Magnetic Properties of Compounds $(Mn,Cr)_{1+x}Sb$, $V_{1+x}Sb$ and $(Mn,V)_{1+x}Sb$ with B8-type Structures

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Investigations of the compounds $(Mn,Cr)_{1+x}Sb$, $V_{1+x}Sb$ and $(Mn,V)_{1+x}Sb$ with B8-type structures are described. The homogeneity ranges of $(Mn,Cr)_{1+x}Sb$ and $(Mn,V)_{1+x}Sb$ shift to metal-richer compositions with increasing temperature. These compounds are ferrimagnetic. The magnetic-ordering temperature and the spontaneous magnetization decrease with increasing Cr/Mn and V/Mn ratios, respectively.

The homogeneity range of the high-temperature phase $V_{1+x}Sb$ is situated around the composition $x = 0.40$. $V_{1.40}Sb$ shows nearly temperature-independent (Pauli) paramagnetism (except at low temperature).

Introduction

Metallic B8-type phases usually extend over a considerable range of composition. In this respect these phases look more like alloys than like chemical compounds of definite composition. As a rule, NiAs-type transition-metal pnictides (arsenides, antimonides and bismuthides) have a metal-rich character. The structures of these metal-rich phases are intermediate between the NiAs ($B8_1$) and the Ni_2In ($B8_2$) structure.

The existence of a continuous series of mixed crystals between ferromagnetic MnSb and anti-ferromagnetic CrSb has been reported by Hirone c.s. (*1*) and by Lotgering and Gorter (*2*). The latter authors observed small amounts of antimony in samples of gross composition $Mn_{1-x}Cr_xSb$. This indicates that the mixed crystals, as well as the pure compounds (*3*, *4*), have a metal-rich character. With increasing temperature the homogeneity ranges of MnSb (*3*) and CrSb (*4*) shift to compositions with a higher metal content. On heating quenched metal-rich $Mn_{1+x}Sb$ samples, precipitation of Mn_2Sb has been observed (*3*).

Little is known about the B8-type phase in the V–Sb system. Grison and Beck (*5*) found that specimens near the equiatomic composition, which were annealed at 1000°C, had the NiAs-type structure. Meiszner and Schubert (*6*), however, reported a nearly homogeneous alloy of composition $V_{63}Sb_{37}(V_{1.70}Sb)$, annealed at 1250°C, to have a B8-type structure.

According to Sondermann (*7*) it is possible to substitute Mn by V in the NiAs-type compound MnTe. The possibility of substituting Mn by V in MnSb has not yet been reported.

In this paper we report investigations on the existence and the magnetic properties of B8-type compounds of compositions $(Mn,Cr)_{1+x}Sb$, $V_{1+x}Sb$ and $(Mn,V)_{1+x}Sb$. In a previous paper (*8*) we reported results on B8-type compounds of composition $Mn_{1+x}Sb_{1-y}Sn_y$. The results of zero-field nmr investigations on these compounds will be published elsewhere (*9*).[1]

Experimental

Samples of gross compositions $(Mn,Cr)_{1+x}Sb$, $V_{1+x}Sb$ and $(Mn,V)_{1+x}Sb$ were prepared by mixing weighed quantities of the pulverized elements in silica tubes; the tubes were evacuated to a pressure of about 10^{-4} Torr and sealed. These

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[1] More details of these investigations are given in (*10*).

ampoules were heated during one day in a furnace at about 800°C. After quenching to room temperature, the samples were pulverized in a mortar and annealed in sealed and evacuated silica tubes at 800°C during four to seven days. The binary V-Sb samples were annealed at 1100°C. The reaction products were quenched from the annealing temperature.

All samples were examined by X-ray powder diffraction at room temperature and, in some cases, also at higher temperatures. As a rule the homogeneity of a sample was deduced from a Guinier photograph and/or a powder diffracto-gram. Unit-cell dimensions of the B8-type com-pound, present in a sample, were calculated from powder diffractograms by a least-squares method. The standard deviations in the calculated unit-cell dimensions range from 0.001 to 0.003 Å.

