NEUTRON DIFFRACTION AND MAGNETIC PROPERTIES OF Mn1+xSb1-ySny

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NEUTRON DIFFRACTION AND MAGNETIC PROPERTIES OF $Mn_{1+x}Sb_{1-y}Sn_y$

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Résumé. — On a déterminé la région d'homogénéité à 650 °C des composés $Mn_{1+x}Sb_{1-y}Sn_y$ avec la structure du type NiAs (B 8), en utilisant la diffraction des rayons X. On a trouvé une série complète de solutions solides entre $y = 0$ et $y = 1$, avec x changeant graduellement de $x = 0$-0,2 ($y = 0$) à $x = 0{,}6$-0,8 ($y = 1$).

Les mesures de l'aimantation et de la susceptibilité magnétique de $Mn_{1+x}Sb_{1-y}Sn_y$ montrent une grande variation des propriétés magnétiques avec la composition.

L'étude de la diffraction de neutrons pour $Mn_{1,15}Sb$ a révélé l'existence de deux sous-réseaux magnétiques ; les moments de Mn sur les sites octahédriques (3,65 ± 0,07 μ_B à 4,2 °K) sont antiparallèles aux moments de Mn sur les sites interstitiels trigonal-bipyramidaux (3,0 ± 0,4 μ_B à 4,2 °K).

Abstract. — The homogeneity region at 650 °C of compounds $Mn_{1+x}Sb_{1-y}Sn_y$ with the NiAs (B 8)-type structure was determined from X-ray crystallographic data. A complete series of solid solutions was found between $y = 0$ and $y = 1$, with x changing gradually from $x = 0$-0.2 for $y = 0$ to $x = 0.6$-0.8 for $y = 1$.

Measurements of the magnetization and the magnetic susceptibility of $Mn_{1+x}Sb_{1-y}Sn_y$ show a strong variation of the magnetic properties with composition.

Neutron diffraction data of $Mn_{1,15}Sb$ show two magnetic sublattices ; the moments of Mn on octahedral sites (3.65 ± 0.07 μ_B at 4.2 °K) are antiparallel to the moments of Mn on the interstitial, trigonal-bipyramidal sites (3.0 ± 0.4 μ_B at 4.2 °K).

I. **Introduction.** — Many metallic compounds with the NiAs (B 8)-type structure have a broad existence region, and show magnetic properties which depend strongly on the composition. Various authors have studied the magnetic properties of the compounds $Mn_{1+x}Sb$ [1, 2, 3, 4, 5] and $Mn_{1+x}Sn$ [6, 7, 8]. In this paper we report an investigation of the homogeneity region, the crystallographic, and the magnetic properties of compounds $Mn_{1+x}Sb_{1-y}Sn_y$ with the NiAs (B 8)-type structure.

The compounds were prepared by heating mixtures of the elements in evacuated, sealed silica tubes during 4 to 7 days at temperatures between 600 and 700 °C, followed by quenching to room temperature. As starting materials we used manganese flakes (4 N 5), antimony shot (5 N), and tin powder (5 N) from Koch-Light Laboratories Ltd.

The samples were examined by X-ray powder diffraction at room temperature. The contamination by other phases was deduced from Guinier photographs and powder diffractograms. Unit-cell dimensions were calculated from Debye-Scherrer photographs.

Magnetic measurements were carried out with a Faraday balance between 77 and 1 000 °K, and with a PAR vibrating-sample magnetometer between 4.2 and 77 °K. Neutron-diffraction powder data were obtained at the High Flux Reactor at Petten.

II. **Homogeneity region of the NiAs (B 8)-type phase.** — The homogeneity region of compounds $Mn_{1+x}Sb_{1-y}Sn_y$ with the NiAs (B 8)-type structure was deduced from the change of the unit-cell parameters with x and y and the presence of other phases ; the result is shown in figure 1. A complete series of solid solutions exists between $y = 0$ and $y = 1$. The homogeneity region changes gradually from $x = 0$-0.2 for $Mn_{1+x}Sb$ (in accordance with ref. [2]) to $x = 0.6$-0.8 for $Mn_{1+x}Sn$ (see also [9]). Near the Mn-rich limit of the homogeneity region the samples were contaminated with Mn_2Sb or $Mn_{3.7}Sn$, near the Sb/Sn-rich limit contaminations of Sb or $MnSn_2$ and β-Sn were observed.

