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High-pressure synthesis of ferromagnetic Mn_3Ge with the Cu_3Au -type structure

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Abstract

A new intermetallic compound, Mn_3Ge , has been synthesized by direct reaction of elemental components at 6.2 GPa and 1000 °C for 30 min using a belt-type high-pressure apparatus. The compound crystallizes into a cubic structure with the space group $Pm\bar{3}m$, namely the $\text{L}1_2$ -type (Cu_3Au -type) structure. The structure was refined by Rietveld analysis of the powder x-ray diffraction data and the lattice constant was determined as $a = 0.380\ 19(3)$ nm. The compound shows metallic conductivity and ferromagnetism with a Curie temperature of 400 K.

1. Introduction

Transition metal silicides and germanides have been widely investigated because of their variety of electrical and magnetic properties and their potential application in solid-state electronic devices. In the binary Mn–Ge system, six intermetallic phases, $\text{Mn}_{3,4}\text{Ge}$, Mn_5Ge_2 , Mn_7Ge_3 , Mn_2Ge , Mn_5Ge_3 , and $\text{Mn}_{11}\text{Ge}_8$, are known to exist in the equilibrium phase diagram [1]. Previously, we have demonstrated that the high-pressure technique is a suitable method for synthesis of new intermetallic phases and successfully synthesized three new manganese germanides (MnGe , Mn_3Ge_5 , and MnGe_4) under high-pressure conditions: 4–6 GPa [2–4].

Most of Mn–Ge intermetallic phases exhibit antiferromagnetism or ferrimagnetism with relatively low magnetic ordering temperatures. However, two phases, Mn_5Ge_3 ($T_C = 304$ K) [5] and MnGe_4 ($T_C = 340$ K) [4], are known to exhibit ferromagnetism with Curie temperatures above room temperature.

In this paper, we report the synthesis of a new manganese germanide, Mn_3Ge with the cubic Cu_3Au -type structure, which exhibits ferromagnetic behaviour with the Curie temperature of 400 K.

Table 1. Atom coordinates for Mn₃Ge.

Atom	Site	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Mn	3c	1.0	0.0	0.5	0.5	0.21(3)
Ge	1a	1.0	0.0	0.0	0.0	0.53(5)

2. Experimental details

Powders of electrolytic manganese (99.9%) and germanium (99.99%) were used as starting materials. These powders were mixed in the desired proportion and encapsulated into a hexagonal boron nitride crucible. High-pressure/temperature synthesis was carried out by using belt-type high-pressure equipment. The detailed cell construction of the belt-type equipment is described in our earlier paper [2]. High-pressure/temperature syntheses were carried out at 3–6.2 GPa and 800–1000 °C for 30 min and then the sample was quenched to room temperature prior to releasing the applied pressure. The sample obtained was analysed by the x-ray diffraction technique and the crystal structure was refined by Rietveld analysis of the powder x-ray diffraction data using the RIETAN program [6]. Magnetic measurements were performed using a SQUID magnetometer and a magnetic torsion balance.

3. Results and discussion

The x-ray diffraction study of quenched samples revealed that a new cubic phase with the composition Mn₃Ge could be synthesized and metastably quenched from the reaction at 3–6.2 GPa and 800–1000 °C. Single-phase compound was obtained by reaction at 6.2 GPa and 1000 °C.

The x-ray diffraction pattern of Mn₃Ge was completely indexed on a cubic unit cell with the lattice parameter of $a = 0.3802(1)$ nm, suggesting a possible Cu₃Au-type structure. The compound seemed to be stoichiometric because the experiments on different nominal compositions ($2.8 < \text{Mn/Ge} < 3.2$) gave the same lattice constant within experimental error. The structure refinement was carried out by the Rietveld method assuming that the compound was isostructural with Cu₃Au (space group *Pm3m* (No 221)). Figure 1 shows the observed, calculated, and difference plots for the x-ray diffraction data of Mn₃Ge. The refinement revealed that Mn₃Ge crystallizes into the cubic Cu₃Au-type (*L1₂*-type) structure with the lattice parameter of 0.38019(3) nm. The final refinement gave reliability factors of $R_I = 6.69\%$ and $R_F = 5.53\%$ with the *S*-value (goodness-of-fit) of 1.28. The atom coordinates are given in table 1.

Figure 2 shows the crystal structure of Mn₃Ge. The structure is an ordered fcc structure in which manganese atoms are located at the face-centred positions. Each manganese atom is surrounded by eight manganese and four germanium atoms at equal distances (0.2688 nm). On the other hand, each germanium atom is surrounded by twelve manganese atoms.

Similar atomic arrangement can be seen in the perovskite-type Mn₃MC (*M* = Ga, Al, Zn, In, Sn), in which the additional carbon atom is located at the body-centred position in figure 2 [7, 8]. The perovskite-type Mn₃MC compounds and their solid solutions are known to exhibit complex magnetic behaviour in spite of their simple crystallographic arrangements of manganese atoms [7, 8].

The electrical resistivity measurement revealed that Mn₃Ge exhibited metallic conductivity with the resistivity of 2.7×10^{-4} Ω cm at room temperature.

