

High-Pressure Synthesis and Magnetic Properties of the Solid Solution MnCr_xSb and CrMn_ySb ($0 \leq x, y \leq 1.0$)

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Solid solutions between MSb and $\text{MM}'\text{Sb}$ have been studied by many investigators, mainly in the case of $M = \text{Mn}$ (1-6). They had made an attempt to examine the changes of crystallographic, magnetic, and electrical properties by adding metal atoms to the trigonal bipyramidal interstice (2(*d*) site) in the ferromagnetic MnSb with the NiAs -type structure. An intermediate structure between NiAs - and filled-up NiAs -type structure of Ni_2In -type structure is denoted as a partially filled-up NiAs -type structure by Pearson (7). Guillaud (1) found that both Curie temperature and saturation magnetization decreased with increasing Mn contents in the system MnMn_xSb ($0 \leq x \leq 0.22$). Yamaguchi *et al.* (4) measured the magnetization of 2(*d*) site Mn atoms using a polarized neutron technique and reported that no magnetic moment of 2(*d*) site Mn atoms was found. Recently, Reimers *et al.* (8) examined the polarized neutron diffraction study of the single crystal $\text{Mn}_{1.09}\text{Sb}$ and reported that increasing Mn excess led to a decreasing magnetic moment magnitude/Mn atom. Furthermore, Yamaguchi and Watanabe (6) studied the distribution of two kinds of transition metal atoms on 2(*a*) and 2(*d*)

sites and the magnetization of two sublattices in MnM_xSb ($M = \text{Cr, Fe, Co}$; $0 \leq x \leq 0.12$). Both magnetization and Curie temperature decreased with increasing x at the same ratio as in the case of the system MnMn_xSb ($0 \leq x \leq 0.22$) (1). Although many investigators have carried out the crystallographic and magnetic studies of the systems MnM_xSb , it is necessary to extend the composition range from the previous maximum value of $x = 0.22$ to MnMSb ($x = 1$) in order to conduct the detailed studies in these solid solution series. In the present study, the full solid solutions of MnCr_xSb and CrMn_ySb ($0 \leq x, y \leq 1.0$) were synthesized under high temperature-pressure conditions.

Starting materials of MnCr_xSb and CrMn_ySb ($0 \leq x, y \leq 1.0$) were prepared by mixing manganese (99.9%), chromium (99.9%), and antimony (99.99%) powders in the desired ratios. The powders were put into a cylindrical BN capsule, which was placed in a carbon heater. The assemblage was put into pyrophyllite cube. The cube was subjected to high temperature-pressure conditions using a cubic anvil type apparatus (9). The reaction was carried out at 5.0 GPa and 900°C for 1 hr. The sample was quenched to room temperature prior to the release of applied pressure. Products were identified by X-ray diffraction. Lattice con-

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TABLE I
LATTICE PARAMETERS a AND c , UNIT CELL VOLUME V , AND AXIAL RATIOS c/a OF THE INTERSTITIAL SOLID SOLUTIONS OF MnCr_xSb AND CrMn_ySb

Composition	a (nm)	c (nm)	V (10^{-3} nm^3)	c/a
$x = 0$	0.4128	0.5789	85.43	1.402
$x = 0.2$	0.4197	0.5713	87.16	1.361
$x = 0.4$	0.4264	0.5653	89.01	1.326
$x = 0.6$	0.4292	0.5635	89.90	1.313
$x = 0.8$	0.4301	0.5619	90.02	1.306
$x = y = 1$	0.4292	0.5623	89.71	1.310
$y = 0.8$	0.4278	0.5612	88.94	1.312
$y = 0.6$	0.4250	0.5598	87.57	1.317
$y = 0.4$	0.4213	0.5578	85.75	1.324
$y = 0.2$	0.4187	0.5527	83.91	1.320
$y = 0$	0.4127	0.5451	80.40	1.321

stants were determined by a least-squares method from high-angle powder patterns. Silicon was used as an internal standard. Magnetic measurements were performed using a magnetic torsion balance in the temperature range of 80–873 K.

