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Magnetism in Mixed *Heusler* Alloys $(Ni_{1-x}Cu_x)_2MnSn$

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Quarternary *Heusler* alloys of composition $(Ni_{1-x}Cu_x)_2MnSn$ were prepared with $x = 0$—1. They were all single phased with $L2_1$ structure. Alloys were investigated by magnetic measurements. For Mn, the only atom carrying a moment in this kind of *Heusler* alloys, the usual value ($\sim 4\,\mu_B$) was found and a corresponding μ_{eff} in the paramagnetic region. A shallow minimum of the *Curie* temperatures can be explained on the basis of d_i-d_l interaction.

(Keywords: Ferromagnetic properties; Heusler alloys; Magnetism; Paramagnetic properties)

Magnetismus von quarternären Heusler-Legierungen $(Ni_{1-x}Cu_x)_2MnSn$

Quarternäre *Heusler*-Legierungen der Zusammensetzung $(Ni_{1-x}Cu_x)_2MnSn$ wurden über den Konzentrationsbereich $x = 0$—1 hergestellt. Alle waren einphasig und zeigten $L2_1$-Struktur. Magnetische Messungen wurden sowohl im ferromagnetischen als auch im paramagnetischen Bereich durchgeführt. Sie ergaben für Mn, das einzige Atom das in dieser Art von *Heusler*-Legierungen ein Moment zeigt, den üblichen Wert von ca. $4\,\mu_B$ und ein ihm entsprechendes μ_{eff} im paramagnetischen Bereich. Ein flaches Minimum der *Curie*temperatur kann mit Hilfe von d_i—d_l-Wechselwirkung erklärt werden.

Introduction

Heusler alloys are intermetallic compounds with composition X_2YZ and $L2_1$ structure. Although from this general formula a great number of different *Heusler* alloys is imaginable our special interest is due to alloys with $Y = Mn$. From numerous investigations it is well known that Mn carries a localized moment of approximately $4\,\mu_B$ whereas in the case of X atoms only Co displays a small moment[1]. The Mn atoms are far apart ($\sim 4{,}2$ Å) therefore an indirect exchange interaction only

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can be held responsible for ferromagnetism. To isolate the different influence of the electronic state investigations of quarternary *Heusler* alloys seem to be fruitful. There are many reliable data on ternary *Heusler* alloys and a few on quarternary phases known from recent investigations. There are little investigations about *Heusler* alloys with Cu however especially in the paramagnetic region. Systematic research yielding a solid experimental basis is more promising for an understanding of ferromagnetism in *Heusler* alloys than the refinement of models which fail in their basic predictions. This proceeding was proposed already by *Price* et al.[2] and just recently by *Dubiel* et al.[3].

The aim of this paper is to provide experimental data for new theoretical models on the one side and to use these experimental results to check models known from literature as to their usefulness. Special attention is given to a comparatively new model[4,5] based on indirect d_i–d_l interaction. In spite of data from *MacDonald* and *Stager*[6] it was worthwhile to look at this system again. There are several reasons for this undertaking: The authors had difficulties to prepare the copper rich samples single phased. They were not successful in preparing Cu_2MnSn either. They present no data of measurements in the paramagnetic region.

Experimental

Sample Preparation

Samples of composition $(Ni_{1-x}Cu_x)_2MnSn$ ($x = 0$; 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 0.95; 1.0) were prepared using 99.9% metal powders. After weighing in they were mixed, pressed to pills and sealed in evacuated quartz tubes. Since the melting point of Sn is much lower than the ones of the other components Sn was brought in reaction with them by slowly heating the samples (6 h 200 °C; 12 h 230 °C; 12 h 300 °C). Afterwards the samples were sintered at the following temperatures (Cu_2MnSn 645°, $Ni_{0.1}Cu_{1.9}MnSn$ 660°, $Ni_{0.2}Cu_{1.8}MnSn$ 690°, $Ni_{0.4}Cu_{1.6}MnSn$ 720°). All the samples with higher Ni content were sintered at 800 °C. According to the sintering temperature the heating time was 3 d—1 week. From these temperatures the ingots were quenched in ice water and to make quenching faster ampoules were broken under water. Specimen prepared that way were analysed using X-ray methods. If they were single phased, samples were powdered, mixed and sealed in quartz ampoules a second time. The sintering temperature and quenching procedure was the same as before.

