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High-Pressure Synthesis and Electrical and Magnetic Properties of MnGe and CoGe with the Cubic B20 Structure

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MnGe and CoGe with the cubic B20 structure were synthesized at 4–5.5 GPa and 600–1000°C for 1–3 hr using the belt-type high-pressure apparatus. Both MnGe and CoGe are antiferromagnetic with Néel temperatures of 197 and 120 K, respectively. One expects an electron transfer of 0.7 electron from germanium to transition metal in these compounds. The anomalous temperature dependences of the electrical resistivity, the thermoelectric power, and the magnetic susceptibility of MnGe and CoGe are due to a "temperature-induced local moment." © 1988 Academic Press, Inc.

Introduction

First row transition metal monosilicides with the cubic B20 structure show a variety of electrical and magnetic properties. CrSi is metallic and paramagnetic with a temperature-independent susceptibility (*1*). MnSi is metallic and an itinerant helimagnet with a long period (18 nm) propagating along the (111) direction (*2, 3*). FeSi exhibits the semiconductive conduction below 200 K, but is metallic above 200 K and its magnetic properties show an unusual behavior with a broad maximum of susceptibility at about 500 K (*1, 4*). CoSi is semimetallic and diamagnetic with a temperature independent susceptibility (*1*). It has been reported that the itinerant characters of *d*-electrons in these compounds play an important role on their electrical and magnetic behavior (*1–4*).

It is expected that the first row transition metal monogermanides with the B20 structure have electrical and magnetic properties similar to those of the silicides, but no systematic investigations have been carried out yet because of little synthesis of compounds. Only two compounds, CrGe and FeGe with the B20 structure, were synthesized at ambient pressure condition. CrGe is paramagnetic and metallic (*5, 6*) and FeGe is a ferromagnet with a Curie temperature of 280 K (*7*).

A few years ago, Larchev and Popova (*8*) reported that CoGe having the monoclinic structure transformed to the B20 structure under high pressure. But the electrical and magnetic properties of CoGe with the B20 structure were not studied. The compound corresponding to the chemical formula of MnGe has not been synthesized yet. Since the B20 structure is the closest-packed structure consisting of both atoms of 13-fold coordination, high-pressure synthesis

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may be a suitable method for the synthesis of first row transition metal monogermanide with the B20 structure.

In the present study, MnGe and CoGe with the B20 structure were synthesized under high pressure–temperature conditions, and their electrical and magnetic properties were examined.

Experimental

Manganese and cobalt powders (>99.9% in purity) and germanium powder (>99.99% in purity) were mixed in the desired molar ratio using agate mortar and uniaxially pressed at 100 MPa at room temperature to form pellets, 5 mm in diameter and 3 mm in thickness. The pellets were put into a cylindrical BN capsule, which was placed in a carbon heater. The assemblage was put into a cell constructed with NaCl and subjected to high pressure–temperature conditions using the belt-type apparatus. The high temperature–pressure reactions were carried out at 4–5.5 GPa and 600–1000°C for 1–3 hr, and then the samples were quenched to room temperature prior to releasing the applied pressure. The detailed operating procedures were described in the previous paper (*9*). The phase of product was identified by means of X-ray powder diffraction analysis. Lattice parameters were determined by a least-squares method using silicon as an internal standard. The electrical resistivity of the sintered sample was measured by a standard four probes method in the temperature range 80 to 300 K. The thermoelectric power measurement was performed in the temperature range 80–300 K. Magnetic properties were measured using a magnetic torsion balance at 7 kOe in the temperature range 80–300 K.

TABLE I

X-RAY POWDER DIFFRACTION DATA OF MnGe

h k l	$d^{-2}_{obs.}$ (nm^{-2})	$d^{-2}_{calc.}$ (nm^{-2})	$I_{obs.}$	$I_{calc.}$[a]
1 1 0	8.70	8.699	vw	0.9
1 1 1	13.04	13.048	m	7.7
2 0 0	17.40	17.397	m	5.2
2 1 0	21.73	21.746	vs	100.0
2 1 1	26.11	26.096	s	26.5
2 2 0	—	34.794	—	0.3
2 2 1	39.16	39.144	w	3.3
3 1 0	43.51	43.493	vw	0.2
3 1 1	47.83	47.842	w	4.8
2 2 2	—	52.192	—	0.05
3 2 0	56.53	56.541	vw	0.7
3 2 1	60.94	60.891	m	3.0
4 0 0	69.56	69.589	vw	3.9

[a] Intensities are calculated by using the *u* parameter of 0.14 for Mn and 0.845 for Ge.

