Physical properties of the tetragonal CuMnAs: a first-principles study

F. Máca and J. Kudrnovský, and V. Drchal
Institute of Physics ASCR, Na Slovance 2, CZ-182 21 Praha 8, Czech Republic

K. Carva, P. Baláž, and I. Turek
Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, CZ-121 16 Praha 2, Czech Republic

(Dated: August 24, 2017)

Electronic, magnetic, and transport properties of the antiferromagnetic (AFM) CuMnAs alloy with tetragonal structure, promising for the AFM spintronics, are studied from first principles using the Vienna ab-initio simulation package. We investigate the site-occupation of sublattices and the lattice parameters of three competing phases. We analyze the factors that determine which of the three conceivable structures will prevail. We then estimate formation energies of possible defects for the experimentally prepared lattice structure. Mn\textsubscript{Cu}- and Cu\textsubscript{Mn}-antisites as well as Mn\leftrightarrow Cu swaps and vacancies on Mn or Cu sublattices were identified as possible candidates for defects in CuMnAs. We find that the interactions of the growing thin film with the substrate and with vacuum as well as the electron correlations are important for the phase stability while the effect of defects is weak. In the next step, using the tight-binding linear muffin-tin orbital method for the experimental structure, we estimate transport properties for systems containing defects with low formation energies. Finally, we determine the exchange interactions and estimate the Néel temperature of the AFM-CuMnAs alloy using the Monte Carlo approach. A good agreement of the calculated resistivity and Néel temperature with experimental data makes possible to draw conclusions concerning the competing phases.

PACS numbers: 75.25.+z, 75.30.Et, 75.47.Np, 75.50.Ee

I. INTRODUCTION

The tetragonal antiferromagnetic (AFM) CuMnAs phase prepared by the molecular-beam epitaxy (MBE) on the GaAs(001) and GaP(001) substrates has attracted recently considerable experimental and theoretical interest in connection with the so-called AFM spintronics.\textsuperscript{1-4} The combined experimental and theoretical study\textsuperscript{2} has lead to a proposal of basic structural parameters that were used in first-principles calculations assuming an ideal structure without defects.\textsuperscript{2} On the other hand, the experiment for this phase provides the basic physical parameters: the residual resistivity around 90 $\mu$\Omega\textperiodcentered cm for $T = 5$ K (Ref. 2), the Néel temperature around 480 K (Ref. 2), and the local Mn moments around 3.6 $\mu_B$ at room temperature (Ref. 2); its value at lower temperature will be higher (see also Sec. III D). The transport studies (the residual resistivity) thus indicate the presence of defects whose origin and concentrations are known only very approximately (sample grown on the GaAs substrate).\textsuperscript{2} Identification of possible defects and their formation energies thus represent a challenge for the theory. The same concerns also an estimate of the residual resistivity and the Néel temperature. The Néel temperature is closely related to corresponding exchange interactions and, in turn, also to the values of local Mn magnetic moments.

Another interesting issue concerns the sample preparation. The CuMnAs in the bulk phase crystallizes in the orthorhombic phase\textsuperscript{5} while the studied tetragonal phase does not exist as a bulk phase in the Nature and can be only prepared as a film by the MBE on a suitable substrate.

The aim of the present study is thus two-fold. First, we will determine theoretically the structure of the tetragonal phase by optimizing the lattice parameters ($a=b$ and $c$ in the present case) and positions of Cu, Mn, and As atoms inside the unit cell. We also investigate the effect of the substrate, defects, and of electron correlations on the phase stability. Moreover, we estimate the formation energies of possible defects. Second, we will calculate relevant physical quantities such as the local Mn-moments, exchange interactions, and the Néel temperature as well as the residual resistivity due to specific defects. These quantities will be determined in the framework of the unified first-principle electronic structure model and compared with the experiment.