X-Ray diffraction patterns of all samples synthesized under high temperature–pressure conditions were completely indexed as the hexagonal NiAs-type structure. Lattice parameters, axial ratios and unit-cell volumes for these solid solutions are listed in Table I. In order to compare the present experimental results with those in the system $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$ ($0 \leq z \leq 1.0$) having the NiAs-type structure (10), the composition dependence of the lattice parameters for three systems of MnCr_xSb , CrMn_ySb , and $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$, is shown in Fig. 1. It was noted that there was a striking difference in the change of lattice parameter between MnCr_xSb or CrMn_ySb and $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$. It is considered that these results were due to the existence of metal atoms on trigonal bipyramidal interstices in the former systems. It is seen from Fig. 1 that the a axis increased with increasing x or y in both solid solutions. It is expected that the increase of the a axis was due to the exis-

tence of excess atoms located on the 2(d) interstitial site in NiAs-type structure. The similar increase of the a axis due to the existence of excess atoms has been observed generally in many solid solutions with the partially filled-up NiAs-type structure (2, 5, 6, 11, 12). On the other hand, the c axis of MnCr_xSb decreased with increasing x , but that of CrMn_ySb increased with increasing y .

The temperature dependences of magnetization of the systems MnCr_xSb ($0.2 \leq x \leq 0.8$) and CrMn_ySb ($0.4 \leq y \leq 0.8$) are shown in Figs. 2 and 3. The temperature dependences of reciprocal magnetic susceptibility of both solid solutions are shown in Figs. 4

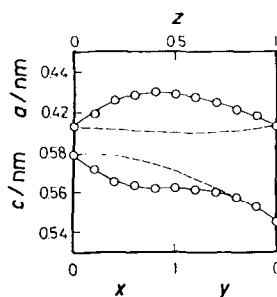


FIG. 1. Composition dependences of lattice parameters of MnCr_xSb (solid line), CrMn_ySb (solid line), and $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$ (broken line).

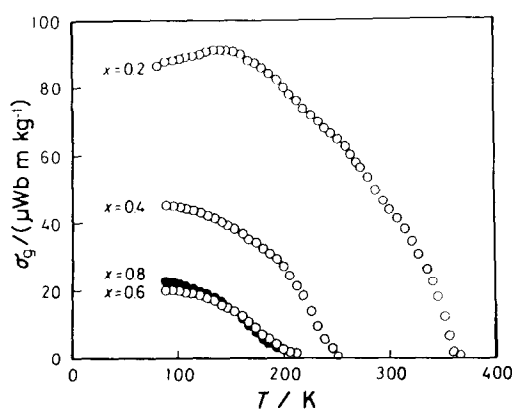


FIG. 2. Magnetization as a function of temperature for MnCr_xSb .

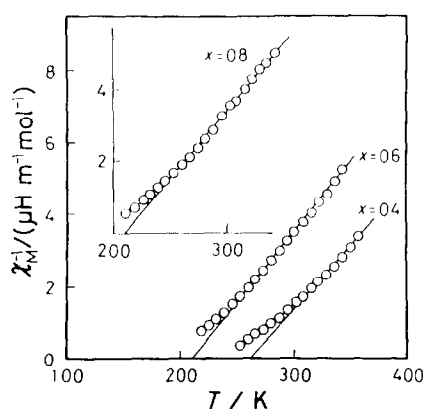


FIG. 4. Temperature dependence of reciprocal magnetic susceptibility of MnCr_xSb .

and 5. All samples obeyed the Curie–Weiss law in the paramagnetic region. The fact that the paramagnetic Curie temperatures of samples MnCr_xSb ($0 \leq x \leq 1.0$) and CrMn_ySb ($0.6 \leq y \leq 1.0$) were positive, indicates that the predominant magnetic interactions were ferromagnetic. The magnetic parameters of MnCr_xSb and CrMn_ySb ($0 \leq x, y \leq 1.0$), are listed in Table II. From the magnetic phase diagram as shown in Fig. 6, it was found that, in the composition range from $x = 0$ to $x = 0.12$, the present results were in good agreement with those reported by Yamaguchi and Watanabe (6). In Figure 6, the composition dependences of Curie temperature of the isostructural solid solutions $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$ ($0 \leq z \leq 1.0$) are also shown. From the results of the neu-

