CROATICA CHEMICA ACTA CCACAA 57 (4) 669—672 (1984)

YU ISSN 0011—1643
CCA-1481 UDC 546.56
Original Scientific Paper

The Crystal Structure and Magnetic Properties of the $Cu_2MnAl_{1-x}Hg_x$ System*

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Received November 26, 1983

Among a great number of newly synthesized alloys containing mercury, the system $Cu_2MnAl_{1-x}Hg_x$ was studied by X-Ray diffraction, neutron diffraction and magnetic susceptibility technicques. The aim of the study was to determine the degree of order with respect to the possible transition between the B2 and $L2_1$--Types and its effect upon the magnetic properties. It was found that the Curie temperature strongly depends upon the Hg concentration. All compounds with $x > 0.4$ are ferromagnetics. Neutron diffraction powder patterns taken on aged samples indicate that they became disordered *i. e.* B2-Type.

INTRODUCTION

Over a period of many years a number of intermetallic phases containing mercury have been studied, in this laboratory. Among them special attention has been given to those which may form so called Heusler alloys.[1,2]

The Heusler alloys form an interesting group of compounds for crystallographic and magnetic investigations, because the magnetic order is strongly dependent upon the state of chemical order. The original Heusler alloys are ferromagnetic and based on the composition Cu_2MnX, where X is a B- sub--group metal such as aluminium, tin or indium. When ordered by suitable heat treatment, their structure, as first shown by Bradley and Rodgers,[3] corresponds to the »Strukturbericht type« $L2_1$. The Cu atoms are in the A(000), and C($\frac{111}{222}$) sites, the Mn atoms are on the B($\frac{111}{444}$) sites, and the Al atoms are on the D($\frac{333}{444}$) sites.

The generalized structure, as described, is composed of four interpenetrating f. c. c. sublattices giving rise to nonzero Bragg reflections only when Miller indices of the scattering planes are either all even, or all odd.

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

Today, the name »Heusler alloys« means a ternary intermetallic compounds of varying composition X_2YZ with the structure $L2_1$-Type structure and also those of the composition XYZ with the $C1_b$-Type structure.

Typical elements occupying X sites are Cu, Co, Ni, Rh, or Pd, while the Z site elements are In, Sn, Sb, Al or Ga. The Y sites are usually occupied by Mn but some alloys may contain V, Ti, Zr or Hf at that position.[4]

The majority of Heusler alloys are ferromagnetics with quite high values of Curie temperature.[5]

Magnetization and neutron diffraction studies of X_2MnZ compounds indicate that the magnetic moment per Mn atom is $4\mu_B$. In the case of Co_2MnZ alloys, the magnetic moment is localized on both Mn and Co atoms.

In view of the large separation of the Mn ions (~ 4 Å) the ferromagnetic coupling between their spins is thought to arise from an indirect interactions rather than by direct d—d overlap. A survey of the magnetic properties of Heusler alloys has been reported elsewhere.[5]

In this paper we report the results of X-ray diffraction and magnetometric measurements performed on polycrystalline samples of $Cu_2MnAl_{1-x}Hg_x$ for $0 < x < 1.0$. The aim of this study is to determine their crystal structure and magnetic properties.

EXPERIMENTAL

All samples were prepared from extrapure elements by reacting the appropriate mixtures in evacuated quartz vials at 800 °C over a period of at least 1 hour. The single phase nature of all alloys was checked by X-Ray analysis on Philips PW 1100 and DRON-3 diffractometers, using CuKαNi filtered radiation. A neutron diffraction test for ordering was also performed.

All data were refined by a least squares method and the results are shown in Table I.

TABLE I

Structural and Magnetic Parameters of $Cu_2MnAl_{1-x}Hg_x$

x	a (Å)	T_c (K)	O_p (K)	μ_{eff} (μ_B)	μ_n (μ_B)
0	5.950(3)	587(1)	586(5)	4.6(1)	3.45(5)
0.2	5.955	512	462	4.0	3.40
0.4	5.960	457	454	3.9	3.36
0.6	6.030		51	3.9	
0.8	6.267		20	4.0	
1.0	6.267		15	4.3	

RESULTS AND DISCUSSION

Substituting Hg for Al atoms leads to an increase in the lattice constanta. This results is attributed to the fact that Hg atoms are larger than Al atoms.

In the second step the chemical ordering was determined. For an ordered Heusler alloy, Cu_2MnX, the structure factors become:

$$F_{111} = 4\,[f_{Mn} - f_X]$$

$$F_{200} = 4\,[2f_{Cu} - (f_{Mn} + f_X)]$$

$$F_{220} = 4\,[2f_{Cu} - f_{Mn} + f_X]$$

For compounds with $x > 0$, only peaks with even Miller indices are observed in the X-ray diffractogram. This suggests that the alloys have a $B2$ (CsCl type) structure.

