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Structural Studies on Some 3d Heusler Alloys (Ⅰ)*

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〈Abstract〉

3d transition metal Heusler alloys, usually denoted as X_2YZ (X=Cu, Ni, Co, Fe, Y=Mn, Cr, V, Ti, Sc, Z=ⅢA or ⅣA elements) are magnetically and crystallographically interesting. In recent years, some research works have been done on structural and magnetic properties of non-stoichiometric Heusler alloys, $X_{3-n}Y_nZ$. In this paper, two types of non-stoichiometric alloys are reported about their structural studies. One is $X_{3-n}Y_nZ$ and the other $X_2Y_{2-n}Z_n$.

$Co_{3-n}Mn_nSi$ series, the former type, showed $L2_1$ structure (Heusler type) in the range $n \leq 1.0$ and a second phase began to appear as n exceeded 1.1. Lattice parameters remained almost constant around 5,654A over the range studied. $Fe_2V_{2-n}Al_n$ series, the latter type, showed $L2_1$ structure in the investigated range $n \geq 0.5$ and lattice parameters increased with Al concentration decreasing. Studies were also made on $Fe_2Ti_{2-n}Al_n$ series.

3d 천이금속 Heusler합금의 결정구조에 관하여 (Ⅰ)*

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〈요 약〉

3d 천이원소 Heusler합금은 보통 X_2YZ(X=Cu, Ni, Co, Fe 등, Y=Mn, Cr, V, Ti, Sc 등, Z=ⅢA나 ⅣA족 원소)로 쓰여지며 천이금속의 자기적 성질을 규명하는데 또 결정학적인 면에서도 많은 흥미를 끌고 있다. 최근에는 $X_{3-n}Y_nZ$로 쓸 수 있는 비정수 조성을 갖는 Heusler합금에 대한 연구가 이루어지고 있다. 본 논문에서는 $X_{3-n}Y_nZ$ 및 $X_2Y_{2-n}Z_n$의 두 가지 형태의 비정수 조성 합금의 결정구조를 조사하여 보았다.

첫번째 형의 합금인 $Co_{3-n}Mn_nSi$에 있어서는 $n \leq 1.0$인 영역에서 $L2_1$구조(Heusler형)를 갖고 있었음이 밝혀졌으며 n이 1.1을 초과함에 따라 입방의 $L2_1$구조 외에 비입방상이 나타나기 시작하였다. 격자상수는 대체적으로 5.654Å 부근에서 별로 변하지 않았다. 두 번째 형의 합금인 $Fe_2V_{2-n}Al_n$에서는 조사한 영역($n \geq 0.5$)에서 전부 $L2_1$구조를 보여주었으며 n=0.5에서 5.795Å인 격자상수는 n이 증가함에 따라 감소 현상을 보였다. $Fe_2Ti_{2-n}Al_n$에 대하여도 조사가 이루어졌다.

Ⅰ. Introduction

Heusler alloys, denoted as X_2YZ (X, Y=transition elements and Z=ⅢA or ⅣA elements), have been studied for their crystallographically and magnetically interesting behaviors. The early works on Heusler alloys were well reviewed by Webster.[1]

The crystal structure of ordered Heusler alloys is characterized as $L2_1A$ type structure which shows a superlattice consisted of four interpen-

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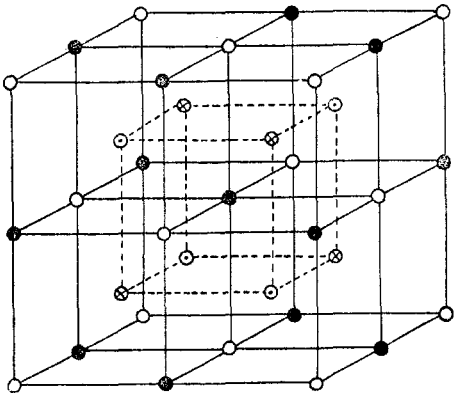