Measurements of the magnetization and the magnetic susceptibility were carried out using a Faraday balance (77–1000° K, 9 kOe) and a vibrating-sample magnetometer (P.A.R. type 150 D, 4.2–120° K, 0–55 kOe). In the figures showing the magnetization vs temperature the experimental points obtained with the Faraday balance are indicated. The drawn curves below 77°K represent the measurements with the magnetometer. The susceptibilities and magnet-izations were corrected for the calculated dia-magnetic contribution of the core electrons of the constituting atoms in the samples.

For compounds with a Curie–Weiss behaviour of the susceptibility in certain temperature ranges, the best values for the Curie constant C and the asymptotic Curie temperature θ were calculated, using a least-squares method. Values of μ_{eff} (= effective moment) and μ (= magnetic

moment) were calculated with $C = N\mu^2_{eff}/3k$ and $\mu^2_{eff} = \mu(\mu + 2)$. The calculation of μ is based on the assumption that the orbital moments are completely quenched ($g = 2$).

Values of μ_f (= spontaneous magnetic moment, extrapolated to 0°K) were deduced from magnet-ization vs field-strength curves at 4.2°K by linearly extrapolating the high-field part of these curves to zero field strength. The Curie temperature T_C was taken as the temperature, at which the extrapolated curve of the square of the magnet-ization as a function of the temperature intersects the temperature axis.

Results

$(Mn,Cr)_{1+x}Sb$

Table I gives a survey of the unit-cell dimensions of the B8-type compounds, present in samples with gross composition $(Mn,Cr)_{1+x}Sb$. X-ray

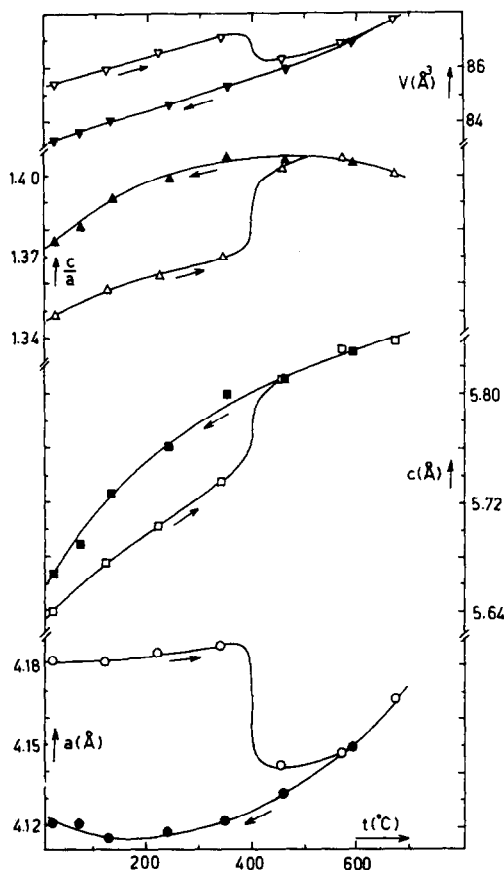
FIG. 1. Unit-cell dimensions of $Mn_{0.50}Cr_{0.75}Sb$ (quenched from 800°C) as a function of the temperature. The open and closed symbols refer to the heating and cooling process, respectively.
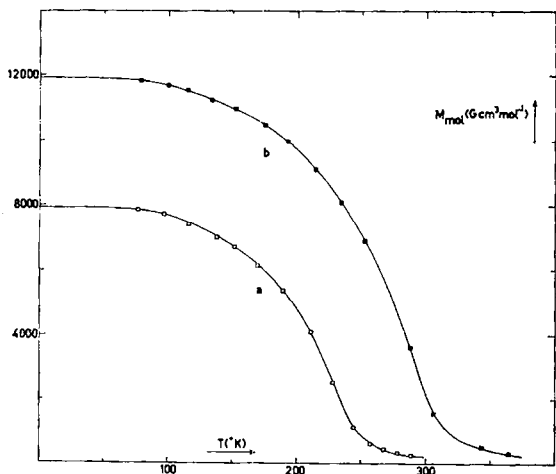
TABLE I

UNIT-CELL DIMENSIONS (AT ROOM TEMPERATURE) OF B8-TYPE COMPOUNDS, PRESENT IN SAMPLES OF GROSS COMPOSITION $(Mn,Cr)_{1+x}Sb$, QUENCHED FROM 800°C.

