Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 61 (2013) 2236–2243

Acta MATERIALIA

www.elsevier.com/locate/actamat

Unexpected crystal and magnetic structures in $MnCu_4In$ and $MnCu_4Sn$

A. Provino [a,b,c], D. Paudyal [a,*], M.L. Fornasini [b], I. Dhiman [d], S.K. Dhar [d], A. Das [e], Y. Mudryk [a], P. Manfrinetti [a,b,c], V.K. Pecharsky [a,f]

[a] The Ames Laboratory, US Department of Energy, Iowa State University, Ames, IA 50011-3020, USA
[b] Department of Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy
[c] CNR-SPIN, Corso Perrone 24, 16152 Genoa, Italy
[d] Department of Condensed Matter Physics and Material Science, TIFR, Homi Bhabha Road, Mumbai 400 005, India
[e] Solid State Physics Division, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India
[f] Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011-2300, USA

Received 4 September 2012; received in revised form 26 December 2012; accepted 30 December 2012
Available online 29 January 2013

Abstract

We discovered a new compound $MnCu_4In$ with its own hexagonal structure type ($hP12$-$P6_3mc$, ternary ordered derivative of the hexagonal $MgZn_2$-type) that becomes ferromagnetic at $T_C = 540$ K. This transition temperature is higher than that found in the $MnCu_2In$ and $MnCu_2Sn$ alloys. In contrast, the homologous compound $MnCu_4Sn$, which crystallizes in the cubic $MgCu_4Sn$-type, orders antiferromagnetically with $T_N = 110$ K. The neutron diffraction studies show ferromagnetic spin orientation in the {1 0 1} plane in $MnCu_4In$ with a magnetic moment of 4.5 μ_B/Mn at 22 K, and a corresponding value of 4.7 μ_B/Mn in the antiferromagnetic $MnCu_4Sn$ with propagation vector $\vec{K} = \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$. The first-principles electronic structure calculations show that the unexpected difference in both magnetic and crystal structures of $MnCu_4In$ and $MnCu_4Sn$ is due to the difference in the Mn-*3d* bands and exchange interactions relating to different crystal anisotropy, coordination numbers, and interatomic distances.

Keywords: Copper alloys; Crystallography; Ferromagnetic shape memory alloy; Heusler alloys; Magnetic properties

1. Introduction

Ferromagnetic compounds with a high ferromagnetic to paramagnetic transition temperature (Curie temperature, T_C) are important materials due to their technological importance. The discovery of Heusler alloys many years ago led to a prolonged, intensive work because of their near or above room temperature T_C.

The half Heusler alloys with the 1:1:1 (molar) stoichiometry XYZ adopt a cubic ($C1_b$) structure. The full Heusler alloys with the XY_2Z stoichiometry generally adopt a different cubic ($L2_1$) structure [1,2]. Here X is an element of groups 3–7 or a heavy lanthanide metal; Y is an element of groups 8–12; and Z is a p-block element of groups 13–17. It has also been established that the properties of these intermetallic compounds can be easily modified by substituting one element for another. The strong interest in these compounds persists due to potential of finding new materials with various high temperature applications.

The Mn-based Heusler alloys in particular have attracted strong attention and have been the subject of substantial experimental and theoretical [3] efforts over the last decade because of their potential applications in ferromagnetic shape-memory [4–6] and recording-media alloys [7,8] and in spintronics devices [9–11]. The first generation of spintronics materials was based on ferromagnetic metallic alloys while the second generation employs semiconductor materials, thanks to the half-metallic properties they exhibit [12,13].

In the search for new magnetic materials with a high transition temperature, the Mn–Cu–In system is promising

* Corresponding author. Tel.: +1 515 294 2041.
E-mail address: durga@ameslab.gov (D. Paudyal).

1359-6454/$36.00
http://dx.doi.org/10.1016/j.actamat.2012.12.043

as it already contains the ferromagnetic Heusler phase $MnCu_2In$ [6,14], which crystallizes with the $MnCu_2Al$ type (a ternary ordered variant of the BiF_3 structure). Besides $MnCu_2In$, the other known phases that have been identified in the Mn–Cu–In systems are: MnCuIn, with an $MgZn_2$ structure-type, $Mn_xCu_3In_{2-x}$ ($x = 1,\ 0.5$), with an $MgCu_2$ structure [15,16], and $MnCu_4In$, with a structure proposed as an $MgZn_2$ ternary derivative but without any detailed studies of stoichiometry or crystallographic ordering (see Ref. [17] and references therein).