Structural Analysis

All specimens were identified and characterized by *Debye-Scherrer* powder photographs using vanadium filtered CrKα radiation. They were single phased with a highly ordered $L2_1$ structure. There were no traces of any impurity phases to be detected.

Magnetic Measurements

Magnetization as well as susceptibility measurements employed a *Faraday* pendulum magnetometer*. The temperature range available was 80–1 200 K at fields up to 12.3 kOe. Measurements were performed under a high purity helium/argon atmosphere.

The apparatus was calibrated with Ni[7] for magnetization measurements and with $CuSO_4 \cdot 5\,H_2O$ ($\chi_g^{293} = 6.00 \cdot 10^{-6}$ emu g^{-1}) for susceptibility measurements.

Spontaneous magnetization σ_{OT} was obtained by an extrapolation of the magnetization at different fields, σ_{HT}, against H. σ_{00}, the spontaneous magnetization at $T = 0$ was obtained by using a $T^{3/2}$ law. The smoothness of the shape of the magnetization curve was given special attention to make sure that only one ferromagnetic phase was present. The sudden decrease of magnetization on heating yielded the *Curie* temperatures (copper rich alloys). In the case of the nickel rich alloys *Kouvel* plots were used for the determination of Θ_F. In the paramagnetic region the influence of ferromagnetic impurities on resulting susceptibilities was eliminated by using the *Honda-Owen* method.

Results and Discussion

The Ternary Heusler Alloys

Results for the ternary *Heusler* alloys Cu_2MnSn and Ni_2MnSn are presented together with values from literature in Tab. 1 and 2. The results compare very well. An investigation on Cu_2MnSn (Ref.[8]) yielded the *Curie* temperature (~ 630 K) by using an extrapolation.

The Quarternary Heusler Alloys

The results of the magnetic measurements are compiled in Tab. 3 and 4 and shown in Figs. 1 and 2. Since it is well known from many contributions that Mn in this system of *Heusler* alloys carries a moment of $4\,\mu_B$ the results could be compared with calculated values. As displayed in Fig. 3 there is a slight decrease in magnetization because of an increasing mass per formula unit whereas μ_{00} stays constant ($4\,\mu_B$).

An interesting very flat minimum in Θ_F values can be seen at $Ni_{1.6}Cu_{0.4}MnSn$ which was detected by *MacDonald* and *Stager*[6] as well. Beginning with $Ni_{0.6}Cu_{1.4}MnSn$ a determination of Θ_F by the use of *Kouvel* plots became impossible because of phase transitions similar to those in Cu_2MnSn. Therefore Θ_F was determined from the steep decrease of magnetization. In the cases of Cu_2MnSn and $Cu_{1.9}Ni_{0.1}MnSn$ even this procedure failed because of phase transitions at lower temperatures than Θ_F. A careful description of this behaviour is given

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Table 1. *Lattice parameter* a (Å), *quenching temperature* (°C) *and ferromagnetic moment* μ_{00} (μ_B) *of* Cu_2MnSn

a (Å)	Quenching t. (°C)	μ_{00} (μ_B)	Lit. data
6.1608	640	4.14	[12]
6.16	>500	—	[13]
6.173	625	4.11	[14]
6.18	630	3.41	[15]
6.14	640	—	[16]
6.176	600	—	[17]
6.170	660	4.11	[18]
6.166	645	4.00	this work

Table 2. *Lattice parameter* a (Å), *Curie temperature* Θ_F (K), *paramagnetic Curie temperature* Θ_P (K), *ferromagnetic moment* μ_{00} (μ_B) *and paramagnetic moment* μ_{eff} (μ_B) *of* Ni_2MnSn

a (Å)	Θ_F (K)	Θ_P (K)	μ_{00} (μ_B)	μ_{eff} (μ_B)	Lit. data
6.048	410	—	—	—	[19]
6.057	—	—	—	—	[20]
6.052	344	—	4.05	—	[21]
6.032	342	—	3.69	—	[22]
6.034	—	—	—	—	[23]
6.050	358	—	3.8	—	[24]
6.062	345	359	4.04	5.05	[25]
6.053	345	—	4.07	—	[6]
6.05	340	—	3.25	4.55	[26]
6.052	342	363	3.98	4.90	this work