Composition	a (Å)	c (Å)	c/a	V (Å^3)
$Mn_{1.20}Sb$	4.211	5.714	1.357	87.8
$Mn_{1.00}Cr_{0.20}Sb$	4.204	5.706	1.357	87.3
$Mn_{0.80}Cr_{0.40}Sb$	4.191	5.687	1.357	86.5
$Mn_{1.25}Sb$	4.232	5.705	1.348	88.5
$Mn_{0.93}Cr_{0.32}Sb$	4.225	5.678	1.344	87.8
$Mn_{0.75}Cr_{0.50}Sb$	4.206	5.665	1.347	86.8
$Mn_{0.50}Cr_{0.75}Sb$	4.181	5.638	1.348	85.4
$Mn_{0.25}Cr_{1.00}Sb$	4.152	5.564	1.340	83.1

FIG. 2. Magnetization (per grammol) vs temperature for $Mn_{0.50}Cr_{0.75}Sb$ (a) and $Mn_{0.75}Cr_{0.50}Sb$ (b).

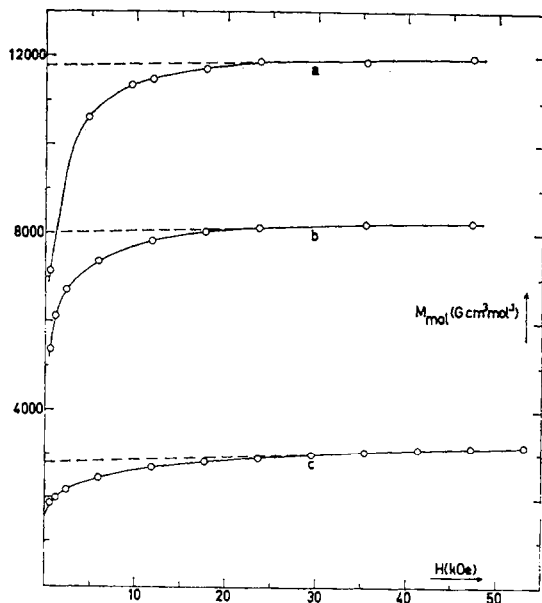diagrams of these samples did not show reflections of a second phase. Reflections of Mn_2Sb could be seen on the X-ray diagrams of a sample with gross composition $Mn_{1.00}Cr_{0.40}Sb$.

A high-temperature Guinier photograph of the compound $Mn_{0.50}Cr_{0.75}Sb$ revealed that on heating this quenched sample there is a sudden change of the lattice parameters at about 400°C (Fig. 1). The sudden change of the lattice parameters at 400°C during the heating process

FIG. 3. Magnetization (per grammol) vs field strength at 4.2°K for $Mn_{0.75}Cr_{0.50}Sb$ (a), $Mn_{0.50}Cr_{0.75}Sb$ (b) and $Mn_{0.25}Cr_{1.00}Sb$ (c).

probably arises from a transition from the quenched state to a state of thermodynamic equilibrium. On cooling the sample slowly from 700°C a gradual change of the unit-cell dimensions with the temperature is observed (Fig. 1). The
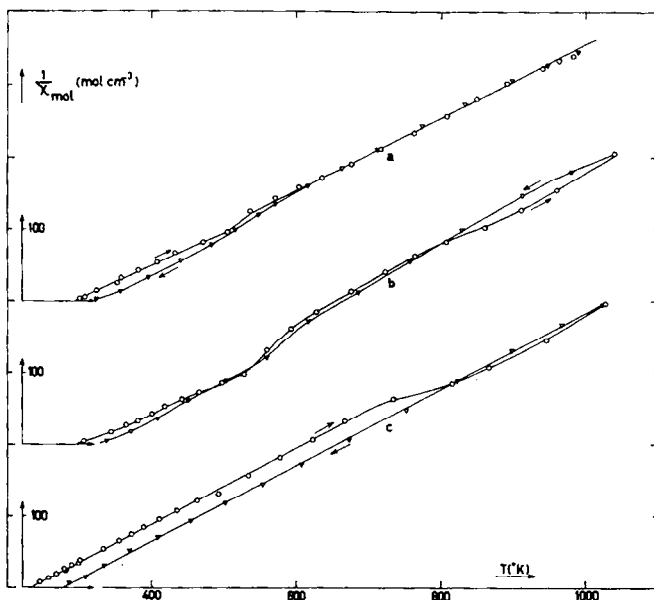

FIG. 4. Reciprocal magnetic susceptibility (per grammol) vs temperature for $Mn_{0.93}Cr_{0.32}Sb$ (a), $Mn_{0.75}Cr_{0.50}Sb$ (b) and $Mn_{0.50}Cr_{0.50}Sb$ (c). Heating and cooling runs are indicated by symbols o and ∇, respectively.

