Tuning magnetostructural phase transition in CoMn$_{0.88}$Cu$_{0.12}$Ge by application of hydrostatic pressure

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Structural and magnetic properties of the CoMn$_{0.88}$Cu$_{0.12}$Ge compound have been investigated using X-ray diffraction (XRD) and differential scanning calorimetry (DSC) accompanied with investigation of magnetic properties under applied hydrostatic pressure up to 12 kbar. It has been found that the orthorhombic crystal structure of the TiNiSi-type, which is dominant at low temperatures, turns into the hexagonal Ni$_2$In-type one, slightly above 200 K. The structural transition is of the first-order type as confirmed by presence of distinct thermal hysteresis exceeding 20 K. The ac magnetic measurements indicate a ferromagnetic order below the Curie temperature $T_C$ of 238 K, followed by additional anomaly at lower temperatures – the latter one being related to the structural transition. Application of hydrostatic pressure leads to temperature separation of the purely magnetic transition, whose Curie temperature $T_C$ slowly increases with applied pressure, and the magnetostructural transition characterized by critical temperature showing much rapid decrease with increasing pressure. Comparison of the DSC data for the investigated compound and the isostructural CoMn$_{0.95}$Cu$_{0.05}$Ge one has made it possible to determine both the structural and magnetic components of entropy change.

keywords: intermetallic compounds, X-ray diffraction (XRD), ferromagnetic materials, magnetic properties, pressure-temperature phase diagram

I. INTRODUCTION

Magnetostructural coupling in the MM’Ge compounds, where M and M’ are transition 3d elements, has been extensively investigated in recent years. The coupling is strictly related to the structural phase transition between the low-temperature orthorhombic martensite (M) phase and the high-temperature hexagonal austenite (A) one. Stoichiometric CoMnGe has an orthorhombic crystal structure of the TiNiSi-type (space group $Pnma$) at room temperature. The structure undergoes a martensite structural transformation into the high-temperature hexagonal Ni$_2$In-type structure (space group $P6_3/mmc$) around $T_s$ $\approx$ 500 K. The compound shows a second order magnetic transition from paramagnetic to ferromagnetic state at the Curie temperature $T_C$ $\approx$ 350 K [2,3]. Doping of substitutional and/or interstitial atoms as well as introducing metal vacancies leads to gradual reduction of the difference between $T_s$ and $T_C$, finally resulting in appearance of a magnetostructural phase transition where both the structural and magnetic transitions occur at the same temperature. This magnetostructural transition is accompanied with large magnetocaloric effect [4,5].

Especially interesting are compounds with the Mn atoms partially substituted by the Cu atoms, as the neutron diffraction studies indicate that the Mn sublattice is a dominant source of magnetism in this class of materials [6,7]. Until now, the X-ray diffraction data at room temperature as well as the calorimetric and magnetic properties in function of temperature for the CoMn$_{1-x}$Cu$_x$Ge system with $x = 0 – 0.15$ [2,3] and $x = 0.08 – 0.1$ [8] have been reported. On the basis of these data, the structural and magnetic ($T, x$) phase diagram has been determined (see Fig. 6b in Ref. [2] and Fig. 5 in Ref. [3]). The temperature of the structural phase transition between the high-temperature hexagonal phase and the low-temperature orthorhombic one has been reported to decrease with increasing Cu content $x$ from about 500 K for $x = 0$ down to about 100 K for $x = 0.15$, while the Curie temperature decreases from about 350 K for $x = 0$ down to about 250 K for $x = 0.15$ [2,3]. The X-ray diffraction data, collected at room temperature, show dominant contribution arising from the orthorhombic structure for $x = 0.08$, while the hexagonal structure being dominant for $x > 0.08$ [8]. A giant magnetocaloric effect has been reported for the Cu concentration range where the first-order magnetostructural transition occurs, i.e. the temperatures of the structural and magnetic transitions coincide. According to Refs. [2,3], the magnetostructural coupling has been found for $0.09 \leq x \leq 0.11$, while partial coupling has been reported for $x = 0.12$. Ref. [8] reports magnetostructural coupling even for $x = 0.08$ and 0.085.
netic entropy change, under magnetic flux change of 0-5 T, has been reported to reach around 50 J·kg⁻¹·K⁻¹ for \( x = 0.11 \) \textsuperscript{2,3} or for \( x = 0.08 \) and 0.085 \textsuperscript{2}.

