Defects and magnetic structure of CuMnSb

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Abstract.
Total energy calculations show that the antiferromagnetic (111) order is not the ground state for the ideal CuMnSb in contrast to the results of neutron diffraction experiments. The magnetic phases of the CuMnSb Heusler alloy were investigated with the aim to clarify the role of defects which exist in real samples (Mn-antisites on Cu, Mn-interstitials, and Cu-Mn swaps). The full-potential supercell approach and the Heisenberg model were used to find the magnetic structure of the CuMnSb with defects. Results of both types of calculations indicate that already low defect concentrations can promote the (111) antiferromagnetic structure.

1. Introduction and formalism

The antiferromagnetic (AFM) Mn-based Heusler alloy, CuMnSb, has attracted the theoretical interest in the past, in particular as concerns its magnetic structure [1]. The situation can be quite complex as indicated in the theoretical study of (Cu,Ni)MnSb random alloys [2], where we found that the AFM100 phase has a lower total energy than the observed AFM111 phase. Real CuMnSb samples show large residual resistivities [1] indicating the presence of defects and neutron diffraction experiments confirm the existence of low defect concentrations (≈ 2%) [3]. We therefore investigate the influence of defects on the magnetic structure of CuMnSb.

We consider the most probable defects, namely, Mn antisites on the Cu-sublattice, Mn\textsubscript{Cu}, Mn atoms at interstitial sites for the non-stoichiometric case, and the Cu\leftrightarrow Mn swaps for the stoichiometric CuMnSb. Two independent approaches are used to study the magnetic structure: (i) the supercell approach employing the full-potential Vienna ab-initio simulation package (VASP) [4], and (ii) the Heisenberg model whose parameters are determined by the tight-binding linear muffin-tin orbital (TB-LMTO) method in which the effect of randomness is included using the coherent potential approximation (CPA) [5]. We include electron correlations in narrow Mn d-bands using the LDA+U approach (the effective Hubbard \( U = 0.13 \) Ry), use the experimental lattice constant \( a = 6.088 \) Å, and neglect small volume changes due to defects. It should be noted that both approaches agree reasonably for model with one single defect in the supercell. Predictions of both models can differ in more complex cases e.g. for two defects in the unit cell where the mutual defects interaction depends on their relative positions inside the supercell.

The exchange interactions among Mn magnetic moments which enter the definition of the Heisenberg model are constructed using the first-principles Lichtenstein mapping procedure adapted to random alloys in the framework of the TB-LMTO-CPA method [6]. The exchange integrals are determined from the reference disordered local moment state (DLM, the paramagnetic state) [7] so that no specific magnetic configuration is used in their construction.
2. Results

We have considered three possible AFM magnetic structures for CuMnSb Heusler alloy with and without defects: the AFM111, AFM100, and AFM40 ones: the first two consist of alternating [111]/[100] planes of Mn atoms with opposite spins while the AFM40 is a tetragonal structure [8] with alternating double layers of opposite spins along the [210]-direction. The supercell approach gives as the lowest total energy for ideal CuMnSb the AF40 structure. In Heisenberg model the magnetic part of total energy is estimated from the classical Heisenberg Hamiltonian [6] with exchange integrals $J_{ij}$ between Mn moments at sites $i$ and $j$. When searching for its magnetic ground state we assume that magnetic moments have fixed size, but variable directions.

![Figure 1](image1.png)

**Figure 1.** The total energy differences $E[111]_{ap} - E[40]$ between the reference AFM111$_{ap}$ state and the AFM40 phase as a function of concentrations for the following defects: Mn antisites on Cu-sublattice, Mn interstitials, and Cu$\rightarrow$Mn swaps as obtained from the VASP (a) and Heisenberg model (b) calculations. Index ap denotes the AFM phase with the antiparallel alignment of defect Mn-moments to the moments on the native Mn-sublattice.

![Figure 2](image2.png)

**Figure 2.** Exchange interactions between Mn-moments on the native Mn-sublattice (a) and between Mn moments on Mn- and Cu-sublattices (b) as a function of the distance $d$ between them (in the units of the lattice constant) for CuMnSb with varying concentrations of Mn$_{Cu}$ antisites.

Results for total energy differences based on the supercell calculations are shown in Fig. 1a with following conclusions: (i) The most favorable defect stabilizing AFM111 phase is the Mn-antisite on Cu lattice. The Mn$\uparrow$ substituting Cu prefers the Mn nearest neighbors (NN) with magnetic moments $\uparrow\downarrow\downarrow$, its magnetic moment (lower than magnetic moments of atoms on the Mn-sublattice) is oriented in our naming convention antiparallel. The critical concentration for which the AFM111 is stabilized is less than 3%. (ii) Mn interstitials also stabilize the AFM111
phase although their effect is not so strong, the AFM111 phase is stabilized above about 6%.
(iii) We have verified that lattice relaxations have a small effect on the magnetic structure and
that Cu-antisites on Mn-lattice are not favorable for the stabilization of the AFM111 phase
while electron correlations promote it.

Results based on the Heisenberg Hamiltonian are shown in Fig. 1b. We see a good agreement
with the supercell results although the calculated critical concentrations are larger. A possible
relevance of local environment effects on the magnetic stability can be illustrated on Cu\rightarrow Mn
swaps in both models: while the Heisenberg model predicts the stabilization of the AFM111
by swaps the supercell approach does not. The explanation consists in very different ways of
modeling of swaps in both approaches: in the supercell approach we assume NN Cu\rightarrow Mn swaps
in the whole crystal, in the Heisenberg model based on the CPA we have completely uncorrelated
Cu and Mn antisites (the CPA is a more realistic model in this case).

Exchange integrals allow us to understand the driving mechanism behind the AFM111
stabilization. We show corresponding integrals derived from the DLM state in Figs. 2a,b for
the case of Mn_{Cu} antisites with conclusions: (i) The calculated negative (AFM-like) first NN
interactions and the positive (FM-like) second NN interaction for the ideal case (x=0, Fig. 1a)
contradicts the formation of the AFM111-phase [9] in the framework of the two NN model
(J_{Mn,Mn}^{\text{Mn}} \text{ should be negative}); and (ii) The leading intersublattice interactions (Fig. 2b) are much
larger than those on the native lattice (the reduction of NN Mn-Mn distance) and becomes
strongly AFM-like with increasing antisite concentration x. This is also true for the J_{Mn,Mn}^{\text{Mn}}
interaction although less pronounced. The interactions, whose weight increases with increasing
defect concentration x, are responsible for the crossover to AFM111 phase although weakening
of the positive J_{Mn,Mn}^{\text{Mn}} with increasing concentration x also supports the crossover.

3. Conclusions
The controversy between the experimentally observed AFM111 ground state of the CuMnSb
alloy and the total energy calculations which predict different ground state for the ideal alloy is
resolved by assuming presence of defects confirmed experimentally in real samples. The main
conclusions are: (i) The magnetic ground state of ideal CuMnSb crystal is not the AFM111
phase; (ii) The experimentally observed AFM111 phase is the ground state of CuMnSb samples
with low concentrations of Mn defects which occupy the nearest neighbor sites of the native
Mn sublattice, namely, Mn-antisites on Cu lattice, and Mn-interstitials; (iii) The crossover to
the AFM111 phase is due to the very strong AFM intersublattice interactions among the NN
Mn-moments with distances shorter than those on the native Mn lattice.

Acknowledgments
We acknowledge the financial support from the Czech Science Foundation (project 14-37427G)
and from the National Grid Infrastructure MetaCentrum (programme CESNET LM2015042).

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