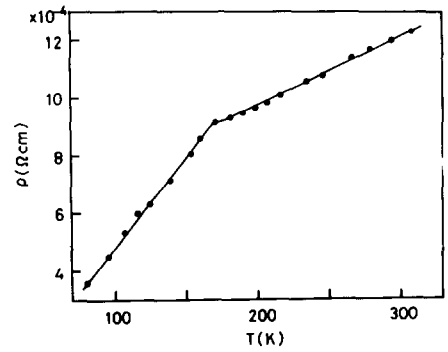

FIG. 1. Temperature dependence of electrical resistivity of MnGe.

Experimental Results

MnGe was synthesized at 4–5.5 GPa and 600–1000°C for 1–3 hr. The X-ray powder diffraction data of MnGe are listed in Table I. All diffraction patterns of MnGe were completely indexed as the cubic B20 (FeSi-type) structure. The lattice constant was calculated to be $a = 0.4795$ nm. MnGe was metastable under ambient pressure condition and decomposed to $Mn_{11}Ge_8$ and Ge by annealing at 600°C in an evacuated silica tube.

The electrical resistivity and the thermoelectric power of MnGe were measured. The results are shown in Figs. 1 and 2. The

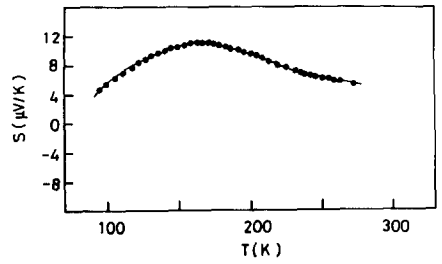

FIG. 2. Temperature dependence of thermoelectric power of MnGe.

electrical resistivity increased linearly with increasing temperature, which indicated that MnGe was metallic. Change in slope of ρ vs T curve was observed at about 170 K. The thermoelectric power had a maximum value at 170 K, and then decreased with increasing temperature. The temperature dependences of magnetic susceptibility and reciprocal magnetic susceptibility is shown in Fig. 3. From the results of magnetic susceptibility measurements, MnGe was antiferromagnetic with the Néel temperature of 197 K. In the paramagnetic region, χ_g obeyed the Curie–Weiss-type relation of $M\chi_g = M\chi_p + C/(T - \theta_p)$, where M is the formula weight. The Pauli paramagnetic susceptibility, χ_p, Curie constant, C, and the paramagnetic Curie temperature, θ_p, are calculated to be 2.17×10^{-6} emu/g, 1.138 emu · K/mol, and 187 K, respectively. The large positive value of θ_p indicated that Mn–Mn ferromagnetic exchange interactions exist in MnGe. The cusp of magnetic susceptibility observed at about 105 K might be due to the small amount of impurity phase which could not be detected by X-ray powder diffraction analysis.

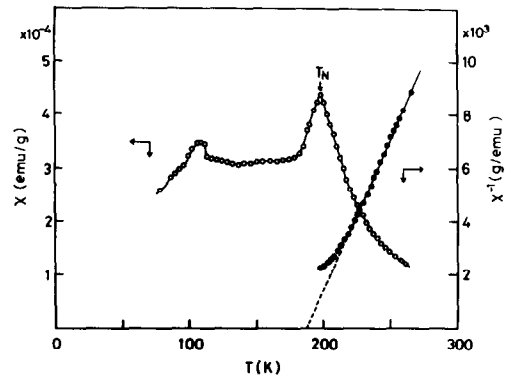

FIG. 3. Temperature dependences of magnetic susceptibility and reciprocal magnetic susceptibility of MnGe.

CoGe with the B20 structure was synthesized at 4 GPa and 800–1000°C for 1–3 hr. The lattice constant was calculated to be $a = 0.4631$ nm, which was in good agreement with that reported by Larchev and Popova (*8*). The high-pressure phase of CoGe with the B20 structure was metastable under ambient pressure condition and transformed to the monoclinic phase which was stable at lower pressure condition by annealing at 600°C in an evacuated silica tube.