In order to better understand the complex magnetostuctural properties of the CoMn\(_{1-x}\)Cu\(_x\)Ge system, in this work we report the results of X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements accompanied with investigation of magnetic properties under applied hydrostatic pressure up to 12 kbar, as performed for CoMn\(_{0.88}\)Cu\(_{0.12}\)Ge, i.e. the composition showing partial magnetostuctural coupling, according to the \((T, x)\) phase diagram presented in Refs. \textsuperscript{2,3}. On the basis of our data, the \((p, T)\) phase diagram has been determined. In addition, the comparison of the DSC data for the investigated compound and the isostructural CoMn\(_{0.95}\)Cu\(_{0.05}\)Ge one has made it possible to determine both the structural and magnetic components of entropy change.

II. EXPERIMENTAL DETAILS AND RESULTS

A. Sample synthesis

Polycrystalline sample of CoMn\(_{0.88}\)Cu\(_{0.12}\)Ge has been obtained by arc melting of the constituent elements (purity better than 99.9 wt. %) under argon atmosphere, followed by annealing in vacuum (\( \sim 10^{-3} \) mbar) for 5 days at 1123 K (850 °C) and subsequent furnace cooling down to room temperature.

B. Crystal structure

Thermal evolution of the powder X-ray diffraction pattern for CoMn\(_{0.88}\)Cu\(_{0.12}\)Ge clearly indicates a temperature-induced structural transition – see Fig. 1a. In purpose to determine the exact crystal structures, a Rietveld refinement of the X-ray diffraction data has been performed using the FullProf software \textsuperscript{2,3}. Figs. 1b and 1c show the XRD patterns collected at 100 and 300 K, respectively, together with the results of the Rietveld refinement. The experimental data indicate that CoMn\(_{0.88}\)Cu\(_{0.12}\)Ge at 100 K (Fig. 1b) is a mixture of two crystal phases, namely, the orthorhombic one (88.8 wt. %) of the TiNiSi-type (space group \( Pnma, \) No. 62) in which each element occupy the \( 4c \) site \((x, \frac{1}{2}, z)\) with different values of the \( x \) and \( z \) parameters, and the hexagonal phase (11.2 wt. %) of the Ni\(_2\)In-type (space group \( P6_3/mmc, \) No. 194) with the Co atoms occupying the 2d site \((\frac{1}{3}, \frac{2}{3}, \frac{2}{3})\), while the Mn and Cu atoms occupying the same \( 2e \) site \((0, 0, 0)\) and the Ge atoms located in the \( 2c \) site \((\frac{1}{3}, \frac{2}{3}, \frac{1}{3})\). CoMn\(_{0.88}\)Cu\(_{0.12}\)Ge at 300 K (see Fig. 1c) is single-phase, consisting of the hexagonal phase solely.

Figure 2 shows thermal evolution of: fractions of the orthorhombic and hexagonal phases, lattice parameters \( a, b \) and \( c \) as well as unit cell volume \( V \), as determined from X-ray powder diffraction. The orthorhombic phase, which is dominant at low temperatures, undergoes an inverse martensitic transition to the hexagonal phase at 219 K, while the high-temperature hexagonal phase transforms into the orthorhombic one on cooling (martensitic transition) at 193 K. The transition temperatures have been defined as inflection points in the phase fraction vs. temperature curves. A comparison of the lattice parameters characterizing the orthorhombic and hexagonal phases can be done considering the relationships: \( a_o = c_h, b_o = a_h, c_o = \sqrt{3}a_h \) and \( V_o = 2V_h \). A first order character of the structural transition is confirmed by a large volume contraction \( \frac{\Delta V}{V_o} = 3.7 \% \), step change of selected lattice parameters, namely, \( \frac{\Delta a}{a_o} = 10.2 \% \) and \( \frac{\Delta c}{c_o} = 7.2 \% \) as well as thermal hysteresis visible in the phase fraction vs. temperature curves.