Some important structures are:

Type		Site occupancies (for Fe_2MnSi)			
		A	*B*	*C*	*D*
$A2_1$	$A=B=C=D$	all identical			
B2A	$A=C\neq B=D$	$\frac{1}{2}$(MnSi)	Fe	$\frac{1}{2}$(MnSi)	Fe
$L2_1A$	$A\neq C\neq B=D$	Si	Fe	Mn	Fe
$L2_1C$		Si	$\frac{1}{2}$(FeMn)	Fe	$\frac{1}{2}$(FeMn)
XA	$A\neq D\neq B\neq C$	Si	Fe	Fe	Mn
XC		Si	$\frac{1}{2}$(FeMn)	$\frac{1}{2}$(FeMn)	Fe
DO_3	$A\neq B=C=D$	Si	$\frac{1}{3}$(Fe_2Mn)	$\frac{1}{3}$(Fe_2Mn)	$\frac{1}{3}$(Fe_2Mn)
$L2_1B$	$A\neq C\neq B=D$	Mn	$\frac{1}{2}$(FeSi)	Fe	$\frac{1}{2}$(FeSi)
XB	$A\neq D\neq B=C$	Mn	$\frac{1}{2}$(FeSi)	$\frac{1}{2}$(FeSi)	Fe
YA	$A\neq B\neq C\neq D$	$\frac{1}{2}$(FeSi)	Fe	$\frac{1}{2}$(MnSi)	$\frac{1}{2}$(FeMn)

Fig 1. Unit cell of 4 interpenetrating Sublattices,
$A(\bigcirc)(0,0,0)$, $B(\odot)\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$, $C(\bullet)\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ and $D(\otimes)\left(\frac{3}{4},\frac{3}{4},\frac{3}{4}\right)$.

etrating *f c c* sublattices(Fig. 1). Each sublattice is occupied by the elements quite distinctively even between neighbouring transition metals.

Magnetic structures of the Heusler alloys are more interesting for the various possible magnetic interactions within the crystals. Many theoretical approaches have been made to explain the magnetic structure of Heusler alloys. The theoretical efforts include *X-Y* direct exchange interactions,[2,3] indirect exchange interactions like RKKY model,[4] superexchange interactions[5], double resonance scattering of virtual d-states[6] and even de Gennes's double exchange model[7].

Yet no one's theoretical model seems to be able to explain by itself all the magnetic behaviors of various Heusler alloys satisfactorily.

Recently some experimental works have been reported on magnetic and structural properties of non-stoichiometric Heusler alloys in the hope that clues on magnetic interactions in the system might be obtained. For instances, Booth et al[8] and Yoon and Booth[9] reported Fe_{3-x} Mn_x Si alloy system and Görlich et al [10] on Co_{2-x} Ni_x Ti Sn system.

In this paper, structural studies using x-ray diffraction for some non-stoichiometric Heusler alloys of 3-d elements are reported. Attempts

were made on two different types of non-stoichiometry, say, $X_{3-n}Y_nZ$ and $X_2Y_{2-n}Z_n$. This report is preliminary one in a way since further investigations like neutron diffractions are essential for the completion of the structural studies on such transition metal alloys. Results from further investigations will shortly be published as the next of the series of the paper.

Ⅱ. Experiments and Results

1. Sample preparation and X-ray diffraction

Jhonson and Matthey's high purity elements (99.99%) were used for alloying. Each constituent elements were weighed in 0.1 mg scale for 30 gram ingots of the alloy. The mixtures of constituent metals were melted in an argon arc furnace. The ingots were powdered in a stainless steel mortar to obtain x-ray diffraction specimens.

The powdered specimens were annealed at about 800°C for 24 hours in a quatz tube which was filled with about half an atmosphere of argon. The tubes were then rapidly quenched into cold water. This heat treatment was made in order to ensure the structural stability and the homogeneity and to remove any mechanical strains which might occur during the powdering. Each alloy was weighed before and after melting and the weight losses calculated. Alloys with weight losses in excess of 1% were rejected.