II. FORMALISM

The AFM-CuMnAs prepared by the MBE has a tetragonal structure\textsuperscript{5} with the space group P4/nmm (No. 129).\textsuperscript{5} The experimental lattice parameters are $a=b=3.82$ Å and $c=6.318$ Å. The atomic basis contains two formula units (6 atoms). Cu atoms are in the basal plane of the tetragonal lattice, (Wyckoff position 2$a$), there are two parallel layers of As atoms (Wyckoff position 2$c$) and two layers of Mn atoms (Wyckoff position 2$c$) with oppositely oriented moments (see Fig. 1). The interstitial sites are located in the Wyckoff positions 2$b$. The relative positions of atoms (in units of $c$) are $z_{\text{Cu}}=0.0$, $z_{\text{Mn}}=0.25$, $z_{\text{As}}=0.5$.
The lattice structure of the phase I of tetragonal AFM CuMnAs consisting of two nonmagnetic Cu-/As-sublattices (black/grey color), and two Mn-sublattices with the antiparallel spin orientations (indicated by arrows). The possible interstitial positions (Wyckoff positions 2b) are shown by hatched circles. For the phase II the positions of Cu- and Mn-atoms are interchanged.

The exchange interactions depend on the reference magnetic state from which they are extracted. In particular, in the present case we employ two reference states, namely, the AFM state and the disordered local moment (DLM) state. The DLM approach describes the paramagnetic state above the critical temperature with fluctuating Mn-moments and it is thus better suited for the estimate of the critical (Néel) temperature for the transition between the AFM and paramagnetic states as compared to the AFM reference state corresponding to zero temperature. The DLM state is treated as a random equiconcentration binary alloy of moments pointing randomly in opposite directions and can be thus naturally treated using the CPA. In both cases, however, local moments on Cu- and As-atoms are strictly zero. It should be noted that due to the two Mn-sublattices we will have two sets of exchange parameters, intra- and inter-sublattice ones. We remark that the DLM state will be also used in transport studies.

To study the thermodynamic properties of CuMnAs we employed classical Monte Carlo (MC) simulations based on the Metropolis algorithm applied to the constructed Heisenberg Hamiltonian. For simulations we used a three-dimensiona supercell composed of $16 \times 16 \times 16$ elementary CuMnAs cells with periodic boundary conditions. The simulations were carried out assuming zero applied magnetic field and disregarding magnetocrystalline anisotropy. The local Mn magnetic moments, as large as 3.80 $\mu_B$, were assumed to be independent of temperature. We started the simulation from an initial temperature 900 K which decreased by a step $\Delta T = 10$ K. At each temperature $2 \times 10^4$ MC steps were performed. To accumulate the statistics we simultaneously simulated 5 independent identical systems.
III. RESULTS AND DISCUSSION

A. Ground state of the ideal tetragonal AFM-CuMnAs

Assuming the ideal tetragonal AFM-CuMnAs, two natural questions arise: (i) the occupation of atomic positions inside the elementary cell by Cu, Mn, and As atoms, i.e., which phase (I, II or III) corresponds to the ground state; and (ii) optimal lattice parameters for Cu, Mn, and As inside the cell. This structure allows both the FM alignment (like, e.g., in CrMnAs) and the AFM-alignment (like in CuMnAs), but also more complex magnetic structures could exist, if one considers larger unit cells, but here we limit ourselves to the case of six atoms per unit cell observed in the experiment.

Results of extensive calculations in the framework of the VASP and GGA-PBE are summarized in Table I for the optimized phases I and II together with distances between atoms. We have also included results for the experimental geometry.

|       | phase I | phase II |
|-------|---------|---------|
| a [Å] | 3.82    | 3.82    |
| c [Å] | 6.32    | 5.94    |
| V [Å³]| 92.20   | 88.05   |
| z_{Cu}| 0.00    | 0.00    |
| z_{Mn}| 0.670   | 0.682   |
| z_{As}| 0.266   | 0.270   |
| m_{Mn} [μB] | 3.70 | 2.96    |
| ΔE_{tot} [eV] | 0.0 | -0.102  |
| d_{Cu-Cu} [Å] | 2.70 | 3.45    |
| d_{Cu-Mn} [Å] | 2.82 | 2.82    |
| d_{Cu-As} [Å] | 2.55 | 2.55    |
| d_{Mn-As} [Å] | 3.45 | 2.70    |
| d_{As-As} [Å] | 3.82 | 3.82    |