TABLE II

MAGNETIC PROPERTIES OF $(Mn, Cr)_{1+x}Sb$. THE TEMPERATURE RANGES (°K) IN WHICH APPROXIMATE CURIE–WEISS BEHAVIOUR IS OBSERVED, ARE INDICATED IN PARENTHESES

Composition	$\mu_f(\mu_B/\text{molecule})$	$T_C(°K)$	θ (°K)	$C_{mol}(\text{cm}^3 \text{ °K mol}^{-1})$	$\mu_{eff}(\mu_B/\text{molecule})$	$\mu(\mu_B/\text{molecule})$
$Mn_{1.00}Cr_{0.20}Sb$	2.73					
$Mn_{0.80}Cr_{0.40}Sb$	2.37	330				
$Mn_{0.93}Cr_{0.32}Sb$		286	286	2.02 (600–1000)	4.02	3.14
$Mn_{0.75}Cr_{0.50}Sb$	2.11	295	292	1.83 (600–1000)	3.83	2.96
$Mn_{0.50}Cr_{0.75}Sb$	1.43	235	$\begin{cases}232\\276\end{cases}$	1.89 (300 → 650) 1.89 (1000 → 300)	3.89 3.89	3.02 3.02
$Mn_{0.25}Cr_{1.00}Sb$	0.50					

differences between the unit-cell dimensions of the slowly cooled sample and those of the quenched sample indicate that the composition $Mn_{0.50}$-$Cr_{0.75}Sb$ falls outside (at the metal-rich side) the homogeneity range at room temperature. On the Guinier photograph no reflections of a second phase were observed, however.

Magnetization vs temperature curves of $Mn_{0.50}Cr_{0.75}Sb$ and $Mn_{0.75}Cr_{0.50}Sb$ are shown in Fig. 2. Curves giving magnetization as a function of the field strength at 4.2°K are shown in Fig. 3. The magnetic-ordering temperature and the magnetization decrease with increasing Cr/Mn ratio.

Figure 4 shows reciprocal susceptibility vs temperature curves. Differences between heating and cooling curves were observed, especially for $Mn_{0.50}Cr_{0.75}Sb$. After the high-temperature measurements the Curie temperatures of all three samples were higher than those of the original quenched samples. The same effect has been observed by Teramoto and Van Run for metal-rich MnSb samples (3). These results indicate

that the compositions of the original quenched B8-type compounds lie outside (at the metal-rich side) the homogeneity range at low temperature. Therefore, during the susceptibility measurements a second metal-richer phase can precipitate at low temperature (e.g. Mn_2Sb or Cr).

The sudden change of the lattice parameters of $Mn_{0.50}Cr_{0.75}Sb$ at 400°C is reflected in the heating curve of the reciprocal susceptibility (Fig. 4). Table II gives a survey of the magnetic properties of the compounds $(Mn,Cr)_{1+x}Sb$.

$V_{1+x}Sb$

Table III gives a survey of the unit-cell dimensions of the B8-type compounds, present in samples with gross composition $V_{1+x}Sb$, and of the contaminations therein. The data in Table III show that at 1100°C (the temperature from which these samples were quenched) the B8-type phase has a small existence region around the com-

TABLE III

UNIT-CELL DIMENSIONS (AT ROOM TEMPERATURE) OF B8-TYPE COMPOUNDS, AND CONTAMINATIONS, PRESENT IN SAMPLES OF GROSS COMPOSITION $V_{1+x}Sb$, QUENCHED FROM 1100°C

x	a (Å)	c (Å)	c/a	V (Å³)	Contamination(s)
0.25	4.277	5.451	1.274	86.4	VSb_2, Sb
0.30	4.280	5.455	1.275	86.5	VSb_2, Sb
0.40	4.290	5.447	1.270	86.8	
0.50	4.297	5.444	1.267	87.1	V_3Sb
0.75	4.296	5.444	1.267	87.0	V_3Sb