Magnetometer specimens for next studies were made from small pieces of material selected during the crushing process.

X-ray powder diffraction photographs were obtained using Debye-Scherrer camera and Diffractometer with Fe $K\alpha$ radiation. Lattice parameters were determined by the Nelson-Riley[11] extrapolation of the lattice parameters corresponding to each line using the least square method.

2. Structures of Co_{3-n} Mn_n Si Series.

The lattice parameters were given in table 1.

Table 1. The lattice parameters and structures of the Heusler alloys Co_{3-n} Mn_n Si in the range of $0.7 \leq n \leq 1.5$.

n	lattice parameter(Å)	Structure	comment
1.5	5.647±0.002	$L2_1$+tetragonal	two phase
1.2	5.953±0.002	$L2_1$+tetragonal	two phase
1.1	5.653±0.001	$L2_1$+tetragonal	two phase
1.0	5.654±0.001	$L2_1$	single phase
0.9	5.653±0.002	$L2_1$	single phase
0.8	5.653±0.002	$L2_1$	single phase
0.7	5.655±0.001	$L2_1$	single phase

Figure 2 shows the variation of lattice parameter a_0 with Mn concentration n of Co_{3-n} Mn_n Si alloys in the range of $0.7 \leq n \leq 1.5$.

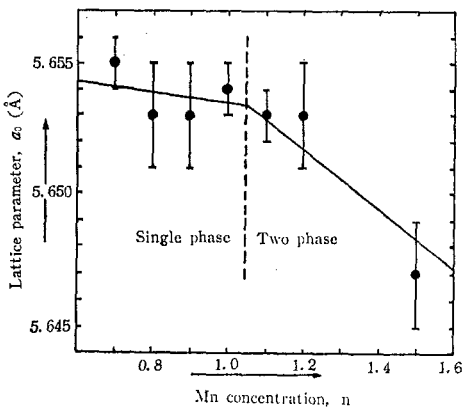

Fig. 2. Variation of lattice parameter a_0 with Mn concentration n of Co_{3-n} Mn_n Si alloys.

Alloys having Mn concentration in excess of $n=1.0$ exhibited a second phase, while the alloys in the range of $0.7 \leq n \leq 1.0$ appeared to be single-phase.

The lattice parameter decreased linearly with increasing Mn concentration from 5.655 Å to 5.647Å as shown in figure 2. The lattice parameter of the single phase alloys in the range of $0.7 \leq n \leq 1.0$, however, is almost

constant around 5.654. Å.

X-ray powder photography showed that the crystal structure of the alloys in the single phase range is a four inter-penetrating *f c c* lattice with four chemical formula units in a unit cell. The two-phase alloys seemed to have a small amount of a tetragonal phase in addition to the cubic phase for which lattice parameters a_0 agreed with those of the single phase alloys.

3. Structures of Fe_2 V_{2-n} Al_n Series

The latlice parameters of the alloys Fe_2 V_{2-n} Al_n in the range of $0.5 \leq n \leq 0.75$ were given in table 2.

Table 2. The latlice parameters and structures of the Heusler alloys Fe_2 V_{2-n} Al_n in the range of $0.5 \leq n \leq 0.75$.

n	heat treatment	lattice parameter(Å)	Structure
0.5	as-cast	5.795±0.001	$L2_1$(single phase)
0.5	800°C, 24hr.	5.795±0.002	〃
0.625	800°C, 24hr.	5.792±0.001	〃
0.75	800°C, 24hr.	5.790±0.001	〃