The following conclusions are made: (i) The ground state is the phase II, but with the energy preference with respect to the phase I being only about 0.1 eV per unit cell. The lattice parameter c is about 6% smaller as compared to the grown sample while the lattice parameter a is similar; (ii) In the phase I the result is just opposite: the lattice parameter c is similar to that in the grown sample, but the lattice parameter a is smaller by 3.5%; (iii) Theoretical volumes for phases I and II were smaller as compared to the experimental one thus indicating a possible role played by the substrate; (iv) The energy preference of the phase II as compared to the phase I (by about 0.08 eV per unit cell) is obtained also for the experimental structure; (v) The values of local Mn moments are strongly underestimated in both phases II and III as compared to experiment; and (vi) The total energy of the phase III (with As atoms in the basal plane) was estimated for the experimental lattice parameters, but with optimized atom positions. It was higher than that of the phase I by 2.97 eV. Calculated interatomic distances among atoms (Table I) also indicate a possible experimental test – using the Extended X-ray Absorption Fine Structure (EXAFS) experiment which could distinguish between possible phases, namely, by checking the nearest-neighbor Mn-Mn distances which differ significantly and do not interfere with distances between other atom pairs. Additional arguments in favor of the phase I will be given below based on the transport studies and an estimate of the Néel temperature.

For the phase I at the experimental geometry we have also estimated total energies of the FM and nonmagnetic CuMnAs phases (+0.29 eV and +2.82 eV), respectively. Corresponding total energies are higher as compared to the AFM total energies so that they can be excluded as possible ground state candidates. On the other hand, the energy difference between the AFM and FM states is smaller for the phase II as compared to phase I (+0.069 eV and +0.29 eV, respectively). Such result is compatible with exchange interactions of both phases I and II, namely with dominating AFM interactions for the former and competing FM and AFM interactions for the latter (see Figs. 4b and 4c below).

While the semilocal GGA exchange-correlation potential is generally considered to be an optimal choice for the structure optimization, the GGA+U approach is sometimes used to fine the theoretical description in some systems, tuning of band gaps, magnetic moments, the critical temperatures, etc. (see, e.g., a recent study of the AFM-MnTe). We present here a similar study of the effect of electron correlations on the lattice structure and magnetic moments in the AFM-CuMnAs assuming that the Hubbard parameter U is limited to d-orbitals of Mn atoms, which is an acceptable model for narrow Mn-bands.

### Table I: Total energies per elementary cell of the phase II with respect to the phase I (energy zero) are shown assuming the (frozen) experimental geometry (label 0) as well as the optimized one. Also shown are lattice parameters a, c, the relative z-coordinates of Cu, Mn, As atoms inside the unit cell, its volume V, and the local Mn-moments m_{Mn}.

|       | phase I | phase II |
|-------|---------|---------|
| a [Å] | 3.82    | 3.85    |
| c [Å] | 6.32    | 5.94    |
| V [Å³]| 92.20   | 88.05   |
| z_{Cu}| 0.00    | 0.00    |
| z_{Mn}| 0.670   | 0.682   |
| z_{As}| 0.266   | 0.270   |
| m_{Mn} [μB] | 3.70 | 2.96    |
| ΔE_{tot} [eV] | 0.0 | -0.102  |
| d_{Cu-Cu} [Å] | 2.70 | 3.45    |
| d_{Cu-Mn} [Å] | 2.82 | 2.82    |
| d_{Cu-As} [Å] | 2.55 | 2.55    |
| d_{Mn-As} [Å] | 3.45 | 2.70    |
| d_{As-As} [Å] | 3.82 | 3.82    |

### Table II: Total energy differences (per elementary cell) between the phases I0 and II0, ΔE_{tot} = E_{I0} − E_{II0}, as a function of the on-site Hubbard parameter U.