In the particular case of Cu_2MnHg, an additional measurement of neutron diffraction was performed at room temperature ($\lambda = 1.28$ Å). In the neutron diffraction pattern the (111) reflection does not appear. This suggests that the crystal structure of Cu_2MnHg is of the $B2$ type (disorder between Mn and Hg sites). These results are confirmed by the calculation (Table II).

TABLE II

The Calculated and Measured Intensities of Nuclear Peaks for Cu_2MnHg

hkl	Intensity		
	observed	calculated for $L2_1$ and $B2$	
111	0	82.6	0
200	13.1	7.0	7.0
220	100.0	100.0	100.0

Magnetometric measurements were carried out in the temperature range 80 to 600 K using an electronic balance with a maximum field of 10 kOe. The temperature dependence of the magnetization and reciprocal magnetic susceptibility are shown in Figure 1. For samples with $0 < x < 0.45$ spontaneous magnetization is observed at low temperatures. The values of the Curie temperature decrease with increasing x.

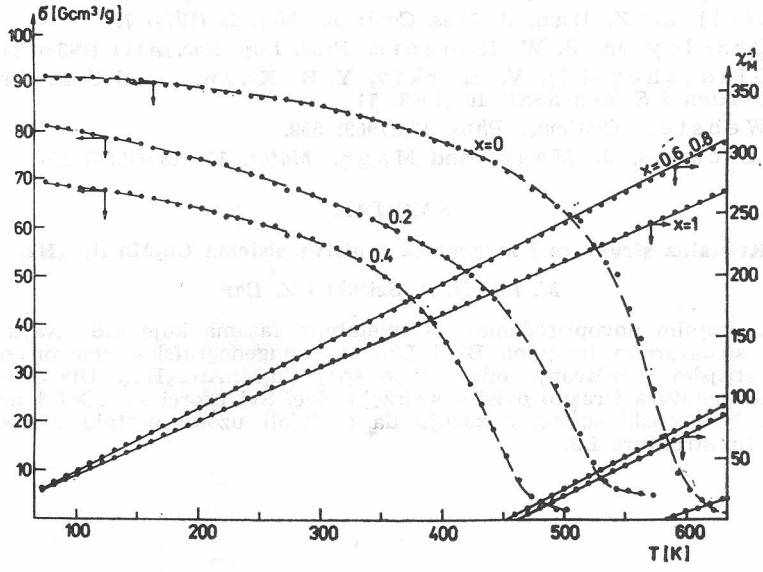

Figure 1. The temperature dependence of the magnetization and reciprocal magnetic susceptibility of $Cu_2MnAl_{1-x}Hg_x$ in the range of 80 to 600 K.

For samples with $0.6 < x < 1.0$ the reciprocal susceptibility obeys the Curie-Weiss law in the temperature range 80—600 K.

The Curie temperatures, the asymptotic Curie-Weiss temperatures Θ_p, as well as the magnetic moments in the saturation and paramagnetic states were also established from these measurements. The results are listed in Table I and presented graphically in Figure 1.

The values of Curie and Curie-Weiss temperatures decrease with increasing z. The positive values of Θ_p suggest that a ferromagnetic interaction becomes dominant. From the magnetic measurements it follows that:

— the Curie temperature strongly depends upon the Hg concentration,
— the compounds with $x < 0.4$ are ferromagnetic with high Curie temperatures, the latter decrease with increasing x,
— the remaining compounds are paramagnetic within the investigated temperature range.

Increasing Hg concentration leads to an increase in the lattice constant due to the difference in atomic radii (1.50 Å for Hg *v. s.* 1.43 Å for Al). This causes an increase of the distance between Mn atoms carrying the magnetic moment. This is consistent with the strong dependence of T_c upon the Mn—Mn distance and confirms the hypothesis of Stearns[6] concerning the nature of the magnetic moment with increasing Hg-concentration which results in a change in the electronic structure. The cause is that Hg and Al differ with respect to electronic configuration /... $5d^{10}\,6s^2$ and ... $3s^2\,3p^1$/. So, the substitution of one for the other results in a drastic change in the electronic structure of the whole compound.

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SAŽETAK

Kristalna struktura i magnetska svojstva sistema $Cu_2MnAl_{1-x}Hg_x$

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Među brojnim novopriređenim intermetalnim fazama koje sadržavaju živu, a pripadaju strukturnim tipovima B2 i $L2_1$, za rendgenografsko, neutronografsko i magnetometrijsko istraživanje odabran je spoj $Cu_2MnAl_{1-x}Hg_x$. Utvrđeno je da Curieva temperatura izrazito ovisi o sadržaju žive. Svi uzorci sa $x > 0.4$ jesu feromagnetici. Neutronski snimci pokazuju da odstajali uzorci postaju nesređeni, tj. prelaze u tip strukture B2.