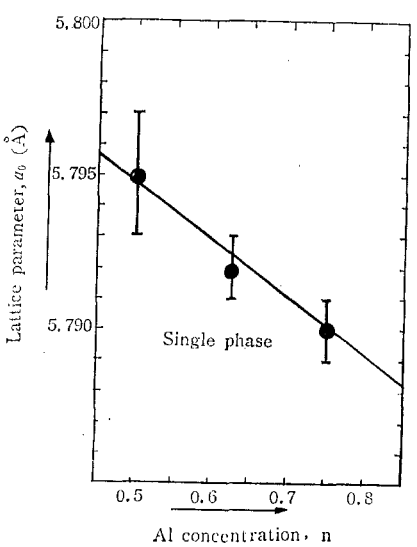

Fig. 3. Variation of lattice parameter a_0 with Al concentration n of Fe_2 V_{2-n} Al_n alloys.

Figure 3 shows the variation of lattice parameter with Al concentration n. In the range of $0.5 \leq n \leq 0.75$, the alloys were found to be single phase.

The lattice parameters of the alloys decreased linearly with increasing Al concentration n from 5.795Å (n=0.5) to 5.790Å (n=0.75).

X-ray powder photography showed that the crystal structure of the alloys is a four interponetrating *f c c* latlice with four chemical formula units in a unit cell.

4. Structure of Fe_2 Ti_{2-n} Al_n

In the Al concentration n=1.0, the alloy Fe_2 Ti Al appeared to be single phase by the X-ray powder diffraction photography.

The alloy Fe_2 Ti Al was found to have a *f c c* crystal structure with four formula units in a unit cell. The latlice parameter is 5.887Å. In the Al concentration n=0.5, Fe_2 $Ti_{1.5}$ $Al_{0.5}$ Showed a complicated multiphase.

5. Magnetic properties at room temperature.

The alloys Co_{3-n} Mn_n Si were found to be ferromagnetic in the range of Mn concentration $0.7 \leq n \leq 1.5$ at room temperature. Bulk magnetism increases monotonically in the range of $0.7 \leq n \leq 1.0$, but decreases in the range of $1.0 \leq n \leq 1.5$ with increasing Mn concentration n. The alloys Fe_2 V_{2-n} Al_n and Fe_2 Ti_{2-n} Al_n were found to be non-ferromagnetic at room temperature.

Ⅲ. Discussions and Conclusions

The lattice parameters of the alloys Co_{3-n} Mn_n Si were about 5.654Å in the single phase range of $0.7 \leq n \leq 1.0$ and decreased linearly with increasing Mn concentration. The alloys having Mn concentration in excess of n=1.0 were not single phase and contained a small amount of a tetragonal phase.

The alloys Fe_2 V_{2-n} Al_n were found to be

single phase with latlice parameters which decreased from 5.795Å to 5.790Å with increasing n in the range of $0.5 \leq n \leq 0.75$.

Fe_2 Ti Al showed $f\ c\ c$ structure with lattice parameter of 5.887Å.

The crystal structure of these alloys Co_{3-n} Mn_n Si, Fe_2 V_{2-n} Al_n and Fe_2 Ti_{2-n} Al_n were found to be consisted of four interpenetrating $f\ c\ c$ sublattices A, B, C, D with origins at the point (0,0,0), $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$, $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$, $\left(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}\right)$ as shown in figure 1.

The determination of crystallographic order between adjacent transition metal elements is hardly possible by X-ray diffraction, since the X-ray scattering factors for atoms which are close to each other in the periodic table are very similiar.

However, a tendency of selective occupancies of the sublattice among 3d metal-ⅢA or ⅣA elements and even between 3d metal-3d metal elements forming $L2_1A$ structure was strongly supported by Burch et al[12]. They have examined the spin echo spectra of (Fe T)$_3$ Si alloys where T is a 3d metal and found that all solutes to the left of Fe in the periodic table prefer "C" site and those to the right of Fe "B" and "D" sites.

Co_{3-n} Mn_n Si exhibited ferromagnetism at room temperature while other series of alloys studied were non-ferromagnetic.

Further studies like neutron diffraction and magnetization measurements are undergoing and will shortly be published.

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