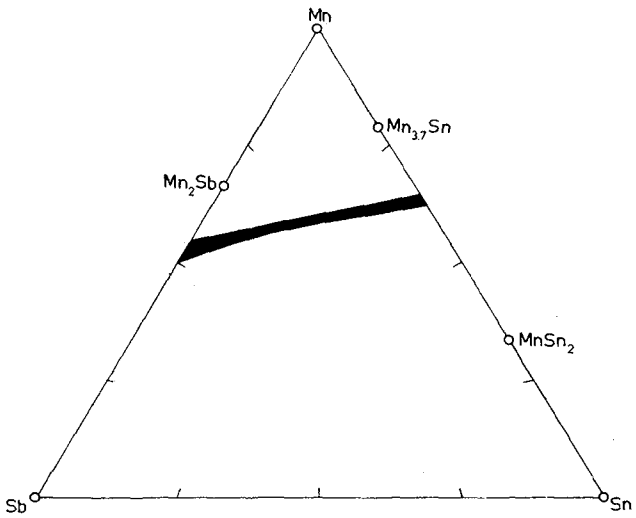

FIG. 1. — Part of the phase diagram of the Mn-Sb-Sn system at about 650 °C. The black area indicates the NiAs-type phase homogeneity range. The compound $MnSn_2$ is not stable at 650 °C ; it is formed at lower temperature, by reaction of $Mn_{1+x}Sn$ with β-Sn.

The unit-cell parameters of some of the samples are given in Table I.

TABLE I

Unit-cell dimensions and magnetic properties of $Mn_{1+x}Sb_{1-y}Sn_y$. *The effective paramagnetic moment* μ_p *and the corresponding number of unpaired spins* n_p *are calculated from* C_{at}. *The* μ_f *values were determined in a field of* 23.5 kOe.

Composition	a (Å)	c (Å)	c/a	V (Å^3)	C_{at} (°K.cm^3.gat^{-1})	μ_p (μ_B)	n_p	θ (°K)	T_c (°K)	μ_f (μ_B) at 4.2 °K
$Mn_{1.00}Sb$	4.128	5.787	1.402	85.4	2.06	4.06	3.19	573	573	3.55
$Mn_{1.15}Sb$	4.189	5.728	1.368	87.1	1.95	3.95	3.07	462	462	2.94
$Mn_{1.33}Sb_{0.75}Sn_{0.25}$	4.261	5.612	1.317	88.2	2.35	4.33	3.45	60	193	1.26
$Mn_{1.38}Sb_{0.75}Sn_{0.25}$	4.275	5.603	1.311	88.7	2.26	4.25	3.37	23	171	0.98
$Mn_{1.44}Sb_{0.50}Sn_{0.50}$	4.303	5.535	1.286	88.8	2.82	4.75	3.85	− 190	140	0.94
$Mn_{1.53}Sb_{0.25}Sn_{0.75}$	4.339	5.502	1.268	89.7	2.0	4.0	3.2	22		
$Mn_{1.56}Sb_{0.25}Sn_{0.75}$	4.342	5.509	1.269	90.0	2.14	4.14	3.26	− 30	197	1.30
$Mn_{1.63}Sn$	4.367	5.517	1.263	91.1	2.10	4.10	3.22	88		
$Mn_{1.75}Sn$	4.387	5.509	1.256	91.8	2.12	4.12	3.24	47	252	1.27

III. **Magnetic properties of** $Mn_{1+x}Sb_{1-y}Sn_y$. — The magnetic properties of compounds

$$Mn_{1+x}Sb_{1-y}Sn_y$$

with the NiAs (B 8-type structure) are given in Table I The Curie-Weiss θ and the Curie constant per gramatom Mn, C_{at}, were determined from high-temperature susceptibility data, the Curie temperature T_c and the saturation moment μ_f from magnetization curves.

Figure 2 shows the reciprocal susceptibility $1/\chi_{at}$ and the magnetization M_{at} of $Mn_{1.15}Sb$. The departure from linearity of the $1/\chi_{at}$ vs T curve, and the tail of M_{at} above T_c, are probably caused by the presence

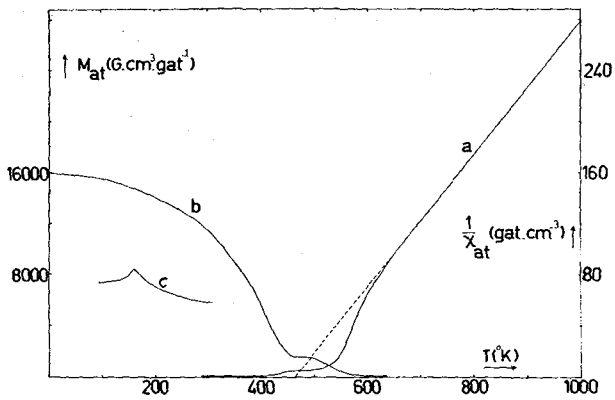

FIG. 2. — Reciprocal susceptibility (curve a) and magnetization (curve b) vs temperature of $Mn_{1.15}Sb$ for $H = 9$ kOe. Curve c represents the magnetization M_{at} for $H = 955$ Oe.

of some Mn_2Sb, a ferrimagnetic compound with $T_c = 550$ °K [2, 3]. The presence of Mn_2Sb could not be seen from X-ray and neutron diffractograms.

The magnetization in low field (curve c of Fig. 2) has a maximum at 160 °K. Similar maxima were observed in $Mn_{1.00}Sb$ at 510 °K for $H = 583$ Oe, and in $Mn_{1.08}Sb$ at 355 and 320 °K for $H = 587$ and 1 145 Oe, respectively. Takei and al. [10] reported for two MnSb samples low-field magnetization maxima at 520 and 320 °K. The maxima are caused by a change of the direction of easy magnetization, from perpendicular to the c-axis at low temperatures to parallel to the c-axis at high temperature. Our data agree with data for the magnetic anisotropy of $Mn_{1+x}Sb$ [3, 4].