The aim of this work is to study the crystal structure and magnetic properties of $MnCu_4In$ together with that of the already known phase $MnCu_4Sn$, crystallizing in the cubic $MgCu_4Sn$-type ($cF24$, $F\bar{4}3m$; ternary ordered derivative of the $AuBe_5$-type) [18]. Moreover, to understand the magnetic behavior of these two compounds, first-principles calculations have been performed and the results are compared with those obtained for the $MnCu_2Al$-type $MnCu_2In(Sn)$ phases. Manganese Heusler alloys, such as $MnCu_2In$ and $MnCu_2Sn$, also adopt the $L2_1$-type cubic structure and order ferromagnetically at ~500 K [6,14].

We report the formation of stoichiometric compound $MnCu_4In$, crystallizing in its own prototype. Surprisingly, we discovered that $MnCu_4In$ orders ferromagnetically at $T_C = 540$ K, which is higher than the magnetic ordering temperatures of cubic $MnCu_2In$ and $MnCu_2Sn$, despite Mn–Mn distances being shorter in the two Heusler compounds which also have higher molar concentration of the magnetic constituent Mn. On the other hand, $MnCu_4Sn$ orders antiferromagnetically at $T_N = 110$ K.

2. Experiment

Samples were prepared using commercially available high-purity metals (99.99 wt.% Mn; 99.999 wt.% for Cu, In, Sn). To avoid any weight losses due to possible volatilization of manganese during reaction and melting because of the high vapor pressure of this metal, the alloys were prepared in sealed crucibles. The weighed amounts of the metals (small pieces for Cu, In and Sn and of surface-cleaned Mn chips; total mass of about 5 g) were loaded together into outgassed tantalum crucibles, which were sealed by arc welding under a pure Ar flow. Samples were then melted by heating the crucibles in a high-frequency induction furnace up to about 1500 K, shaken to ensure homogenization and remelted twice. The crucibles were then sealed under vacuum in quartz tubes and the samples annealed at 870 K in a resistance furnace. The as-received alloys were brittle and stable in air, and had a metallic yellow-gold luster. Metallographic examination was performed by both optical and scanning electron microscopy; the semi-quantitative analysis of the phases was performed by electron microprobe analysis.

Differential thermal analysis (DTA) was performed on specimens of the alloys, prepared as above (about 0.8 g) and closed by arc welding into Mo crucibles, which were transferred to the DTA equipment and subjected to heating and cooling cycles at the rates of 5 or 10 K min^{-1} (the temperature measurements being accurate to within ±5 K). The detected liquidus temperature was 963 and 958 K for $MnCu_4In$ and $MnCu_4Sn$, respectively. Small bulk specimens (50–150 mg), with one side flattened, were used for differential scanning calorimetry (DSC).

Several crystals were isolated from a $MnCu_4In$ alloy annealed 21 days at 870 K and their symmetry checked by the Laue method. The data collection was then made for a single crystal mounted on a Bruker-Nonius MACH3 diffractometer, using graphite monochromated Mo Kα radiation. The lattice parameters were determined from X-ray Guinier powder patterns (using monochromated Cu Kα radiation and Si as an internal standard).

High-temperature X-ray powder diffraction data were collected using the Rigaku TTRAX rotating anode diffractometer (Mo Kα radiation) equipped with a high-temperature attachment. Several powder diffraction patterns were collected on heating the $MnCu_4In$ sample from room temperature (300 K) to the highest measured temperature of 823 K, above the peak observed in the DSC measurements. The sample was held at each desired measurement temperature for 10 min before the start of data collection. Partial surface oxidation was visually observed after the sample was taken out from the equipment, which agrees with the appearance of a few broad Bragg peaks on the patterns collected, despite continuous pumping of the sample chamber.

Neutron diffraction patterns were recorded on a multi-position-sensitive detector-based powder diffractometer ($\lambda = 1.249$ Å) at Dhruva reactor, Bhabha Atomic Research Centre, Mumbai, at selected temperatures between 22 and 300 K. The powdered samples were packed in a cylindrical Vanadium container and attached to the cold finger of a closed-cycle helium refrigerator. Rietveld refinement of the diffraction patterns were performed using the FULLPROF program [19].

Magnetization was measured using SQUID and VSM magnetometers. The heat capacity was recorded on PPMS (Quantum Design).

3. Results and discussion

3.1. Crystal structure of $MnCu_4In$

The structure of $MnCu_4In$ was solved with SIR97 [20] in the space group $P6_3mc$ and refined with SHELXL-97 [21] (wR2 = 0.045; R1 = 0.021). Table 1 gives the atomic coordinates and equivalent isotropic displacement parameters.[1] The structure of $MnCu_4In$ can be described as ternary ordered derivative of the $MgZn_2$ Laves phase, but with a lower symmetry space group, which allows an ordered

[1] Further details of the crystal structure investigations (crystal data, refinement details and bond distances) are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 424277.