| U [eV] | 0 | 0.41 | 0.83 | 1.25 |
|--------|---|------|------|------|
| m_{I0}^{Mn} [μB] | 3.70 | 3.80 | 3.90 | 3.99 |
| m_{II0}^{Mn} [μB] | 2.96 | 3.15 | 3.31 | 3.46 |
| ΔE_{tot} [eV] | -0.078 | +0.102 | +0.278 | +0.443 |
Electron correlations stabilize the phase $I_0$ as compared to the phase $I_0'$. Already for $U=0.4$ eV the phase $I_0$ has a lower total energy than the phase $I_0'$. Assuming $U$ around 1 eV, the local Mn-moment (3.9 − 4.0 $\mu_B$) agrees also reasonably well considering the fact that it was measured at room temperature. We have as well tested the effect of lattice relaxations and found only slight qualitative modifications not changing the qualitative picture.

There are two other effects which could influence the calculated phase stability, namely, that samples are grown on the particular substrate and the presence of impurities in the sample. The real samples are grown on the As-terminated GaAs(001)/GaP(001) faces. We have tried to elucidate a possible role of the substrate using a simple model which simulates this case, namely, the system consisting of five layers of GaP simulating the substrate with an extra layer of P atoms (P-rich conditions) which interface with four multilayers of CuMnAs, either in the phase I (the bottom layer is Cu one) or in the phase II structure (the bottom layer is Mn one). Such system separated by a vacuum layer is periodically repeated and studied by the supercell method. We used the VASP-GGA, fixed the substrate layers, but allowed relaxation of extra layer of P atoms, and atoms inside CuMnAs. We also varied spin orientations, the AFM orientation was either between Mn-layers or inside each Mn-layer. In all cases, the AFM orientation between Mn-layers was preferred. Finally, we have also tested models with frozen experimental sample geometry. In all cases we have obtained the preference of the phase I, the energy difference in its favor was quite substantial and varied between 0.8 and 1 eV per elementary cell with 42 atoms.

The present model fulfills the basic requirement for comparison of total energies, namely, the same number of atoms in supercells. The model correctly includes sample/vacuum and sample/substrate interfaces as it is in a real system. On the other hand, it has certain limitations as we do not consider possible switching between the phases I and II during the growth. One should keep in mind that theoretical calculations assume zero temperature and give the global minimum of energy while a real system. On the other hand, it has certain limitations as we do not consider possible switching between the phases I and II during the growth. One should keep in mind that theoretical calculations assume zero temperature and give the global minimum of energy while a real system. On the other hand, it has certain limitations as we do not consider possible switching between the phases I and II during the growth. One should keep in mind that theoretical calculations assume zero temperature and give the global minimum of energy while a real system.

We refer the reader to the end of the next Section as concerns a possible effect of impurities on the phase stability.

## B. Formation energies of defects in AFM-CuMnAs

Structural studies and measurements of residual resistivity (90 $\mu$2cm) indicate that the samples contain defects. An estimate of the formation energies (FE) of defects is a tool that can identify possible candidates. A complete study of all possible defects, similar to that done for a cubic FM-NiMnSb, is beyond the scope of the present paper. Rather, we choose a few possible candidates as in the study for related CuMnSb alloy. We have estimated FE for chosen substitutional defects including vacancies, as well as for Mn-interstitial and listed them in Table III.

TABLE III: The formation energies FE for various substitutional defects in the tetragonal AFM-CuMnAs. Also studied was the Mn-interstitial (Mn$_{\text{int}}$, see Fig. I). The symbol XY denotes the X-defect on the Y-sublattice. Defects are sorted according to their formation energies, the values for unrelaxed atom positions are given in brackets.