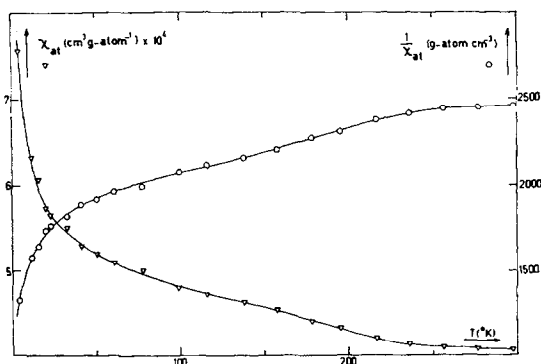FIG. 5. Magnetic susceptibility (symbols ∇) and reciprocal magnetic susceptibility (symbols o) per gram-atom V vs temperature for $V_{1.40}Sb$.

TABLE IV

UNIT-CELL DIMENSIONS (AT ROOM TEMPERATURE) OF B8-TYPE COMPOUNDS,
AND CONTAMINATIONS, PRESENT IN SAMPLES WITH GROSS COMPOSITION
$(Mn,V)_{1+x}Sb$, QUENCHED FROM 800°C

Composition	a (Å)	c (Å)	c/a	V (Å^3)	Contamination(s)
$Mn_{0.80}V_{0.20}Sb$	4.184	5.716	1.366	86.7	Sb, ?
$Mn_{0.50}V_{0.50}Sb$	4.223	5.630	1.333	87.0	Sb, ?
$Mn_{1.00}V_{0.10}Sb$	4.209	5.715	1.358	87.7	Sb, ?
$Mn_{1.00}V_{0.20}Sb$	4.218	5.711	1.354	88.0	
$Mn_{0.90}V_{0.30}Sb$	4.202	5.704	1.357	87.2	
$Mn_{0.80}V_{0.40}Sb$	4.205	5.687	1.352	87.1	
$Mn_{0.75}V_{0.50}Sb$	4.233	5.674	1.340	88.1	
$Mn_{0.50}V_{0.75}Sb$	4.237	5.614	1.325	87.3	
$Mn_{0.25}V_{1.00}Sb$	4.253	5.537	1.302	86.7	?
$Mn_{1.00}V_{0.30}Sb$	4.251	5.691	1.339	89.1	
$Mn_{1.00}V_{0.40}Sb$	4.282	5.663	1.323	89.9	V_3Sb
$Mn_{1.00}V_{0.50}Sb$	4.280	5.668	1.324	89.9	V_3Sb

position $V_{1.40}Sb$ (58.3 at. % V). Near the Sb-rich limit of the homogeneity range the samples were contaminated with VSb_2 and Sb, near the V-rich limit contaminations of V_3Sb were observed. The unit-cell dimensions of the B8-type phase are in good agreement with the results of previous investigations (5, 6). Our conclusion about the existence region is not in agreement with these previous investigations, however. A sample with gross composition $V_{1.00}Sb$, annealed at and quenched from 750°C, showed a complicated

X-ray pattern in which no reflections of a B8-type compound were observed. This is in accordance with the results of Meiszner and Schubert (6).

The magnetic susceptibility of the single-phase sample $V_{1.40}Sb$ is shown in Fig. 5. The susceptibility does not show a Curie–Weiss behaviour. The susceptibility increases slightly with decreasing temperature above about 40°K, and increases rapidly below this temperature. The magnetization of $V_{1.40}Sb$ at 4.2 °K increases linearly with
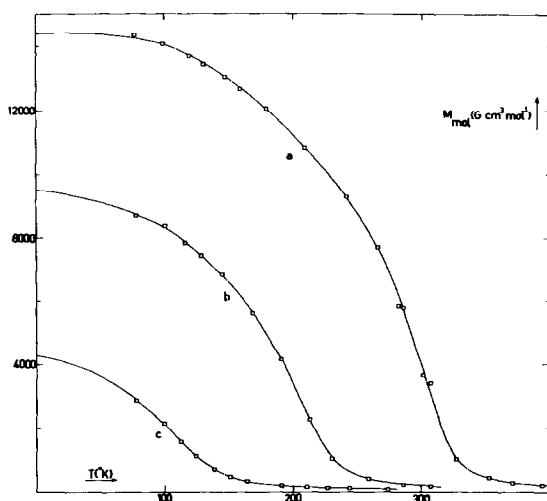

