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MAGNETIC AND CRYSTALLOGRAPHIC PROPERTIES OF SEVERAL Cl_b TYPE HEUSLER COMPOUNDS

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The compounds NiMnSb and IrMnGa were studied by neutron diffraction. The former compound has the cubic Cl_b crystal structure with an ideal site occupancy of the atoms. Below 750 K the compound is ferromagnetically ordered. The magnetic moments are confined to the Mn atoms ($4.0\mu_B$/Mn). The compound IrMnGa has a crystal structure related to the Cl_b type but characterized by a high atomic disorder. Results of magnetic measurements are presented for NiMnSb, CuMnSb and IrMnGa. The results of these measurements are in accord with the occurrence of high atomic ordering in the first two compounds but point to high atomic disorder in the latter material. Total energies and Mn moments derived from band-structure calculations are presented for three different types of site occupancies in NiMnSb. The lowest total energy as well as the correct value for the Mn moment correspond to the site occupancy found by means of the neutron diffraction.

1. Introduction

Band-structure calculations reported recently for Mn-base Heusler compounds of the Cl_b structure showed that several of these intermetallics have unique features making them distinct from other intermetallics or alloys: They are normal metals for the majority spin electrons but semiconductors for the minority spin electrons [1]. The presence of the energy gap near E_F in the minority spin band is intimately connected with the point symmetry at the Mn-sites. This symmetry is lower in the Cl_b type compounds than in the normal $L2_1$ type Heusler compounds, owing to the fact that one type of atomic sites of the latter is unoccupied in the former. To be more specified, in the $L2_1$ type Heusler compounds one discerns four types of sites

$$A(0\ 0\ 0),\quad B(\tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{1}{4}),\quad C(\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}),\quad D(\tfrac{3}{4}\ \tfrac{3}{4}\ \tfrac{3}{4}),$$

the C site being unoccupied in the Cl_b type of structure. It is essential for the occurrence of the energy gap in the minority spin band that the Mn atoms occupy the B sites. This site occupancy of the Mn atoms is currently accepted to occur in Mn-base Cl_b type compounds and was also tacitly assumed in the band-structure calculations mentioned above [1]. However, there is some dubiousness associated with this site occupancy since Szytuła et al. [2] proposed a different site occupancy for Mn in NiMnSb. For clarifying this point we have reinvestigated this compound by neutron diffraction. In order to broaden the experimental basis for the study of the phenomenon of half-metallic ferromagnetism we included magnetic measurements in our investigation. Several of the Mn-base Cl_b type compounds such as CuMnSb and IrMnGa order antiferromagnetically at low temperatures. This opens the possibility that apart from half-metallic ferromagnets there might also

exist a class of materials that can be characterized as half-metallic antiferromagnets. In the present study we have investigated whether the site occupancy in the antiferromagnetic Cl_b compounds is favourable for the occurrence of half-metallic antiferromagnetism.

2. Experimental

The compounds NiMnSb. CuMnSb and IrMnGa were prepared by arc melting in an atmosphere of purified argon gas. The purity of the starting materials was 99.9%. X-ray diffraction showed these materials to be single-phase. The magnetic properties of the three compounds were studied in the range 4.2–300 K using the Faraday method. For NiMnSb magnetic isotherms were studied at various temperatures in magnetic fields up to 1440 kA/m by means of a vibrating sample magnetometer. The Curie temperature of this compound was determined also by differential scanning calorimetry (DSC) in purified argon, using a heating rate of 50 K/min.

Neutron diffraction data of NiMnSb and IrMnGa were collected on the powder diffractometer at the HFR reactor at Petten at 4.2 K. Neutrons of wavelength 2.5904(5) Å were obtained after reflection from the (111) planes of a copper crystal. The λ/n contamination had been reduced to less than 0.1% using a pyrolytic graphite filter. Soller slits with a horizontal divergence of 30′ were placed between the reactor and monochromator and in front of the four ^{3}He counters. The maximum absorption correction for NiMnSb was 2.4%, $\mu R = 0.309$ [3]. Because of the high linear absorption coefficient of IrMnGa ($\mu = 8.4$ cm^{-1}) a powdered sample of this compound was diluted with Al powder. An intensity gain by a factor of a about 8 was obtained by this procedure. Nevertheless it still proved necessary to correct the data for absorption, the maximum absorption being 23%, $\mu R = 1.0$.