| Defect | FE [eV] | Defect | FE [eV] |
|--------|---------|--------|---------|
| Vac$_{\text{Mn}}$ | −0.13 (−0.23) | Mn$_{\text{int}}$ | +1.62 (+2.15) |
| Vac$_{\text{Cu}}$ | −0.13 (−0.10) | As$_{\text{Cu}}$ | +1.73 (+2.66) |
| Mn$_{\text{Cu}}$ | −0.04 (−0.06) | As$_{\text{Mn}}$ | +1.77 (+1.90) |
| Cu$_{\text{Mn}}$ | +0.33 (+0.27) | Mn$_{\text{As}}$ | +2.00 (+1.95) |
| Cu$_{\text{As}}$ | +1.15 (+1.06) | Vac$_{\text{As}}$ | +2.18 (+2.22) |

The supercell VASP method and GGA-PBE was applied to the reference 48-atoms supercell Cu$_{16}$Mn$_{16}$As$_{16}$ and to corresponding supercells containing specific defects. For example, Cu$_{15}$Mn$_{17}$As$_{16}$ supercell simulates the Mn$_{\text{Cu}}$ defect concentration of 6.25%. We have used the experimental lattice parameters. The accurate determination of FE is a challenging task (see, e.g., a recent review). Here we employ the simplest possible approach in which the FE is defined as $E_\text{tot}[\text{def}] - E_\text{tot}[\text{id}] - \sum_i n_i E_i$, where $E_\text{tot}[\text{def}]$ and $E_\text{tot}[\text{id}]$ are total energies of the supercells with (def) and without (id) defects, $n_i$ indicates the number of atoms of type i (i=Cu, Mn, As, vacancy) that have been added to (ni > 0) or removed from (ni < 0) the supercell when the defect is formed, and $E_i$ are total energies of atoms in their most probable bulk phase. Strictly speaking, one should employ instead of $E_i$ corresponding chemical potentials of these species which may depend on the temperature, defect concentration, the presence of other defects, etc. The above choice represents a rough, but acceptable approximation. It was used, e.g., in Refs. 23-25 for cubic semi-Heusler NiMnSb and CuMnSb alloys. We have chosen for $E_i$ the total energies of fcc-Cu, AFM-Mn (L1$_0$ lattice), and rhombohedral As. The choice for Mn is the same as in Ref. 24 although in the OQMD (Open Quantum Materials Database), a more complex structure is used. It should be noted that actual values for the FE may depend on the choice of these energies and on the determination of $E_\text{tot}[\text{def}]$. While the lattice parameters $(a, c)$ were kept fixed in all cases we have optimized atomic positions inside the supercell. We have also tested the model with frozen atomic positions like in the ideal structure, but there were only small quantitative differences. Results are summarized in Table III with the following conclusions: (i) Mn$_{\text{Cu}}$ and Cu$_{\text{Mn}}$ are similarly as in the cubic CuMnSb the most probable candidates for possible defects. In addition, also vacancies on Mn- and Cu-sublattices have small FE. We note that a small FE
for Mn-vacancy$^{24}$ was also found for NiMnSb alloy; (ii) Mn-interstitials have, contrary to CuMnSb or NiMnSb, a much larger FE due to tetragonal vs cubic structure with natural vacancy sites in the latter; (iii) Also Mn$_{\text{As}}$ or As$_{\text{Mn}}$ and related defects have large FE similarly like Mn$_{\text{Sb}}$ and Sb$_{\text{Mn}}$ in NiMnSb or CuMnSb$^{24,25}$, and (iv) Although the FE of Mn$\leftrightarrow$Cu swaps was not explicitly studied, one can roughly estimate it as the sum of FE’s of Mn$_{\text{Cu}}$ and Cu$_{\text{Mn}}$ assuming that they are not correlated.$^{25}$ Consequently, the Mn$\leftrightarrow$Cu swaps are also possible candidates. To resume, we regard the defects with FE in tenths of eV as probable, while those with FE above 1 eV we do not further consider.

