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

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Solid solutions between MSb and MM'Sb have been studied by many investigators, mainly in the case of M = 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 $MnMn_xSb$ ($0 \leqq x \leqq 0.22$). 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 $Mn_{1.09}Sb$ 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 = Cr, Fe, Co; $0 \leqq x \leqq 0.12$). Both magnetization and Curie temperature decreased with increasing x at the same ratio as in the case of the system $MnMn_xSb$ ($0 \leqq x \leqq 0.22$) (*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 $CrMn_ySb$ ($0 \leqq x, y \leqq 1.0$) were synthesized under high temperature–pressure conditions.

Starting materials of $MnCr_xSb$ and $CrMn_ySb$ ($0 \leqq x, y \leqq 1.0$) 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 $(Mn_{1-z}Cr_z)Sb$ ($0 \leqq z \leqq 1.0$) having the NiAs-type structure (*10*), the composition dependence of the lattice parameters for three systems of $MnCr_xSb$, $CrMn_ySb$, and $(Mn_{1-z}Cr_z)Sb$, 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 $(Mn_{1-z}Cr_z)Sb$. 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 existence 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 $MnCr_xSb$ ($0.2 \leqq x \leqq 0.8$) and $CrMn_ySb$ ($0.4 \leqq y \leqq 0.8$) are shown in Figs. 2 and 3. The temperature dependences of reciprocal magnetic susceptibility of both solid solutions are shown in Figs. 4

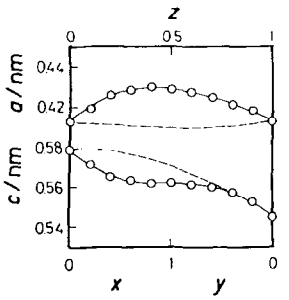

FIG. 1. Composition dependences of lattice parameters of $MnCr_xSb$ (solid line), $CrMn_ySb$ (solid line), and $(Mn_{1-z}Cr_z)Sb$ (broken line).

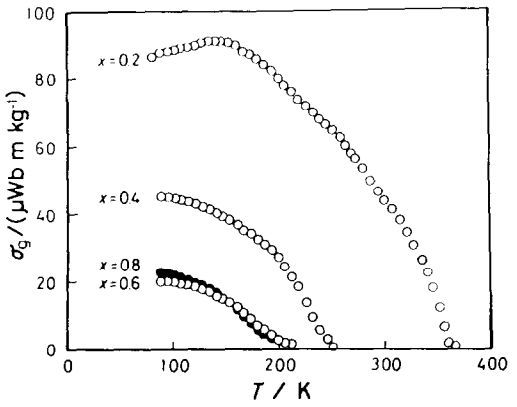

FIG. 2. Magnetization as a function of temperature for $MnCr_xSb$.

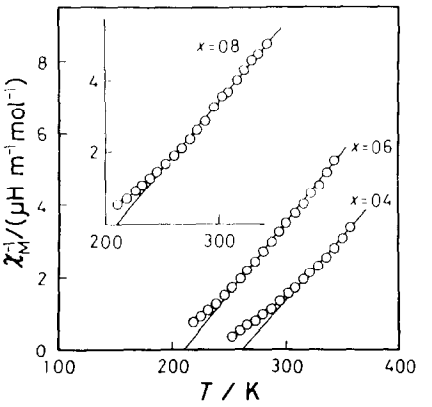

FIG. 4. Temperature dependence of reciprocal magnetic susceptibility of $Mncr_xSb$.

and 5. All samples obeyed the Curie–Weiss law in the paramagnetic region. The fact that the paramagnetic Curie temperatures of samples $MnCr_xSb$ ($0 \leqq x \leqq 1.0$) and $CrMn_ySb$ ($0.6 \leqq x \leqq 1.0$) were positive, indicates that the predominant magnetic interactions were ferromagnetic. The magnetic parameters of $MnCr_xSb$ and $CrMn_ySb$ ($0 \leqq x, y \leqq 1.0$), 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 $(Mn_{1-z}Cr_z)Sb$ ($0 \leqq z \leqq 1.0$) are also shown. From the results of the neu-

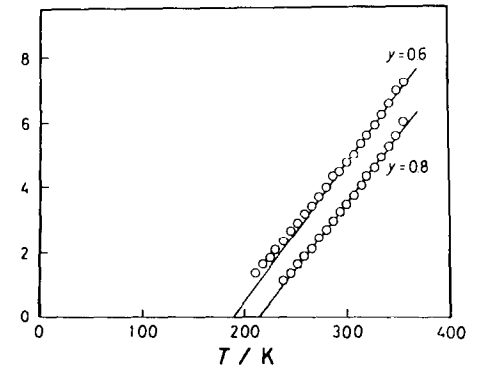

FIG. 5. Temperature dependence of reciprocal magnetic susceptibility of $CrMn_ySb$.

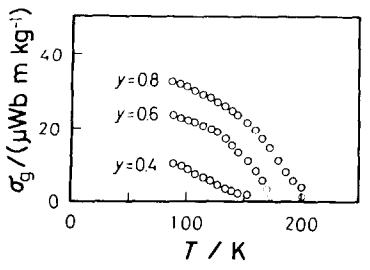

FIG. 3. Magnetization as a function of temperature for $CrMn_ySb$.

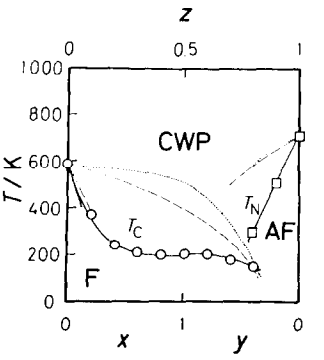

FIG. 6. Magnetic phase diagram (solid line: $MnCr_xSb$ and $CrMn_ySb$, broken line: $(Mn_{1-z}Cr_z)Sb$ (*10*), dotted line: $(Mn_{1-z}Cr_z)Sb$ (*13*), dash-dot line: $Mn_{1+x}Sb$ (*2*), thick broken line: $MnCr_xSb$ ($0 \leqq x \leqq 0.12$) (*6*), F: ferromagnetism, Af; antiferromagnetism, CWP: Curie–Weiss 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

tron diffraction studies on single crystals $(Mn_{1-z}Cr_z)Sb$ $(0 \leqq x \leqq 1.0)$, 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 $(Mn_{1-z}Cr_z)Sb$. Castelitz (*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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