Magnetism of quaternary Heusler alloys: $(Cu,Ni)_2MnSn$ as a case study

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Introduction

Heusler alloys are materials with interesting physical properties and significant potential technological applications (magnetic shape memory, magnetocaloric effects, and spintronics). Structurally, most Heusler alloys crystallize in two different cubic phases, having either $L2_1$ or C_{1b} symmetry. An important feature of Heusler alloys is the presence of chemical or substitutional disorder. Examples are the chemical disorder due to non-stoichiometry or a native chemical disorder which exists even in 'ideal' ordered alloys. The complex quaternary alloys like the semi-Heusler (Ni,Cu)MnSb alloys are another example. Here we present results of our *first-principles* density-functional studies of magnetic, thermodynamical, and transport properties of full quaternary $(Cu,Ni)_2MnSn$ Heusler alloys . Our resistivity calculation includes the effect of both chemical disorder between Cu and Ni atoms and the spin-disorder due to finite temperature effects.

Method

The electronic structure calculations were carried out using the TB-LMTO method in which the effect of disorder is included via the coherent potential approximation [1]. We use the exchange-correlation potential given by Vosko, Wilk, Nusair and employ the experimental lattice constants. The exchange interactions among Mn atoms, influenced by the disorder among Cu and Ni atoms, are obtained via the mapping of the total (band) energy onto a Heisenberg spin-Hamiltonian form suggested by Liechtenstein [2]. Calculated exchange integrals are used to estimate the spin-stiffness and the Curie temperature T_c using both mean field and random phase approximations (MFA and RPA). The residual resistivity is determined by the linear-response theory as formulated in the framework of the TB-LMTO-CPA approach using the Kubo-Greenwood formula [3]. The spin disorder [4] is described in the framework of the disordered local moment (DLM) picture [5] and treated formally as 'substitutional' disorder via CPA [1].

Results

There is an overall good agreement between calculated and measured average moments, which are essentially concentration-independent and have values around 4 μ_B. The contribution from Mn-atom dominates, with the Ni-moments being smaller than 0.2 μ_B and other moments being negligible (not shown).

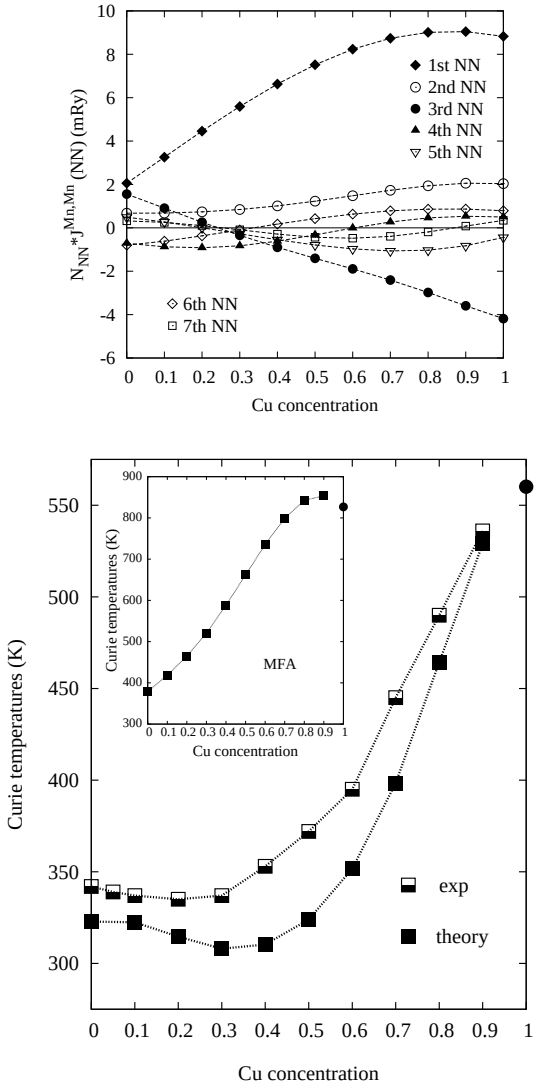

Figure 1: *Top: The first 7 exchange interactions (multiplied by their degeneracies) as a function of Cu- concentration. Bottom: Calculated (RPA) and experimental Curie temperatures as a function of Cu-concentration. The MFA results are shown in the inset.*

Exchange integrals, derived form the DLM reference state and multiplied by degeneracy factors, are shown in Fig. 1 (top panel). The resulting concentration dependence is quite complex, with the first three exchange integrals being dominant. While the first two are ferromagnetic and increase with the Cu-content, the third one decreases almost linearly with Cu-concentration, and changes its sign at about 20% of Cu, giving a hockey-stick like shape to the non-monotonic variation of the Curie temperature with concentration (see Fig. 1, bottom frame). T_cs calculated in the framework of the RPA are in good agreement with the measured values.