Essentially zero (small negative) FE for Mn-Cu swap correlates with the fact that corresponding total energies of phases I and II have very similar energies (see Table I), the phase II has the total energy even slightly lower. Besides the FE’s the formation of defects depends on delicate details of the impurity kinetics which is not considered here. Anyway, defects with low FE’s are more probable candidates than those with larger FE’s even at the non-equilibrium conditions. We will therefore investigate below the influence of these more probable defects on transport properties. It should be noted that defects play less important role on the value of the Néel temperature as compared to the resistivity so that we limit ourselves to defect-free samples when calculating Néel temperature.

We have further studied possible effect of impurities on the phase stability. We have taken two defect types with low and high formation energies (see below), namely Mn$_{\text{Cu}}$ and Mn$_{\text{As}}$ and investigated also the effect of the defect concentrations (supercells simulating the defect concentrations 6.25% and 12.5%, respectively). Neither the defect type nor the higher defect concentration were able to change the energy preference of the phase II.

C. Transport properties of AFM-CuMnAs

We will estimate residual resistivities due to possible defect types found in the previous Section, namely, Mn$_{\text{Cu}}$, Cu$_{\text{Mn}}$, Mn-vacancy, and Mn$\leftrightarrow$Cu swap assuming the defect concentration of 5% in each case.

To this end we employ the linear-response theory as formulated in the TB-LMTO-CPA method$^{18}$ and including disorder-induced vertex-corrections$^{17}$ and neglect possible relativistic effects (spin-orbit interaction) for simplicity.

We will first demonstrate that the present tetragonal AFM-CuMnAs alloy can be described properly by the TB-LMTO method similarly as we did recently$^{15}$ for topological insulator Bi$_2$Te$_3$. Careful tests have lead to the conclusion that we can use a model without empty spheres and assuming the same atomic Wigner-Seitz radii. We present in Figs. 2a and 2b the densities of states (DOS’s) for an ideal tetragonal AFM-CuMnAs as calculated by the VASP and the TB-LMTO methods, respectively, using the VWN exchange-correlation potential in both cases. A very good agreement between both DOS’s is obtained. A similarly good agreement was obtained also for the phase II and for models with empirical Hubbard $U$ (not shown).

Concerning the transport properties, there is an important difference between Mn$_{\text{Cu}}$ defects or Mn$\leftrightarrow$Cu swaps on one side and Cu$_{\text{Mn}}$ defects or Mn vacancies on the other hand. First, the frustration of the Mn$_{\text{Cu}}$ moments is obvious (see Fig. 1). We have therefore considered two limiting models: (i) A collinear moment alignments, both the parallel or antiparallel (P/AP) to the nearest native Mn-sublattices, which have the same total energy, and (ii) the DLM state applied to Mn$_{\text{Cu}}$ moments characterizing an ideal frustrated state. We have found (5% defects) that the total energy for the DLM-Mn$_{\text{Cu}}$ is smaller by negligible 0.17 meV per formula unit. Second, a virtual bound state (VBS) is present at the Fermi energy for Mn$_{\text{Cu}}$ and Mn$\leftrightarrow$Cu swap defects and it is missing for Cu$_{\text{Mn}}$ defects or Mn-vacancies.

The VBS in the DOS for Mn$_{\text{Cu}}$ defect is shown in Fig. 3a and 3b, for the VASP and TB-LMTO methods, respectively. We have assumed the DLM-Mn$_{\text{Cu}}$ model for the TB-LMTO while for the VASP we used again
48-atom supercell with a single Mn-atom on the Cu-site (the concentration 6.25%). It should be noted that a similar VBS was found in the TB-LMTO approach also for the collinear P/AP model and/or for the Mn↔Cu swap model (not shown). The presence of impurity states at the Fermi energy will lead to a stronger scattering due to extra scattering at CuMn defects or Mn-vacancies (no VBS state at the Fermi energy); (iv) The resistivity for Mn↔Cu swaps is slightly larger as compared to that for MnCu defects for the same defect concentrations due to extra scattering at CuMn defects forming the Mn↔Cu swap. The Matthiessen rule is violated, namely, the sum of resistivity for Models B and E is 135 μΩcm while for the Model D it is 124 μΩcm; and (v) The effect of vertex corrections is small.