for Cu_2MnSn[8]. In[6] a relative strong decrease of μ_{00} in the alloys $Ni_{0.4}Cu_{1.6}MnSn$ and $Ni_{0.2}Cu_{1.8}MnSn$ is reported which must be seen in connection with the presence of a second phase which is less magnetic and results from quenching at too low temperatures. An additional comparison is done with the results in[6], which agree very well with the data of this work. Contrary to them it was possible to prepare the copper rich phases too. Furthermore the paramagnetic region could be investigated in case of alloys with a lower copper content. Again a comparison with the moments which can be expected theoretically was good. Θ_P values show the same dependence as Θ_F (Fig. 2). There is a strict linear dependence of lattice parameters and composition as is shown by a linear interpolation between the lattice parameters of the ternary *Heusler* alloys.

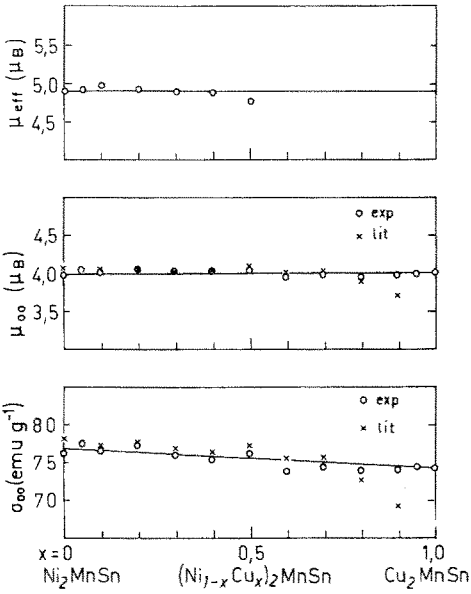

Fig. 1. Paramagnetic moment μ_{eff} (μ_B), ferromagnetic moment μ_{00} (μ_B), spontaneous magnetization σ_{00} (emu g^{-1}) of the system $(Ni_{1-x}Cu_x)_2MnSn$. Literature data (lit) are from *MacDonald* and *Stager*[6]. Straight lines represent calculated values

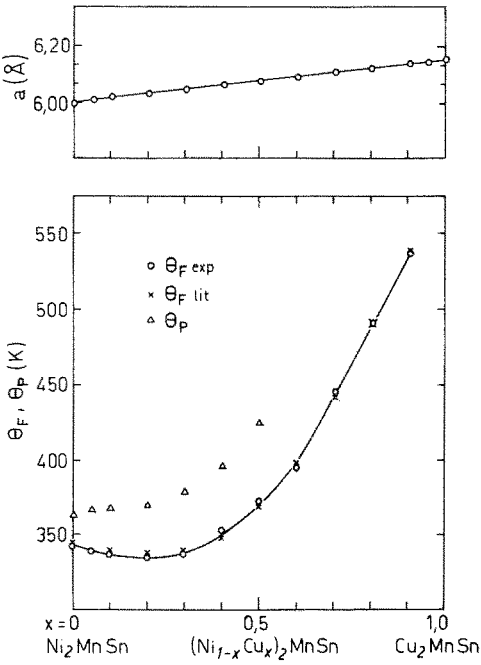

Fig. 2. Lattice parameter a (Å), *Curie* temperature Θ_F (K) and paramagnetic *Curie* temperature Θ_P (K) of the system $(Ni_{1-x}Cu_x)_2MnSn$. The straight line connects the lattice parameters of the ternary alloys. Literature data (lit) are from *MacDonald* and *Stager*[6]

Table 3. *Spontaneous magnetization* $\sigma_{00\ exp}$ (emu g^{-1}), *ferromagnetic saturation moment* μ_{00} (μ_B) *and Curie temperature* Θ_F (K) *of the system* $(Ni_{1-x}Cu_x)_2MnSn$. *Literature data* (lit) *are from MacDonald and Stager*[6]. $\sigma_{00\ lit}$ *and* $\mu_{00\ lit}$ *were calculated from their data. The calculated values* (calc) *are explained in the text*