The electrical resistivity, the thermoelectric power, and the magnetic susceptibility were measured for both low-pressure and high-pressure phases of CoGe. CoGe with the monoclinic structure was metallic conductor with the electrical resistivity of 5.1×10^{-5} Ω cm at 80 K and 1.6×10^{-4} Ω at 300 K and showed the Pauli paramagnetism as having a magnetic susceptibility of 1.3×10^{-6} emu/g. The results of the electrical resistivity, the thermoelectric power, and the magnetic susceptibility measurements of CoGe with the B20 structure are shown in Figs. 4–6.

The high-pressure phase of CoGe with the B20 structure was metallic, but the elec-

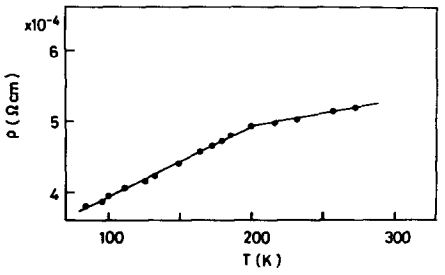

FIG. 4. Temperature dependence of electrical resistivity of CoGe with B20 structure.

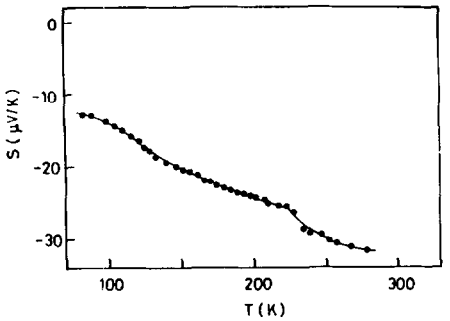

FIG. 5. Temperature dependence of thermoelectric power of CoGe with B20 structure.

trical resistivity was noticeably higher than that of the monoclinic phase. The value of the thermoelectric power was relatively larger than that of the monoclinic phase. These results indicated that the concentration of conduction carriers of CoGe with the B20 structure was lower than that of the monoclinic CoGe. The change in slope of ρ vs T curve was observed at about 200 K and the anomalous change in the thermoelectric power was also observed at near the same temperature.

From the results of magnetic susceptibility measurements, the high-pressure phase of CoGe with the B20 structure was antiferromagnetic with the Néel temperature of 120 K. At high temperatures, χ_g obeyed the Curie–Weiss-type relation with $\chi_p = 1.02 \times 10^{-7}$ emu/g, $C = 0.0082$ emu · K/mol, and $\theta_p = 132$ K. The large positive value of θ_p suggested that ferromagnetic exchange interactions are dominant. It was notable that the results of magnetic properties of CoGe were quite similar to those of MnGe. In the paramagnetic region, the deviation from the Curie–Weiss law was observed below 200 K, which corresponds to the temperature at which the electrical resistivity and the thermoelectric power anomalously change.

Synthetic conditions and characteristics of MGe (M = Cr, Mn, Fe, Co) are listed in Table II.

Discussion

A. Consideration of the B20 Structure

Transition metal monogermanides have several kinds of crystal structures such as the monoclinic, B20, B31, and B35 structures. Among these structures, the B20 structure is the most closely packed structure in which two kinds of atoms are 13-fold coordination. According to the information on high-pressure chemistry, it is expected that the formation of the B20 compound is favored under high-pressure conditions.

The atomic radius ratios (r_M/r_X) in MGe compounds with the B20 structure are limited in a narrow range of $0.90 < r_M/r_X < 1.03$ (*12*). The ratio of r_{Mn}/r_{Ge} in MnGe is 0.94. The ratio of r_{Fe}/r_{Ge} in FeGe is 0.90, which is the lowest limit of the stability range of the B20 structure. FeGe has two polymorphs of the B35 and monoclinic structures at high temperature (*13*). Since the atomic radius ratio of r_{Co}/r_{Ge} in CoGe was 0.89, at ambient pressure condition CoGe had the monoclinic structure which was isostructural with the high-temperature phase of FeGe. Since the ratio of r_{Co}/r_{Ge} in CoGe is very close to the lowest limit of the stability range of the B20 structure, CoGe transforms to the B20 structure under high-pressure condition because germanium