We have also tested the effect of electron correlations in LDA+U model. As an example we have chosen the Model B and the Hubbard parameter \( U = 2.0 \text{ eV} \). Calculated resistivity components are larger due to the larger scattering on MnCu defects which in turn is due to the increase of the local Mn-moments caused by correlations. For example, for the Model B we have an increase of \( \rho_{xx} \) by about 18 μΩcm, or by 15%. We have also considered the phase II. As an example we have again calculated resistivity for the Model B. The resistivity is smaller \( (\rho_{xx} = 42 \text{ μΩcm} vs 111 \text{ μΩcm} \text{ for the phase I case) due to the smaller effective scattering (smaller local MnCu-moments).} \)

As an example of the effect of temperature on transport properties we have calculated the resistivity in the paramagnetic (DLM) state above the Néel temperature (often called the spin-disorder resistivity, SDR). The experiment indicates a large increase of the planar resistivity from about 90 μΩcm at 5 K to about 160 μΩcm at 300 K. Such a large increase cannot be ascribed only to phonons (e.g., a phonon contribution to the resistivity of about 25 μΩcm exists for bcc-Fe at the Curie temperature \( T = 1050 \text{ K} \)). The largest part of contribution to the resistivity of bcc-Fe should be ascribed to spin-fluctuations. To illustrate the effect
also for CuMnAs, one can compare the Model B (Mn-impurity on Cu with the spin-disorder described by the DLM state) and the Model G describing the paramagnetic state (SDR) in which the spin-disorder exists also on the native Mn-sublattices. The calculated SDR is around 230 $\mu\Omega$cm, which looks reasonably because the temperature of measurement (300 K) is appreciably smaller than the Néel temperature (480 K). The contribution due to spin-fluctuations monotonically increases with temperature up to the Néel temperature and then remains constant so that the calculated SDR seems reasonable.

The resistivity depends on the actual occupation of sublattices which is a challenging problem connected with similar scattering crosssections of atoms forming the alloy. In Ref. 5 for a sample grown on GaAs(001) was suggested that the Cu-lattices are fully occupied by Cu-atoms while 8% of Cu- and 8% of Mn-atoms are found on the As-sublattice leaving about 14% vacancies on the Mn-sublattice. A recent analysis for a sample grown on GaP(001) as in Ref. 2 has indicated the presence of 10% vacancies on both the Cu- and Mn-lattices. It should be emphasized that actual compositions should not be taken literally as they depend on the annealing and can also slightly fluctuate from sample to sample. Calculated longitudinal resistivities for GaAs and GaP grown samples are about 180 $\mu\Omega$cm and 88 $\mu\Omega$cm, respectively, indicating a better agreement with experiments for samples grown on GaP.

D. Exchange interactions and the Néel temperature

The exchange interactions in the ideal (defect-free) phase I for both AFM- and DLM- (paramagnetic) reference states are shown in Figs. 4a and 4b, respectively while the corresponding interactions for the phase II and assuming the DLM-reference state are shown in Fig. 4c. In all cases we show interactions among atoms on the same Mn-sublattice (intrasublattice interactions) as well as among atoms on different Mn-sublattices (intersublattice interactions). All other interactions are zero. The following conclusions can be done: (i) Exchange interactions for the AFM reference state exhibit, as expected, a strong leading AFM intersublattice couplings while the intrasublattice ones are much smaller in their absolute values; (ii) More important are interactions derived from the paramagnetic (DLM) state. The paramagnetic state assumes no specific magnetic order and the character of such interactions is a precursor of the possible AFM ground state (see also Ref. 25). The fact that qualitative character of both intersublattice and intrasublattice interactions is the same as in the AFM reference state can be interpreted as a strong indication of the AFM ground state; and (iii) Because dominating (AFM-like) intersublattice interactions in the paramagnetic state are smaller than those derived from the AFM reference state, one can expect a lower Néel temperature derived from the DLM state. We have also estimated exchange interactions for the paramagnetic state for the phase II which are shown in Fig. 4c. The interactions are very different, in particular the intersublattice ones. Consequently, one can expect very different Néel temperature.

