. VI.A) whereas the energy cost of doubled magnetic unit cell is at the level of few meV per f.u.

V. MEASUREMENTS OF THE OPTICAL GAP

Optical transmission measurements offer a straightforward means to prove the presence of a band gap. The measurements were performed using Woollam RC2 Mueller matrix ellipsometer in the spectral range from 0.7 to 6 eV. The data were corrected for the baseline measurement without the sample in optical path, the resulting transmission data is shown in Fig. 8 on a logarithmic scale, with the raw data in the inset. The higher level of noise above 1.2 eV is due to extremely low transmission data is shown in Fig. 8. The spectral dependence of the optical transmission \( T \). Main plot: The same data replotted as \(-\ln T(E)\); fits in the interval 1.2 - 1.4 eV by direct (red, dashed) or indirect band gap model allow to estimate the band gap.

VI. THEORETICAL MODELLING

A. Electronic structure

Magnetic compounds containing manganese in the nominal \( 3d^5 \) configuration often share a generic electronic structure: while the existence of the gap is optional, the anion-based bands provide a background for the spin-split Mn \( d \)-states one of which is below and the other above Fermi level. Previous ab initio calculations[31, 38] predicted that tetragonal XMnAs antiferromagnetic materials (where \( X \) is an alkali metal) do have a gap and, for example, CuMnAs is a metal with low density of states (DOS) at the Fermi level (\( E_F \)), see Fig. 3 in Ref. [24]. Size of the gap obtained by ab initio methods can be problematic and density functional theory (DFT) calculations are known to often give too small gaps even in simple systems (as opposed to strongly correlated ones) such as GaAs.

We chose local density approximations (LDA) as our starting point for DFT. Apart from an undersized gap, a simple LDA calculation leads to Mn magnetic moments about 10% smaller than what is found experimentally. Regardless of the detailed implementation of DFT+U, magnetic moments become larger when \( U \) increases, as a consequence of the larger separation in energy of the ma-
majority and minority Mn \(d\)-states. Symptoms of such gradual changes can be seen in the density of states (DOS) shown in Fig. 9. A compromise among several factors (magnetic moments, gap size, estimates of Néel temperature discussed in the next subsection) directed us to a value of \(U\) around 5 eV. On the experimental side, realistic magnitude of Mn magnetic moments \cite{37} would suggest somewhat smaller \(U\) but the final judgement should depend on a more direct quantity (such as Mn \(d\)-peak characteristics in UPS). In the following, we use both LDA and LDA+U in the atomic sphere approximation (ASA) as implemented within the spin-polarized relativistic Korringa-Kohn-Rostoker (SPRKKR) electronic structure package \cite{54} and cross-check the results using generalised gradient approximation to DFT in linearised augmented-plane-wave (LAPW) method in another package \cite{55}. The latter yield an out-of-plane magnetic anisotropy around 0.2 meV per formula unit free of any strong dependence on the value of \(U\) with a modest correction due to dipolar interactions. This is somewhat larger than in CuMnAs (see App. A of Ref. \cite{56}).

**B. Heisenberg parameters**

Effective spin Hamiltonians allow to study finite-temperature properties of magnetic systems (such as NaMnAs) at a reasonable computational cost (see also discussion in Appendix). Depending on their complexity, they use various parameters as input where Heisenberg exchange parameters \(J_{ij}\) play the central role. In our work, \(J_{ij}\) are determined using the method of Ref. \cite{57} i.e. starting from the perturbed (by \(\delta V_i\), see Appendix) antiferromagnetic ground state (reflected in the \(T\)-matrices) and evaluating

\[
J_{ij} = \frac{1}{4\pi} \int_{-\infty}^{\infty} dE \text{ Im } \text{Tr} \delta V_i T_{ij}^{\uparrow} \delta V_j T_{ji}^{\downarrow} \tag{2}
\]

Herewith, the complicated quantum-mechanical problem (crystal with many electrons, for example) is mapped to a relatively simple lattice model of classical spins with pair interactions only. In this model, total energy (more precisely, its part --- see Appendix) of the system is approximated by Eq. (1) and using a Monte Carlo simulation, various thermodynamic quantities can be estimated. For example, temperature-dependent sublattice magnetisation can be extrapolated to zero and thus Néel temperature obtained.