We find that the MFA overestimates T_c and fails to reproduce correctly (even in a qualitative sense) the variation of T_c with concentration.

We also estimate the spin-stiffness constant $D_{\rm stiff}$ for Ni_2MnSn from exchange constants using the ferromagnetic reference state (see [7] for details). The calculated and experimental values of $D_{\rm stiff}$ for Ni_2MnSn alloy are 160 $\pm$25 and 150 $\pm$10 meV.Å^2, respectively.

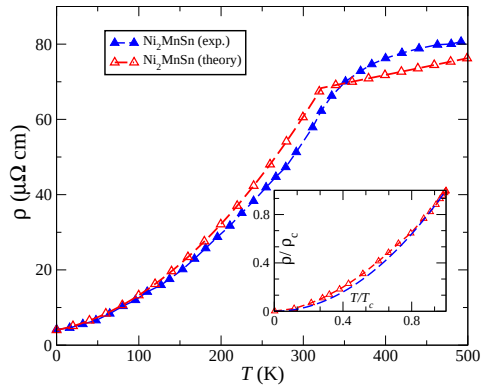

Figure 2: *(Color online) Calculated and experimental T-dependent resistivities of Ni_2MnSn. Validity of a simple model for the effect of spin-disorder on resistivity (see text) is illustrated in the inset.*

In Fig. 2 we display theoretically calculated resistivity of Ni_2MnSn as a function of temperature assuming the form [8] $\rho(T) = \rho_0 + A\,T + B\,T^2$. The quadratic term is due to the spin disorder [4], the linear one is the phonon contribution (which is valid with the exception of very low temperatures), and ρ_0 is the value of the residual resistivity at T=0 K, which is due to all the defects present in the sample. While constants ρ_0 and A are taken from the experiment, constant B is calculated from the expression $B = \rho_c/(T_c)^2$. Here ρ_c denotes the resistivity evaluated at the Curie temperature T_c. We identify ρ_c with the resistivity in the paramagnetic (DLM) state and T_c as calculated above. This approximation is valid if the spin-spin correlation function is small at T_c, a reasonable assumption for a number of transition metals and their alloys, including the Heusler alloys. We demonstrate the validity of this simple model in the inset of Fig. 2, a plot of the reduced resistivity ρ/ρ_c vs reduced temperature T/T_c. The assumed quadratic dependence (dashed line) is supported very well by the experiment for the extracted spin-disorder part (symbols). We obtain very good quantitative agreement between the measured and calculated temperature-dependent resistivity. The theoretical estimate B= 4.7$\times10^{-4}\mu\Omega$ cm K^{-2} compares reasonably well with the experiment (3.94$\times10^{-4}\mu\Omega$ cm K^{-2}). We refer the reader to our recent paper [9] for further details and for results involving other related systems.

Conclusions

We have studied magnetic, thermodynamic, and transport properties of quaternary Heusler alloys $(Ni,Cu)_2MnSn$ by means of the first-principles density functional method. In agreement with experiments, magnetic moments per formula unit depend only weakly on the alloy composition, having values around 4 μ_B.

Exchange interactions were determined using the DLM reference state, which assumes no *a priori* magnetic ordering in the system. The alloy disorder strongly influences values of exchange integrals, resulting in different behaviors of Ni-rich and Cu-rich alloys, which can be ascribed to the 3rd NN exchange integrals. The Curie temperatures, estimated by using the RPA applied to the non-random Mn-sublattice, agree reasonably well with available experimental data.

The residual resistivities are found to obey the weak-scattering Nordheim rule (not shown). This is due to the fact that the strong disorder found in $(Ni,Cu)_2MnSn$ alloys influences the states far from the Fermi energy, which are not relevant for electronic transport. Using a simple model for the spin-disorder, we have estimated the temperature-dependent resistivity at temperatures above T_c. Reasonably good agreement with experimental results is found for calculations which assume that the resistivity above T_c is essentially captured by the DLM model. Using this value of resistivity and calculated Curie temperatures, good agreement with the experiment was obtained also for the temperature-dependence of the resistivity below T_c.

J.K. and V.D. acknowledge financial support from AV0Z 10100520 and the Czech Science Foundation (202/09/0775 and 204/11/1228).

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