The Néel temperatures were determined using the atomistic spin dynamics (ASD) codes which contain the package for the estimate of critical temperatures using the Monte Carlo simulations. We show in Fig. 5 the sublattice magnetizations and the heat capacity as a function of the temperature. The sublattice magne-
FIG. 5: (Color online) (a) Magnetizations of the Mn-sublattices as a function of temperature assuming exchange interactions derived from the paramagnetic (DLM) state of the tetragonal CuMnAs with the phase I structure. By symmetry, the dependence of both sublattice magnetizations on the temperature is the same. (b) The temperature dependence of the heat capacity from which the Néel temperature can be extracted more accurately (about 480 K).

izations at $T = 0$ K (equal to the local Mn-moments) are reduced with temperature due to spin-fluctuations and disappear at the Néel temperature. An internal test of consistency of calculations is that temperature dependence of both sublattice magnetizations should be identical and they indeed are. The magnetization at the Néel temperature is not zero, but rather smeared out due to the finite size of sampling supercells used in the Monte Carlo calculations. It should be noted, however, that the zero sublattice magnetizations do not mean that also local moments are zero. On the contrary, the local Mn-moments in the AFM- and DLM-states are very similar due to the rigidity of Mn-moments with respect to their rotations. The Néel temperature can be more precisely extracted from the maximum of the heat capacity (see Fig. 5b). The Néel temperature estimated in this way, one can exclude the phase II as a ground state.

IV. CONCLUSIONS

We have performed an extensive ab initio study of electronic, magnetic, and transport properties of the tetragonal AFM-CuMnAs alloy with potential technological applications. The VASP approach was used for the phase stability and the estimate of formation energies of possible defects. In the next step, for the experimental lattice structure, the TB-LMTO-CPA approach was adopted to estimate transport properties and the Néel temperature from calculated exchange interactions by the Monte Carlo method. The main conclusions are: (i) The theoretical optimized structure of the bulk tetragonal AFM-CuMnAs is the phase II, but with smaller volume than the experimental one. The same result was obtained for the experimental lattice parameters and optimized atomic positions inside the unit cell; (ii) We have found that electron correlations stabilize the phase I. (iii) There are indications that the presence of the substrate favors the phase I; (iv) The presence of various defects even at higher concentrations does not change the phase preference; (v) $\text{Mn}_{\text{Cu}}$, $\text{Cu}_{\text{Mn}}$, $\text{Mn} \leftrightarrow \text{Cu}$ swaps, and vacancies on Mn- and Cu-sublattices are defects with low formation energies and thus probable candidates that can explain the finite sample resistivity; (vi) Estimated in-plane resistivity of CuMnAs systems with $\text{Mn}_{\text{Cu}}$ defects and $\text{Mn} \leftrightarrow \text{Cu}$ swaps for concentrations around 3.5-5% explains experimentally observed values while much larger concentrations would be needed for $\text{Cu}_{\text{Mn}}$ defects or Mn-vacancies. The origin of larger resistivity can be ascribed to the existence of the well-pronounced virtual bound state at the Fermi energy for $\text{Mn}_{\text{Cu}}$ defect or $\text{Mn} \leftrightarrow \text{Cu}$ swap; and (vii) Estimated Néel temperature for ideal, defect-free AFM-CuMnAs agrees reasonably well with the experiment keeping in mind that sample contains unspecified amount of defects. On the other hand, the ideal phase II gives a paramagnetic state which contradicts experimental findings.

Acknowledgments

We acknowledge the financial support from the Czech Science Foundation (Grant No. 14-37427G) and the National Grid Infrastructure MetaCentrum (project LM2015042) for access to computation facilities.
We have tested the robustness of the estimation of the Néel temperature with the respect to the size of the three-dimensional supercell. The choice $20 \times 20 \times 20$ gives the Néel temperature $500 \text{ K}$. 

---

"Electronic address: maca@fzu.cz"