In Fig. 10 we show Heisenberg parameters obtained from an LDA+U zero-temperature calculation \((U = 5\text{ eV})\) plotted as a function of the distance between individual Mn atoms. This is a simplified representation of the situation created by an anisotropic crystal: the complete layout of \(J_{ij}\)’s in real space is shown in the Appendix. It should be pointed out that the couplings are clearly dominated by the nearest-neighbour (NN) pairs within one plane of Mn atoms (both inter- and intra-sublattice) and the next-nearest-neighbour \(J_{ij}\) are more than an order of magnitude smaller. The antiferromagnetic inter-sublattice NN coupling (corresponding to \(J_0 < 0\) in terms of the discussion in Sec. IV) is further augmented by ferromagnetic intra-sublattice NN interaction. More distant pairs interact feebly and coupling between different layers is also weak. The NN in a different layer, i.e. shortest inter-layer coupling (corresponding to \(J_c\) and highlighted by an arrow in Fig. 10) belongs to the same magnetic sublattice and \(|J_c/J_0| \sim 10^{-2}\).
Comparing LDA to LDA+U calculations, we find that the coupling between Mn magnetic moments decreases with increasing $U$. However, this seems to be compensated by the enhancement of magnetic moments (see the discussion of Monte Carlo simulations in the next subsection). Zhou et al. noted that calculations are robust with respect to the alternative choice of GGA rather than LSDA exchange-correlation functional, thanks to the over-binding artefact of the latter cancelling out in taking the difference. The reduced dimensionality of the magnetic interactions, mainly confined to the (001) Mn planes, can explain the much smaller ordering temperature revealed by experiments and by Monte Carlo simulation, as opposed to cruder early estimates in terms of total energy difference alone, or mean-field theory calculations.

C. Néel temperature

Several approaches to estimating theoretically the ordering temperature are possible and their short review is given in Appendix. Here, we employ Monte Carlo (MC) calculations as implemented the Uppsala Atomistic Spin Dynamics UppASD code. Their input are the Heisenberg parameters discussed in the previous subsection.

The lower $T_N$ of NaMnAs with respect to CuMnAs can be tentatively understood as a consequence of different effective coordination, or local environment, for the Mn atoms within the two materials. While for manganese pnictide CuMnAs the transition metal (Mn atoms) is arranged in a rumpled geometry (2c positions in the CuSb$_2$-type structure), in NaMnAs the manganese creates flat planes (2a positions of the CuSb$_2$ type structure). In combination with the fairly short-ranged $J_{ij}$’s which present only weak coupling across such planes, the magnetic Hamiltonian becomes effectively 2D.

Temperature-dependent sublattice magnetisation for NaMnAs shown in Fig. 11 suggests that ordering temperature is slightly above 350 K. This agrees well with experimental data in Fig. 6.

VII. CONCLUSIONS

We have prepared the room temperature antiferromagnet NaMnAs for the first time in the single crystalline form. The single crystals have layered tetragonal structure and can be easily cleaved within the basal plane, the single crystals are in general very soft. The magnetization measurement showed the Néel temperature to be 350 K being in agreement with the temperature range defined by previous neutron diffraction experiments on polycrystals. Using Ultraviolet photoemission spectroscopy and optical transmittivity measurements we showed that NaMnAs is a p-type semiconductor with a band gap between 0.9 and 1.16 eV depending on whether the band gap is direct or indirect, respectively. The detail studies of the type of band gap and band structure in general will be subject of our further work. In conclusion NaMnAs has been found to be a new room temperature antiferromagnetic semiconductor, together with the layered structure it can be promising material for fabrication of functional devices. However, further studies of basic physical properties and possibilities to modify its electronic properties e.g. by chemical substitutions of formation of multi layers has to be done prior to looking into application sphere.

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