Figure 3 shows a typical result for a ternary compound. Heating and cooling curves of $1/\chi_{at}$ do not coincide between T_c and 600 °K. This is presumably due to the presence, at room temperature, of some Mn_2Sb, not detectable by X-rays. At higher tempera-

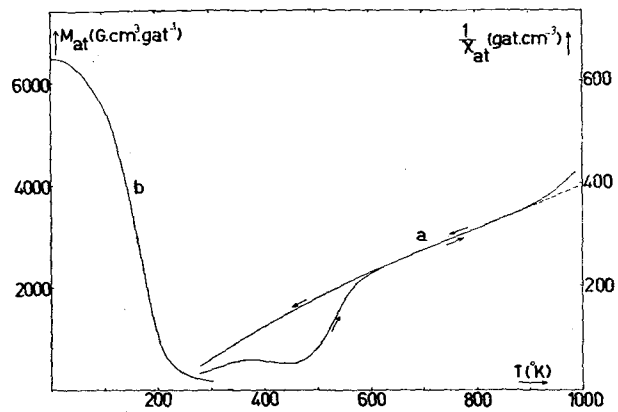

FIG. 3. — Reciprocal susceptibility (heating and cooling ; curves a) and magnetization (curve b) vs temperature of $Mn_{1.33}Sb_{0.75}Sn_{0.25}$ for $H = 9$ kOe.

ture Mn_2Sb dissolves ; cooling (cooling curve of Fig. 3) proceeds too fast for an appreciable precipitation of Mn_2Sb.

Between 600 and 850 °K the $1/\chi_{at}$ vs T cuves show approximatley a Curie-Weiss behaviour. Above 900 °K, χ_{at} decreases, probably as a result of the onset of a decomposition of the compound. This behaviour was also observed for $Mn_{1.00}Sb$, from which Sb begins to separate above 870 °K.

IV. **Neutron diffraction of** $Mn_{1+x}Sb$. — A neutron-diffraction investigation was carried out for $Mn_{1.00}Sb$ and $Mn_{1.15}Sb$. The $Mn_{1.00}Sb$ sample was cooled slowly from 600 °C, the $Mn_{1.15}Sb$ sample was quenched from 750 °C in order to prevent the precipitation of Mn_2Sb.

Neutron powder diffractograms of $Mn_{1.00}Sb$ were obtained at 4.2, 300, 550 and 650 °K, and of $Mn_{1.15}Sb$ at 4.2, 300 and 489 °K. The nuclear and magnetic structures were refined by using a profile refinement method [11]. Nuclear scattering lengths of

$$-0.36 \times 10^{-12} \text{ cm}$$

for Mn [12] and $+0.56 \times 10^{-12}$ cm for Sb were

used (*). The magnetic form factor of Mn was taken from Cromer and Waber's calculations [13].

Good agreement between observed and calculated nuclear intensities was obtained for a NiAs-type structure. In $Mn_{1.00}Sb$ and $Mn_{1.15}Sb$ the octahedral sites are fully occupied by Mn atoms, in $Mn_{1.15}Sb$ there is an occupancy of 15 % of the trigonal-bipyramidal sites by Mn atoms. Thus, the structure of $Mn_{1.15}Sb$ is intermediate between the NiAs ($B\,8_1$)- and the Ni_2In ($B\,8_2$)-type structures, as was already suggested by Teramoto and al. [2].

The neutron-diffraction data show $Mn_{1.00}Sb$ to be a ferromagnet, in agreement with previous investigations [10, 14, 15]. At 4.2 and 300 °K, the magnetic moments are perpendicular, at 550 °K, they are parallel to the c-axis. From the neutron-diffraction data at 4.2 °K we calculate a magnetic moment of

$$3.79 \pm 0.03\ \mu_B/\mathrm{Mn}\ ,$$

a value somewhat larger than that obtained from magnetization data ($\mu_f = 3.55\ \mu_B$).

$Mn_{1.15}Sb$ is a ferrimagnet, with magnetic moments of Mn atoms on octahedral sites antiparallel to the moments of Mn atoms on trigonal-bipyramidal sites. The moments are perpendicular to the c-axis at 4.2 °K, and parallel to the c-axis at 300 °K. At 4.2 °K the magnetic moments of the Mn atoms on octahedral and trigonal-bipyramidal sites are $3.65 \pm 0.07\ \mu_B$ and $3.0 \pm 0.4\ \mu_B$ respectively. This corresponds to a net magnetization of $2.78 \pm 0.11\ \mu_B$ per Mn atom, in good agreement with the observed value of

$$\mu_f = 2.94\ \mu_B\ .$$

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(*) The nuclear scattering length of Sb was determined from a diffractogram of cubic Sb_2O_3, accepting the value of $b_0 = 0.577 \times 10^{-12}$) cm [12].

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