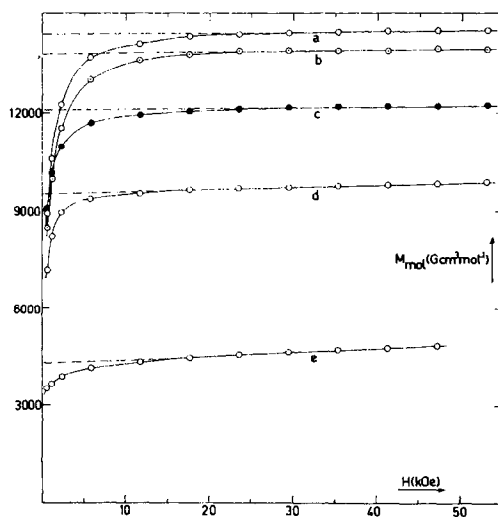FIG. 6. Magnetization (per grammol) vs temperature for $Mn_{1.00}V_{0.20}Sb$ (a), $Mn_{0.75}V_{0.50}Sb$ (b) and $Mn_{0.50}V_{0.75}Sb$ (c).

FIG. 7. Magnetization (per grammol) vs field strength at 4.2°K for $Mn_{1.00}V_{0.20}Sb$ (a), $Mn_{0.90}V_{0.30}Sb$ (b), $Mn_{0.80}V_{0.40}Sb$ (c), $Mn_{0.75}V_{0.50}Sb$ (d) and $Mn_{0.50}V_{0.75}Sb$ (e).
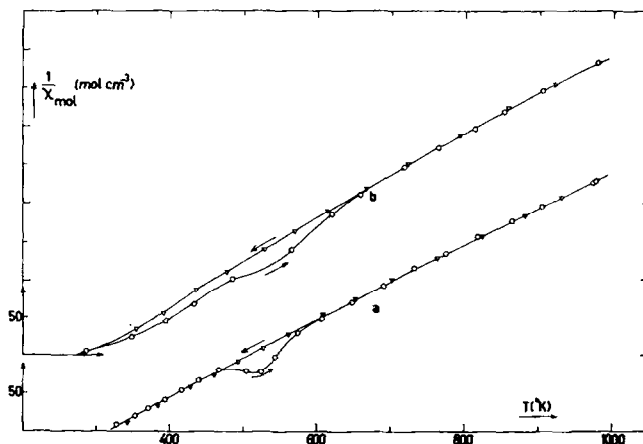
FIG. 8. Reciprocal magnetic susceptibility (per grammol) vs temperature for $Mn_{1.00}V_{0.20}Sb$ (a) and $Mn_{0.80}V_{0.40}Sb$ (b). Heating and cooling runs are indicated by symbols o and ∇, respectively.

the magnetic field strength, with a slope of 0.56×10^{-3} cm^3 g-at^{-1}.

$(Mn,V)_{1+x}Sb$

Table IV gives a survey of the unit-cell dimensions of the B8-type compounds, present in samples with gross composition $(Mn,V)_{1+x}Sb$, and of the contaminations therein. X-ray diagrams of the samples with the smallest total metal content (i.e., the first three samples of Table IV) showed in addition to reflections of a B8-type compound and antimony, reflections of an unidentified phase. The additional reflections in the X-ray diagram of the sample $Mn_{0.25}V_{1.00}Sb$

correspond to the strongest reflections in the X-ray diagram of the sample $V_{1.00}Sb$, quenched from 750°C