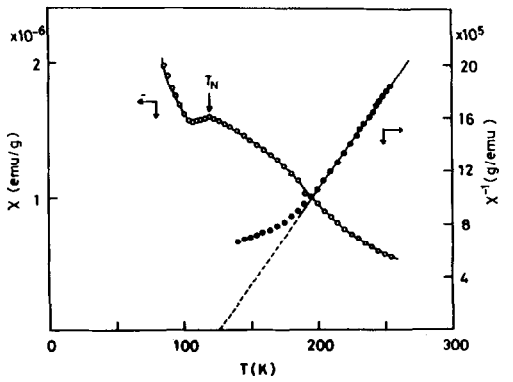

FIG. 6. Temperature dependences of magnetic susceptibility and reciprocal magnetic susceptibility of CoGe with B20 structure.

TABLE II

SYNTHETIC CONDITIONS AND CHARACTERISTICS OF MGe (M = Cr, Mn, Fe, Co)

Compound	Synthetic condition	Crystal structure	Lattice constant (nm)	T_C or T_N (K)	θ_p (K)	μ_{eff} (μ_B)	Reference
CrGe	880°C in an evacuated silica tube	B20	a = 0.4790	—[a]	−376	2.0	(6)
MnGe	4 GPa–800°C	B20	a = 0.4795	197	187	3.0	Present work
FeGe	450°C (halogen transport)	B20	a = 0.4700	280[b]	295	2.1	(7)
	700°C in an evacuated silica tube	B35	a = 0.5003 c = 0.4055	410	220	3.1	(10)
	742°C (halogen transport)	Monoclinic	a = 1.1838 b = 0.3937 c = 0.4934 β = 103.514°	335	—	—	(11)
CoGe	4 GPa–800°C	B20	a = 0.4631	120	132	0.26	Present work
	800°C in an evacuated silica tube	Monoclinic	a = 1.165 b = 0.3807 c = 0.4945 β = 101.1°	—[c]	—	—	Present work

[a] Paramagnet.
[b] Curie temperature, T_C.
[c] Pauli paramagnet.

atom is more compressive than cobalt atom. The phase transformation from monoclinic to B20 structure in CoGe results in the increase of the coordination number of the cobalt atoms from 10 to 13 and in the decrease of the cell volume of 8.4%.

The B20 structure in MGe is composed of four metal atoms and four metalloid atoms in the position (u, u, u), $(u + \frac{1}{2}, \frac{1}{2} - u, u)$, $(u, u + \frac{1}{2}, \frac{1}{2} - u)$, and $(\frac{1}{2} - u, u, u + \frac{1}{2})$. Each atom deviates from the *fcc* position due to the repulsion between both atoms. Each metal atom is surrounded by seven germanium atoms having three different distances and six metal atoms with the same distance.

The interatomic distances in the B20 monogermanides calculated by using the u parameter of 0.14 for metal atom and 0.845 for germanium atom are listed in Table III. The M–M distances are 15–18% longer than the sum of atomic radius, which was the characteristic feature of the B20 compounds compared with the other transition metal monogermanides. On the other hand, the interatomic distances M–Ge were rather shorter than the sum of corresponding atomic radii, which might be caused by the electron transfer from germanium atom to metal atom.

B. Magnetic Properties

The 3*d*-electrons in metals, alloys, and intermetallic compounds show essentially

TABLE III

INTERATOMIC DISTANCES OF MGe WITH THE B20 STRUCTURE (nm)

Compound	M–M	M–Ge(1)	M–Ge(3)	M–Ge(3)
CrGe	0.293	0.239	0.250	0.265
MnGe	0.294	0.240	0.250	0.267
FeGe	0.288	0.239	0.244	0.264
CoGe	0.285	0.237	0.243	0.257

itinerant character. In these compounds, the spin fluctuation in the narrow *d*-band plays an important role on magnetic and transport behaviors (*14*). The amplitude of the spin fluctuation is small and variable in weakly ferromagnetic or nearly ferromagnetic metals, but is large and fixed in localized moment system (*14, 15*).