The values of refined lattice parameters and the unit cell volumes at 100, 300 and 480 K are listed in Table 1.
TABLE I. Lattice parameters $a$, $b$ and $c$ and the unit cell volume $V$ of the orthorhombic and hexagonal phases together with the phase fraction of the hexagonal phase, as determined from the X-ray diffraction data collected at 100, 300 and 480 K.

| $T$ [K] | $a_0$ [Å] | $b_0$ [Å] | $c_0$ [Å] | $V_0$ [Å$^3$] | $a_h$ [Å] | $b_h$ [Å] | $c_h$ [Å] | $V_h$ [Å$^3$] | hex [%] |
|---------|-----------|-----------|-----------|----------------|-----------|-----------|-----------|----------------|--------|
| 100     | 5.876(2)  | 3.8104(8) | 7.066(2)  | 158.22(7)      | 4.075(1)  | 2.981(3)  | 5.69(2)   | 68.10(6)       | 100    |
| 300     | -         | -         | -         | -              | 4.0889(4) | 3.5158(5) | 5.79(2)   | 76.97(2)       | 100    |
| 480     | -         | -         | -         | -              | 4.0976(4) | 3.5472(6) | 77.75(2)  | 112.8(8)       | 100    |

TABLE II. Enthalpy ($\Delta H$) and total entropy ($\Delta S$) changes associated with the structural phase transition in CoMn$_{1-x}$Cu$_x$Ge, $x = 0.05$ and 0.12, as determined from the DSC data collected during heating and cooling.

| $\Delta H$ [J/g] | $\Delta H$ [kJ/mol] | $\Delta S$ [J/(kg·K)] | $\Delta S$ [J/(mol·K)] |
|-----------------|---------------------|------------------------|------------------------|
| $x = 0.05$, cooling | 1.79                | 0.34                   | 5.85                   | 1.09                  |
| $x = 0.05$, heating   | 1.79                | 0.34                   | 5.72                   | 1.07                  |
| $x = 0.12$, cooling   | 4.97                | 0.93                   | 23.7                   | 4.44                  |
| $x = 0.12$, heating   | 5.95                | 1.12                   | 25.5                   | 4.79                  |

The data presented in Fig. 2 and Table I indicate almost linear thermal expansion of lattice parameters of the hexagonal phase.

C. Thermal properties

Differential scanning calorimetry (DSC) measurements were carried in the temperature range 100-350 K with the temperature rate of 10 K/min in DSC 2500 (TA Instruments) calorimeter. The results of the DSC measurements are shown in Fig. 3.

A difference between the peak temperatures obtained during heating and cooling is marked by vertical dashed lines in Fig. 3. A noticeable thermal hysteresis of 21 K indicates first order character of the structural phase transition. Determined values of the enthalpy ($\Delta H$) and total entropy ($\Delta S$) changes are given in Table II.

D. Magnetic properties

High pressure magnetic measurements were carried out in the temperature range 80-400 K under fully hydrostatic conditions. Helium was used as a pressure-transmitting medium. The pressure cell (made of beryllium bronze) was connected to the UNIPRESS GCA-10 three stage gas compressor by a manganin gauge placed in the highest pressure stage of the compressor. Temperature was controlled by a temperature controller equipped with a thermocouple placed directly at the sample position.

The ac magnetic susceptibility $\chi$ for CoMn$_{0.88}$Cu$_{0.12}$Ge during heating and cooling within the temperature range 80-360 K and selected hydrostatic pressures up to 12 kbar. At ambient pressure, a sharp increase of ac magnetic susceptibility with decreasing temperature, characteristic of transition from para- to ferromagnetic state, is visible at $T_C = 238$ K. The Curie temperature has been defined as an inflection point in the $\chi(T)$ curve. A slow increase of $T_C$ with increasing pressure is observed.

A distinct thermal hysteresis in the $\chi(T)$ curves is noticeable below the respective Curie points. An anomaly, defined as a second inflection point in the $\chi(T)$ curve, can be attributed to the magnetostructural transition associated with the (inverse) martensitic transition in CoMn$_{0.88}$Cu$_{0.12}$Ge. The temperature of anomaly ($T_s$) decreases with increasing pressure and shows thermal hysteresis of almost 20 K.

On the basis of the collected ac magnetic measurements, the magnetostructural pressure-temperature ($p$, $T$) phase diagram has been determined (see Fig. 4). The Curie temperature is found to increase slowly with increasing pressure ($dT_C/dp = 0.7(1)$ K/kbar). The characteristic temperature of the magnetostructural transition is lower than the Curie one, and decreases with increasing pressure with much higher rate ($dT_s/dp = -10.4(5)$ K/kbar). The first order character of the latter transition is confirmed by presence of distinct thermal hysteresis of $T_s$.

