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The stability and physical properties of the tetragonal phase of bulk CuMnAs antiferromagnet

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ABSTRACT

The effect of Cu substitution on the stability of the CuMnAs tetragonal phase was studied both experimentally and by *ab initio* calculations. Polycrystalline samples with various compositions $Cu_{1+x}Mn_{1-x}As$ ($x = 0–0.5$) were synthetized. The tetragonal phase of CuMnAs is found to be stabilized by substituting Mn by Cu in the amount of x ~0.1 or higher. This observation is supported by *ab initio* calculations of the total energy of the tetragonal and orthorhombic phases; with increasing Cu content the tetragonal phase is favoured. Small variations of composition thus allow to grow selectively one of these two phases with distinct and unique features for antiferromagnetic spintronics.

Measurements of magnetic susceptibility and differential scanning calorimetry have shown that the tetragonal $Cu_{1+x}Mn_{1-x}As$ has an antiferromagnetic behaviour with the maximum Néel temperature $T_N = 507$ K for the highest Mn content samples, decreasing with the decreasing Mn content.

1. Introduction

The antiferromagnetic semi-metal CuMnAs, which exists in both tetragonal and orthorhombic structure, have been attracting recent attention of experimental and theoretical physicists in the fields of antiferromagnetic spintronic and physics of Dirac fermions [1–3]. A controlled rotation of magnetic moments' orientation by means of an applied electrical field has been demonstrated in tetragonal CuMnAs [4]. This reorientation is achieved by the creation of staggered fields due to the spin-orbit torques in antiferromagnets of specific symmetry [5]. Such effect allows for creation of a unique memory device and paves the way for antiferromagnetic spintronics [6–8]. On the other hand, the orthorhombic CuMnAs has been proposed to be the first candidate for a Dirac semimetal with magnetic order [3]. It is thus desirable to describe the conditions that lead to the formation of the orthorhombic and tetragonal phases.

The crystal structure of the compounds from the ternary Cu-Mn-As system is sensitive to the composition. Three different structures have been reported for this system:

(i) The stoichiometric or almost stoichiometric compound crystallizes in an orthorhombic structure with space group *Pnma* (Fig. 1 b) and with lattice parameters $a = 0.6586$ nm, $b = 0.3867$ nm, $c = 0.7320$ nm [8–10].
(ii) slightly As rich (7%) and/or Cu rich (3%) and Mn deficient samples form a tetragonal structure with space group *P4/nmm* (Fig. 1 a) and with lattice parameters $a = 0.3800(4)$ nm, $c = 0.6328(10)$ nm [11]. Similar lattice parameters $a = 0.3820(10)$ nm, $c = 0.6318(10)$ nm were reported for CuMnAs thin films grown on GaAs (001) substrate [12,13]. Recent studies [14] suggest that the tetragonal thin films grown on GaAs (001) substrate are also Mn deficient.
(iii) when going further to the Mn-rich side of the ternary diagram, namely $Cu_2Mn_4As_3$ (= $Cu_{0.67}Mn_{1.33}As$) and $CuMn_3As_2$ (= $Cu_{0.50}Mn_{1.5}As$) an orthorhombic II structure (Fig. 1c) with doubled unit cell along the a axis compared to stoichiometric orthorhombic CuMnAs is formed [15,16].

Both the orthorhombic and tetragonal phases are reported to be room temperature antiferromagnets [8,9,13,17]. The Néel temperature T_N of the orthorhombic CuMnAs ranges between 330 and 360 K [8,10], a more complex modulated magnetic structure was recently reported in off-stoichiometric orthorhombic $Cu_{0.98}Mn_{0.96}As$ single crystals [10]. The magnetic structure of the tetragonal

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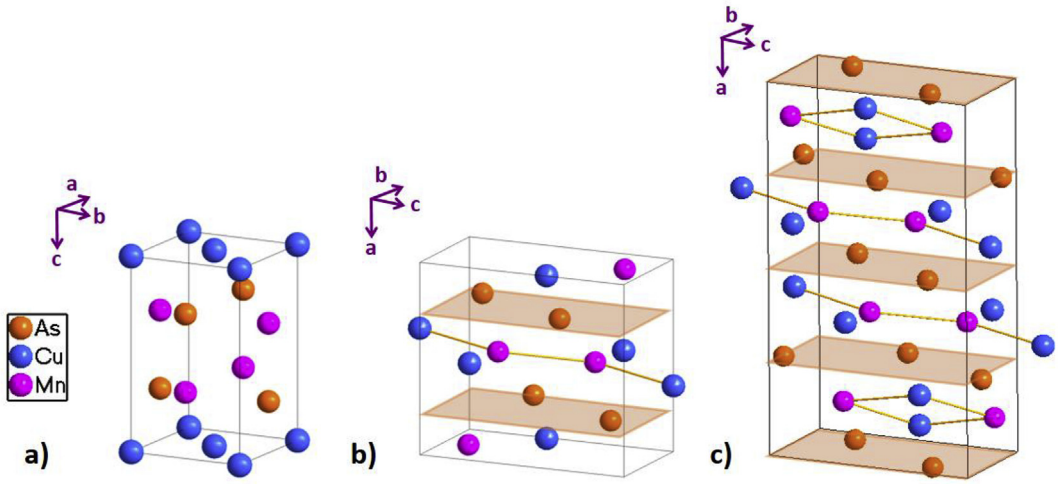