Since the large distances between the metal atoms in the B20 monogermanides should increase the localization of the 3*d*-electrons, the 3*d*-electrons in the B20 monogermanides are considered to have a rather localized character and the amplitude of the spin fluctuation is considered to be large. According to the results reported by Moriya (*15*), there exist cases where the amplitude of the spin fluctuation is strongly temperature dependent and is saturated at a finite temperature. Above saturation point, spin fluctuation is regarded as a set of local moments in the Heisenberg model. The "temperature-induced local moment" (TILM) mentioned above was found in $Co(S_xSe_{1-x})_2$ system with the pyrite structure (*15*) and in FeSi with the B20 structure (*16*). The anomalies in the magnetic and transport behaviors of CoGe and MnGe with the B20 structure are considered to be due to the TILM model. The saturation temperature of the amplitude of the spin fluctuation in CoGe is estimated to be about 200 K from the results of the magnetic susceptibility measurements. The anomalous changes in the transport behaviors of CoGe occur at this saturation point. On the other hand, the temperature at which the character of local moment occurred in MnGe was determined to be 170 K from the results of the electrical resistivity and the thermoelectric power measurements. At 170 K, MnGe is in the antiferromagnetic state and the magnetic susceptibility drastically increases above 170 K.

The effective moments of MnGe and CoGe with the B20 structure are plotted in Fig. 7 together with the reported values of

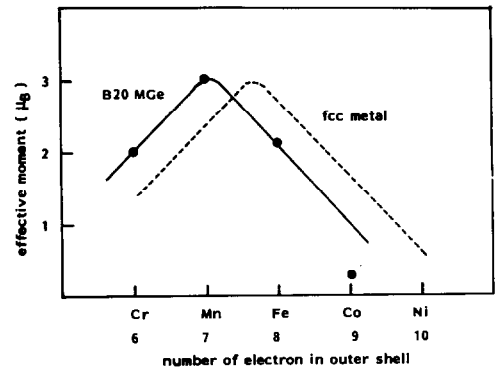

FIG. 7. Effective moment per first row transition metal atom as a function of the number of electron in outer shell for B20 monogermanides.

CrGe (6) and FeGe (7) with the B20 structure. The effective moments of B20 monogermanides change by 1 μ_B in the series of CrGe → MnGe → FeGe, in a similar manner to the *fcc* metals shown as the dotted line in Fig. 7. The value of CoGe is somewhat smaller. The plots of the effective moment vs the number of electrons in the outer shell of the first row transition metal for B20 monogermanides shift to the lefthand side from those of the *fcc* metal. The magnitude of shift is equivalent to 0.7 *d*-electron. These results indicate that each germanium atom donate 0.7 electron to the *d*-band of the transition metal. A similar electron transfer is observed in transition metal boride systems such as M_2B and MB (*17*).

All B20 compounds have a helical magnetic structure (*2, 3, 18, 19*) due to the Dzyaloshinsky–Moriya interaction because the B20 structure is noncentrosymmetric (*19, 20*). Therefore, the antiferromagnetic MnGe and CoGe are considered to have the helical spin structure.

Since the paramagnetic Curie temperatures of MnGe and CoGe are positive, the first nearest magnetic exchange interactions are ferromagnetic. It is well known that the magnetic interaction in alloys or intermetallic compounds containing Mn

atoms is closely related to the nearest Mn–Mn distance. The critical distance of Mn–Mn corresponding to the ferromagnetic and antiferromagnetic exchange interaction is estimated to be 0.28 nm in NiAs-type (*21*) and Ta_3B_4-type (*22*) structures. The nearest Mn–Mn distance was 0.294 nm in MnGe. The long Mn–Mn distance of 0.294 nm and the increase of the number of 3*d*-electrons resulting from electron transfer from germanium atom may lead to a ferromagnetic exchange interaction between Mn atoms in MnGe with the B20 structure.

Summary

MnGe and CoGe with the cubic B20 structure were synthesized under high pressure–temperature conditions and electrical and magnetic properties of the products were examined. Results are summarized as follows.

(1) Formation of the B20 structure in *M*Ge compounds easily occurs under high-pressure conditions because of its closely packed structure with high coordination number.

(2) MnGe and CoGe are antiferromagnetic with the Néel temperatures of 197 and 120 K, respectively. First nearest magnetic exchange interaction in these compounds are ferromagnetic.

(3) The 3*d*-electrons in the B20 monogermanides have a nearly localized character, and the saturation of the amplitude of the spin fluctuation occurs at 170 K in MnGe and 200 K in CoGe.

(4) Each germanium atom donated 0.7 electron to the 3*d*-band of the first row transition metals in the B20 monogermanides.

Acknowledgments

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