III. DISCUSSION

The X-ray powder diffraction data show that the low-temperature orthorhombic crystal structure (TiNiSi-type) of CoMn$_{0.88}$Cu$_{0.12}$Ge undergoes an (inverse) martensitic transition into the hexagonal one (Ni$_3$In-type) with increasing temperature. Distinct jumps in the unit cell volume $V$ as well as the lattice parameters $a$ and $b$ (see Fig. 2) are characteristic of the first order-type transition. The first order of the structural transition is confined by thermal hysteresis found in both the DSC (Fig. 3) and ac magnetic data (Fig. 4). The magnetic data, taken at ambient pressure, reveal that further increase of temperature leads to another phase transition from the low-temperature ferromagnetic state to the high-temperature paramagnetic one. Proximity of two transition temperatures leads to partial coupling of the structural and magnetic transitions at ambient pressure.

The pressure-temperature ($p$, $T$) phase diagram, determined on the basis of the ac magnetic measurements un-
FIG. 2. Phase fraction (weight percentage), unit cell volume and lattice constants vs. temperature for CoMn$_{0.88}$Cu$_{0.12}$Ge. Unit cell parameters of the hexagonal phase have been recalculated to those of the orthorhombic phase using the following relations: $a_o = c_h$, $b_o = a_h$, $c_o = \sqrt{3}a_h$ and $V_o = 2V_h$.

Under hydrostatic pressures up to 12 kbar (see Fig. 4b), shows that increasing pressure breaks the partial coupling of the structural and magnetic transitions, as the Curie temperature increases slowly with increasing pressure (d$T_C$/dp = 0.7(1) K/kbar) while the temperature of the second transition (having magnetostructural character) decreases with increasing pressure with much higher rate (d$T_s$/dp = −10.4(5) K/kbar). A similar effect can be obtained by applying a chemical pressure – compare with the (T, x) phase diagram (Fig. 6b in Ref. [2] and Fig. 5 in Ref. [3]), where x denotes the copper content in CoMn$_{1−x}$Cu$_x$Ge. The chemical pressure increases with increasing copper content as the copper radius (r$_Cu$ ≈ 1.28 Å) is smaller than that of manganese (r$_Mn$ ≈ 1.30 Å) [10].

Total entropy change $\Delta S_T$, associated with a magnetostructural transition, is a sum of the magnetic entropy change $\Delta S_m$ and entropy difference $\Delta S_s$ between two different crystallographic polymorphs, i.e. $\Delta S_T = \Delta S_m + \Delta S_s$ [11]. In order to determine individual components of the sum for CoMn$_{0.88}$Cu$_{0.12}$Ge, additional DSC measurements have been performed for the isostructural CoMn$_{0.95}$Cu$_{0.05}$Ge, where purely magnetic transition occurs for the low-temperature orthorhom-
b) Magnetostuctural (p,T) phase diagram of CoMn$_{0.88}$Cu$_{0.12}$Ge. $T_C$ and $T_s$ denote the Curie and structural phase transitions, respectively, while (h) and (c) indices refer to heating and cooling. The error bars are smaller than the plot symbols.

The current work reports the results of a systematic investigation of structural and magnetic phase transitions in CoMn$_{0.88}$Cu$_{0.12}$Ge by complementary experimental techniques including X-ray diffraction (XRD) and differential scanning calorimetry (DSC) accompanied with investigation of magnetic properties under applied hydrostatic pressure up to 12 kbar. The compound shows at ambient pressure a partial coupling of the structural martensitic transition and the magnetic transition between the ferro- and paramagnetic states. Increasing pressure breaks the partial coupling of the structural and magnetic transitions, as the Curie temperature increases slowly with increasing pressure while the temperature of the second transition (having magnetostructural character) decreases with increasing pressure with much higher rate. Comparison of the DSC data for CoMn$_{0.88}$Cu$_{0.12}$Ge and CoMn$_{0.95}$Cu$_{0.05}$Ge reveals that the structural component dominates over the magnetic one in the total entropy change associated with the magnetostructural transition in CoMn$_{0.88}$Cu$_{0.12}$Ge.

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