Fig. 1. The tetragonal (a), orthorhombic (b) and orthorhombic II (c) structure of $Cu_{1+x}Mn_{1-x}As$ compounds. The shaded planes are a guide to the eye, highlighting similarities between orthorhombic cells.

phase has only been studied in epitaxial thin films, the Néel temperature reaches (480 ± 5) K [17,18] and is therefore significantly higher than in the orthorhombic phase. *Ab initio* calculations have been used to examine both the orthorhombic [8] and the tetragonal phases [13,19]. The Neel temperature obtained by atomistic spin dynamics from the calculated exchange interactions corresponds very well to the experiment in the latter case [19].

In this paper, we aim to describe the synthesis of bulk tetragonal CuMnAs prepared by solid-state reaction as well as the stability of the tetragonal phase for various Mn:Cu ratios from both experimental and a density functional theory perspective. The Néel temperature dependence of the Mn concentration was studied.

2. Experimental and computational details

The polycrystalline samples were prepared by a reaction of high purity Cu, Mn and As. Small pieces of the elements with desired molar ratios and total weigh of 3–4 g were placed in high purity alumina crucibles and sealed under 0.2 bar of Ar atmosphere in fused quartz ampoules. Each sample was then slowly (0.1 °C/min) heated up to 1090 °C where it was kept for 24 h, then it was cooled to 980 °C and held for 7 days to improve homogeneity. These temperatures are above the melting points of MnAs (935 °C) and CuMnAs (950 °C [9]). After the synthesis, only very small amounts of a white film was found at the walls of the ampoules suggest that negligible amount of As sublimated from the sample. The synthesis resulted in shiny polycrystals with relatively large grains of the material.

The composition analysis was performed using scanning electron microscope (SEM) Tescan Mira LMH equipped with an energy dispersive x-ray detector (EDX) based on a non-standard method with precision up to 1–2%. The crystal structure was determined both by powder and single-crystal x-ray diffraction (XRD). Powder XRD data were collected on Bruker D8 Advance diffractometer in standard Bragg-Brentano geometry. Lattice parameters were determined by the LeBail method using Fullprof [20]. The single crystal data were collected at room temperature using a four-circle diffractometer Gemini (Agilent) with kappa geometry, equipped with a Mo sealed X-Rays tube with graphite collimator and with a CCD Atlas detector. Data reduction was made using CrysAlisPro software. The structure resolution and the refinement were done using Jana 2006 software [21].

Polycrystalline samples were subject to differential scanning calorimetry DSC using Setaram Setsys calorimeter in the temperature range 300–600 K and magnetization measurements in temperature the range 300–600 K using a Quantum Design Physical Property Measurement System with the VSM Oven option. Higher temperatures were not used to minimize a risk of As sublimation and subsequent contamination of the equipment.

Calculations were based on the density functional theory employing the Green function tight-binding linear muffintin orbital method [22] and the atomic–sphere approximation (TB-LMTO-ASA) [23]. Moreover, the local spin-density approximation, the Vosko-Wilk-Nursair exchange potential [24], and the *s, p, d* basis are used. We have included relativistic corrections by means of adding the on-site spin-orbit coupling term to the scalar-relativistic TB-LMTO Hamiltonian. Small concentrations of dopants in some of the samples render the coherent potential approximation (CPA) [25,26] to be highly efficient here. The atomic basis contains two formula units (6 atoms) in the case of tetragonal structure and four formula units in the orthorhombic cases. More details on the construction of elementary cell can be found in Ref. 19. For the orthorhombic phase we consider the energetically most favourable magnetic ordering according to the previous study (↑↑↓↓) [3].

3. Results and discussion

3.1. Crystal structure

Samples with compositions $Cu_{1+x}Mn_{1-x}As_{1+y}$ with a small variation of As starting composition (to compensate sublimation) were prepared. The prepared materials were brittle with relatively large grains (submillimetre size). From each polycrystal we isolated a smaller piece for powder XRD and single crystal grains for single crystal XRD. Prior to the XRD measurements the pieces were analysed by SEM EDX. Depending on the composition, the samples had orthorhombic or tetragonal structure. The typical XRD of the tetragonal phases are shown in Fig. 2.

The crystals structure, lattice parameters obtained by PXRD, composition determined by the EDX analysis and starting growth compositions are summarized in Table 1. For completeness of the $Cu_{1+x}Mn_{1-x}As$ system, we also include data from literature. In Fig. 3, the relevant compounds of the Cu-Mn-As ternary system including crystal structure are presented in a ternary diagram; the sample