Alloy	$\sigma_{00\ exp}$ (emu g^{-1})	$\sigma_{00\ calc}$ (emu g^{-1})	$\sigma_{00\ lit}$ (emu g^{-1})	$\mu_{00\ exp}$ (μ_B)	$\mu_{00\ calc}$ (μ_B)	$\mu_{00\ lit}$ (μ_B)	$\Theta_{F\ exp}$ (K)	$\Theta_{F\ lit}$ (K)
Ni_2MnSn	76.3	76.7	78.1	3.98	4.00	4.07	342	345
$Ni_{1.9}Cu_{0.1}MnSn$	77.6	76.6	—	4.05	4.00	—	339	—
$Ni_{1.8}Cu_{0.2}MnSn$	76.5	76.5	77.2	4.00	4.00	4.04	337	340
$Ni_{1.6}Cu_{0.4}MnSn$	77.3	76.2	77.6	4.06	4.00	4.07	335	339
$Ni_{1.4}Cu_{0.6}MnSn$	75.8	76.0	76.7	4.04	4.00	4.04	337	340
$Ni_{1.2}Cu_{0.8}MnSn$	75.4	75.7	76.5	4.04	4.00	4.04	353	348
$Ni_{1.0}Cu_{1.0}MnSn$	76.2	75.5	77.4	4.04	4.00	4.10	372	369
$Ni_{0.8}Cu_{1.2}MnSn$	73.9	75.3	75.6	3.93	4.00	4.02	395	398
$Ni_{0.6}Cu_{1.4}MnSn$	74.6	75.0	75.8	3.98	4.00	4.04	445[a]	442[c]
$Ni_{0.4}Cu_{1.6}MnSn$	73.9	74.8	72.9	3.95	4.00	3.90	490[a]	491
$Ni_{0.2}Cu_{1.8}MnSn$	73.9	74.5	69.3	3.97	4.00	3.72	536[a]	538[c]
$Ni_{0.1}Cu_{1.9}MnSn$	74.3	74.4	—	3.99	4.00	—	[b]	—
Cu_2MnSn	74.3	74.3	—	4.00	4.00	—	[b]	—

[a] Sample shows decomposition while keeping on this temperature.
[b] Θ_F indeterminable (sample decomposes).
[c] Data shows evidence of two phases.

Measurements in the paramagnetic region presented for the first time could be done by using small specimens, guaranteeing a quick temperature equilibrium and thus quick measurement. Even so the results, beginning with $Ni_{1.0}Cu_{1.0}MnSn$ cannot be relied on completely. These values (μ_{eff}, Θ_P) are therefore put into brackets. In the region where a measurement was possible however the result prooves that only Mn carries a moment ($4.9\,\mu_B$).

Table 4. *Paramagnetic moment* $\mu_{eff\,exp}$ (μ_B), *paramagnetic Curie temperature* Θ_P (K) *and lattice parameter of the system* $(Ni_{1-x}Cu_x)_2MnSn$. *Literature data* (lit) *are from MacDonald and Stager*[6]. *Calculated values* (calc) *are explained in the text*

lloy	$\mu_{eff\,exp}$ (μ_B)	$\mu_{eff\,calc}$ (μ_B)	Θ_P (K)	a_{exp} (Å)	a_{lit} (Å)	a_{calc} (Å)
i_2MnSn	4.90	4.90	363	6.052	6.053	6.052
$i_{1.9}Cu_{0.1}MnSn$	4.93	4.90	367	6.058	—	6.059
$i_{1.8}Cu_{0.2}MnSn$	4.98	4.90	368	6.063	6.063	6.065
$i_{1.6}Cu_{0.4}MnSn$	4.93	4.90	370	6.075	6.076	6.075
$i_{1.4}Cu_{0.6}MnSn$	4.91	4.90	379	6.086	6.087	6.085
$i_{1.2}Cu_{0.8}MnSn$	4.88	4.90	397	6.100	6.100	6.100
$i_{1.0}Cu_{1.0}MnSn$	(4.78)	4.90	(425)	6.109	6.105	6.107
$i_{0.8}Cu_{1.2}MnSn$	—	4.90	—	6.120	6.118	6.122
$i_{0.6}Cu_{1.4}MnSn$	—	4.90	—	6.132	6.132	6.133
$i_{0.4}Cu_{1.6}MnSn$	—	4.90	—	6.143	6.145	6.142
$i_{0.2}Cu_{1.8}MnSn$	—	4.90	—	6.155	6.153	6.157
$i_{0.1}Cu_{1.9}MnSn$	—	4.90	—	6.160	—	6.158
u_2MnSn	—	4.90	—	1.166	6.164[a]	6.166

[a] Extrapolation of the data.