Figure 3 shows the magnetic hysteresis loops of Mn₃Ge taken at 4 and 300 K. The temperature dependences of the magnetization and reciprocal magnetic susceptibility are

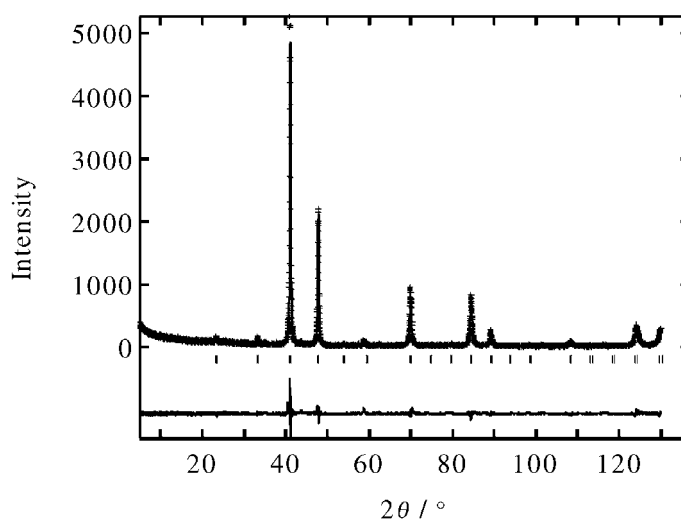


Figure 1. The observed (dots), calculated (curve), and difference x-ray diffraction profiles for Mn₃Ge.

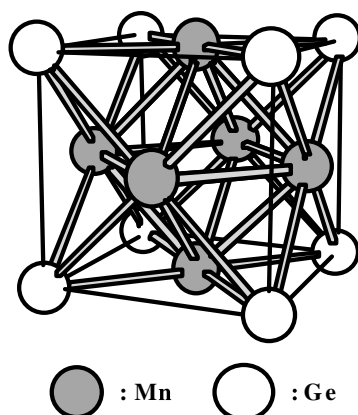


Figure 2. The crystal structure of Mn₃Ge.

shown in figure 4. Mn₃Ge exhibits a ferromagnetic behaviour with a Curie temperature of 400 K. Above the Curie temperature, the magnetic susceptibility obeys a Curie–Weiss-type relation. The saturation magnetic moment is $0.87 \mu_B/\text{Mn}$, while the paramagnetic moment deduced from the Curie–Weiss-type relation is $1.69 \mu_B/\text{Mn}$. This, as well as the metallic conductivity, suggests possible itinerant ferromagnetism of this compound.

It is notable that the isomorphous compounds, Mn₃Pt and Mn₃Rh, are antiferromagnetic, though their lattice constants are nearly the same (0.3833 nm for Mn₃Pt and 0.3813 nm for Mn₃Rh) [9]. Such a difference should be due to the difference in bonding nature between manganese and the other elements. From this point of view, it should be pointed out that electron transfer from the germanium to the metal-atom side occurs generally in transition metal germanides [3]. The observed Mn–Ge distance (0.2688 nm) in Mn₃Ge is somewhat shorter than the sum of the metallic radii, indicating a possible occurrence of electron transfer from germanium to manganese.

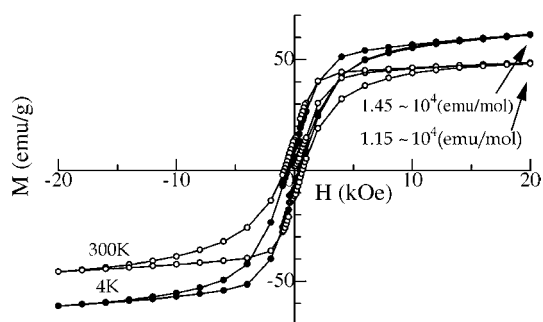


Figure 3. Magnetic hysteresis loops of Mn_3Ge .

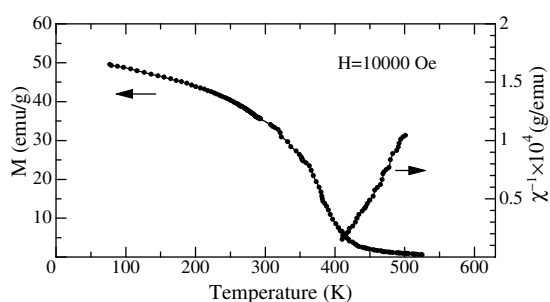


Figure 4. Temperature dependences of the magnetization and reciprocal magnetic susceptibility of Mn_3Ge .

4. Conclusion

In summary, a new intermetallic compound, Mn_3Ge , was successfully synthesized under high-pressure conditions. The compound is a ferromagnet with metallic conductivity. The observed Curie temperature is the highest value among the ferromagnetic Mn–Ge intermetallic compounds. Since the magnetic properties of Mn compounds strongly correlate with the Mn–Mn bonding distance, it would be worth synthesizing other Mn_3X compounds (X: metalloid) with the Cu_3Au -type structure.

Acknowledgment

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