Magnetic measurements were carried out on the single-phase samples, mentioned in Table IV. Magnetization vs temperature curves are shown in Fig. 6. Curves giving the magnetization as a function of the field strength at 4.2°K are shown in Fig. 7. For field strengths above about 20 kOe the magnetization increases linearly with the field. The magnetic-ordering temperature and the magnetization decrease with increasing V/Mn ratio.
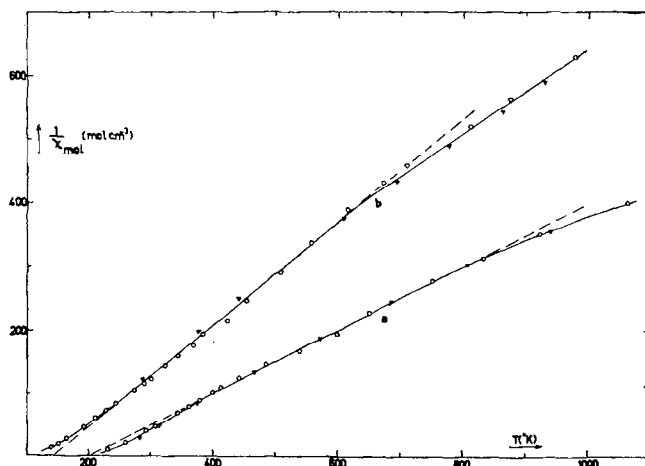
Reciprocal susceptibility vs temperature curves

FIG. 9. Reciprocal magnetic susceptibility (per grammol) vs temperature for $Mn_{0.75}V_{0.50}Sb$ (a) and $Mn_{0.50}V_{0.75}Sb$ (b). Heating and cooling runs are indicated by symbols o and ∇, respectively.

TABLE V

Magnetic Properties of $(Mn,V)_{1+x}Sb$. The Temperature Ranges (°K) in Which Approximate Curie–Weiss Behaviour is Observed, are Indicated in Parentheses

Composition	μ_f(μ_B/molecule)	T_C (°K)	θ (°K)	C_{mol}(cm^3 °K mol^{-1})	μ_{eff}(μ_B/molecule)	μ(μ_B/molecule)
$Mn_{1.00}V_{0.20}Sb$	2.58	315	314	1.96 (350–800)	3.96	3.09
$Mn_{0.90}V_{0.30}Sb$	2.47					
$Mn_{0.80}V_{0.40}Sb$	2.17		280	1.78 (450–850)	3.78	2.91
$Mn_{0.75}V_{0.50}Sb$	1.71	200	200	1.99 (350–850)	3.99	3.11
$Mn_{0.50}V_{0.75}Sb$	0.78	140	$\begin{cases}147\\30\end{cases}$	1.22 (250–700) 1.51 (600–1000)	3.12 3.48	2.28 2.62
$Mn_{1.00}V_{0.30}Sb$	2.10					

are shown in Figs. 8 and 9. The shape of the curves for $Mn_{1.00}V_{0.20}Sb$ and $Mn_{0.80}V_{0.40}Sb$ (Fig. 8) indicates that a small amount of Mn_2Sb precipitates on heating these quenched samples (3, 8). At higher temperature the slopes of the curves of $Mn_{0.75}V_{0.50}Sb$ and $Mn_{0.50}V_{0.75}Sb$ (Fig. 9) decrease; this could be due to a temperature-independent contribution of the vanadium atoms. The results of a Curie–Weiss analysis of the susceptibility curves are given in Table V.

Discussion

Our results confirm the existence of a continuous solid-solution series with B8-type structures between $Mn_{1+x}Sb$ and $Cr_{1+x}Sb$, and the existence of a B8-type phase $V_{1+x}Sb$ at high temperature. A series of solid solutions with B8-type structures exists also between $Mn_{1+x}Sb$ and $V_{1+x}Sb$.

Magnetic measurements on quenched samples indicate that the composition of the metal-rich B8-type compounds changes when the samples are heated. This is due to the precipitation of a second phase. These results, combined with the results of the high-temperature X-ray diffraction study of $Mn_{0.50}Cr_{0.75}Sb$, indicate that with increasing temperature the homogeneity ranges of the B8-type phases shift to metal-richer compositions.

The magnetic structures of $Mn_{1-x}Cr_xSb$ consist of ferromagnetic (001) sheets with the spins in adjacent sheets alternating in orientation (11). In compounds $(Mn,Cr)_{1+x}Sb$ with $x > 0$ the presence of metal atoms in the interstitial trigonal bipyramidal sites may give rise to more complicated spin arrangements. The experi-

mental results obtained so far do not allow a detailed interpretation of the magnetic structure and properties.

The shape of the susceptibility vs. temperature curves of $V_{1.40}Sb$ and $(Mn,V)_{1+x}Sb$ indicate that the V atoms give rise to a (nearly) temperature-independent contribution to the magnetic susceptibility. Apparently, in these compounds the d electrons of V do not produce a local magnetic moment.

Acknowledgments

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