According to the theory of *Stearns*[4,5] the decisive interaction responsible for the occurrence of ferromagnetism is a d_i-d_l interaction. The moment is localized on the Mn atoms. These moments are oriented via d electrons from Cu and Ni. An additional s-d interaction which must be considered according to this theory is not strong enough to explain the large difference in *Curie* temperatures of Cu_2MnSn and Ni_2MnSn (there is a small difference of electrons with s character only and the s-d interaction should stay about the same). As a matter of fact the *Curie* temperature of Cu_2MnSn (630 K) is much higher than the one of Ni_2MnSn (345 K) and this higher again than in the case of Pd_2MnSn (189 K) in spite of the same number of conduction electrons for Pd and Ni.

There is a strong increase in the localized character of d electrons from Ni to Cu however. Therefore the more pronounced itinerant character of Mn can be balanced with Cu easier than with Co or Ni and thus leads to higher *Curie* temperatures. In[6] the minimum in the *Curie* temperatures in the system $(Ni_{1-x}Cu_x)_2MnSn$ is explained as the superposition of two different mechanisms. There should be a s-d interaction which should become stronger with increasing Cu content

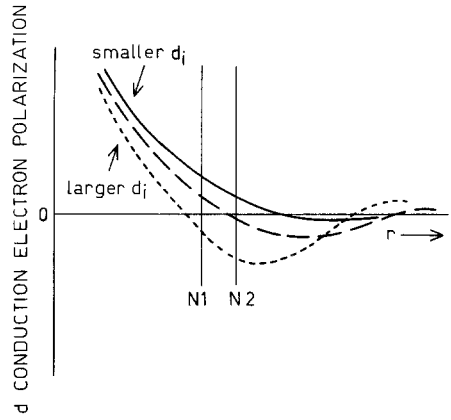

Fig. 3. d conduction electron polarization in the range of the nearest neighbors (N 1 and N 2) depending on the number of d_i electrons

and a direct interaction which should decrease with increasing lattice parameter. From spin wave measurements[9] we learn that the s-d interaction predicts the wrong sign for the first and second nearest neighbor exchange. Additionally *Ishikawa* et al.[10] and *Ishikawa* and *Noda*[11] pointed out that the most important influence comes from the interaction of the nearest (1 NN and 2 NN) neighboring Mn atoms, which depends strongly on the X atoms, the number of conduction electrons and the Z atoms are of minor importance. These facts can be seen in the *Curie* temperatures. Taking into consideration the facts above the explanation of *MacDonald* and *Stager*[6] seems uncertain because of two reasons. Firstly the change in the number of conduction electrons is too small to explain the strong increase in *Curie* temperatures. Secondly the interaction in the region of the 1 NN and 2 NN should dominate in the case of Cu_2MnSn as well. The development of a minimum in such a way cannot be understood easily. Much more plausible seems the following explanation.

Because of the increase in localized d character of the X atoms by increasing Cu content there are much higher *Curie* temperatures. The curve of the d_I-d_I interaction shown in Fig. 3 gives the connection between increasing interaction and increasing number of localized d electrons. Because of larger distances between the interacting atoms there is no immediate ascent however. At the beginning the distances between nearest neighbors are increasing faster than the d_I-d_I interaction, this is due to the growth of the number of localized d electrons. The competition between both mechanisms namely the decrease of the d_I-d_I interaction with larger lattice parameters (enlargement of the lattice by Cu) and the strong increase of the same interaction with higher Cu content (more d_I character) manifests itself in a flat minimum. Starting with Ni_2MnSn the decisive influence comes firstly from the lattice enlargement until at a distinct Cu content this effect is overcome by the number of localized d electrons which dominates finally. There are s-d interactions and superexchange superimposed too. They should stay the same however throughout the whole composition range because of the similar number of s electrons and the same Z atoms (Sn).

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