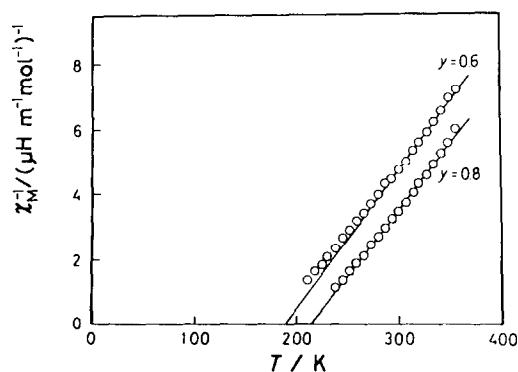


FIG. 5. Temperature dependence of reciprocal magnetic susceptibility of CrMn_ySb .

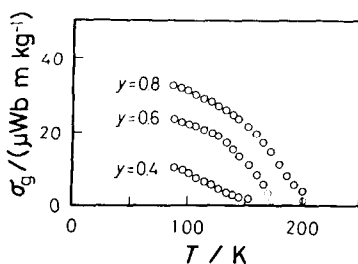


FIG. 3. Magnetization as a function of temperature for CrMn_ySb .

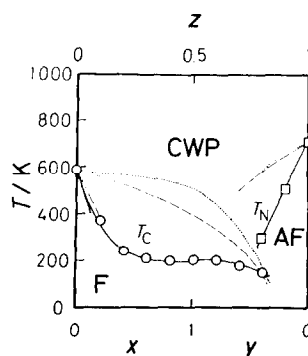


FIG. 6. Magnetic phase diagram (solid line: MnCr_xSb and CrMn_ySb , broken line: $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$ (10), dotted line: $(\text{Mn}_{1-z}\text{Cr}_z)\text{Sb}$ (13), dash-dot line: Mn_{1+x}Sb (2), thick broken line: MnCr_xSb ($0 \leq x \leq 0.12$) (6), F: ferromagnetism, AF: antiferromagnetism, CWP: Curie–Weiss paramagnetism).

TABLE II
CURIE TEMPERATURE T_c , NEEL TEMPERATURE T_N ,
PARAMAGNETIC CURIE TEMPERATURE θ_p ,
FERROMAGNETIC BOHR MAGNETON PER FORMULA
 n_F , AND EFFECTIVE BOHR MAGNETON PER
FORMULA n_p OF THE INTERSTITIAL SOLID
SOLUTIONS OF $MnCr_xSb$ AND $CrMn_ySb$

Compositions	T_c (K)	T_N (K)	θ_p (K)	n_F	n_p
$x = 0$	587		600	3.53	4.32
0.2	375		400	2.72	4.00
0.4	245		260	1.71	3.83
0.6	205		210	1.24	3.63
0.8	195		210	1.11	3.67
$x = y = 1$	198		223	1.17	3.54
$y = 0.8$	200		214	1.26	3.57
0.6	176		189	1.11	3.46
0.4	155	310	-168	0.71	2.82
0.2		510	-385		4.13
0		705	-625		4.79

iron diffraction studies on single crystals ($Mn_{1-x}Cr_x$)Sb ($0 \leq x \leq 1.0$), a more detailed magnetic phase diagram has been examined by Reimers *et al.* (14). It was found that T_c and T_N of the present solid solution systems, changed more rapidly than those of ($Mn_{1-x}Cr_x$)Sb. Castelltz (15), studied the relationship between Curie temperature and metal-metal distance normalized by $3d$ shell radius for many compounds with NiAs-, Ni_2In -, Mn_5Si_3 -, and $MgCuSb$ -type structures. It is expected that the present

experimental results would be explained by her model (15).

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