3. Experimental results

3.1. Magnetic properties

From the temperature dependence of the magnetization of NiMnSb it was derived that this compound orders ferromagnetically near $T_c = 760$ K, confirming earlier results of Castelliz [4] and Szytuła et al. [2] who reported a magnetic ordering temperature of 750 and 730 K, respectively. From the magnetic isotherm at 4.2 K a saturation moment equal to $4.08\mu_B$ per formula unit was derived which is slightly higher than the value $3.80\mu_B$ found by Castelliz. The magnetic properties of NiMnSb close to its Curie temperature were studied in more detail. Results are shown in fig 1 where we have plotted σ^2 versus H/σ (Arrott plot). It is seen that the isotherms below as well as above T_c give rise to straight lines. The Curie temperature is defined by means of the isotherm passing through the origin. By interpolation the value $T_c = 756$ K is found. The DSC trace of NiMnSb obtained in the region 300–900 K showed an endothermic heat effect with a peak at $T_c = 743$ K, which is in satisfactory agreement with the magnetic measurements.

Results of magnetic measurements made on CuMnSb are shown in fig. 2. A Néel type transition is observed at $T_N = 62$ K. Above T_N the
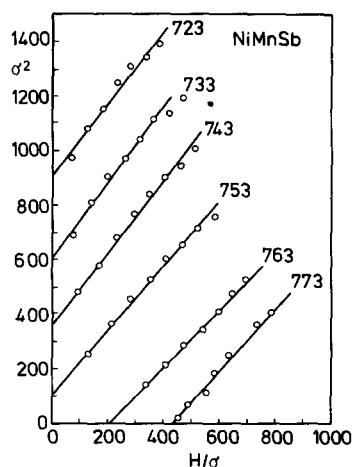

Fig. 1. Arrot plot for NiMnSn. The magnetization σ is in units of emu, the applied field H in units of Oe.
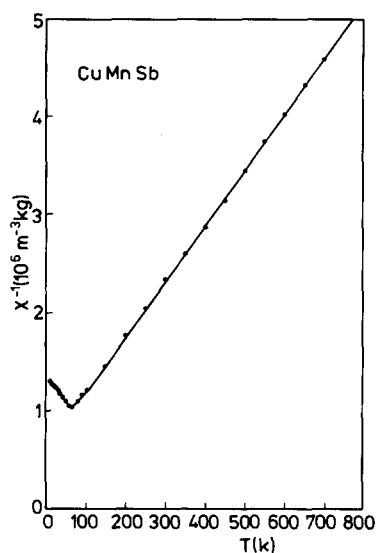
Fig. 2. Temperature dependence of the reciprocal susceptibility in CuMnSb.

reciprocal susceptibility behaves according to the Curie–Weiss law. From the slope and the horizontal intercept of the χ^{-1} versus T plot we derived the values $\mu_{eff} = 5.18 \ \mu_B$/Mn and $\theta_p = -120$ K for the effective moment and asymptotic Curie temperature, respectively. The values of T_N and θ_p differ appreciably from those obtained by Endo ($T_N = 55$ K; $\theta_p = -160$ K) [5].

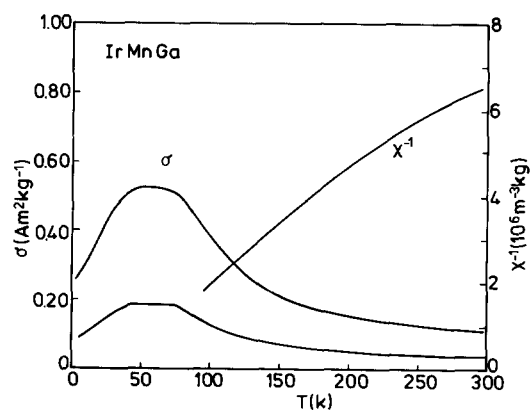Results obtained on IrMnGa are shown in fig. 3. The most likely interpretation of the tempera-

Fig. 3. Temperature dependence of the magnetization σ (240 and 810 A/m) and the reciprocal susceptibility χ^{-1} in IrMnGa.

ture dependence of the magnetization is the occurrence of antiferromagnetic ordering near 60 K, involving a rather smeared out magnetic phase transition. The magnetization at 4.2 K is rather low and more than two orders of magnitude smaller than in NiMnSb. It is rather unlikely therefore that the peculiar $\sigma(T)$ curve is due to the presence of substantial amounts of ferromagnetic impurities or ferromagnetic clusters. A similar type of $\sigma(T)$ curve was also found by Hames and Crangle [6].

3.2. Neutron diffraction

Neutron diffraction measurements were made at 4.2 K and at room temperature. The diffraction patterns observed in both cases were basically the same. Results of neutron measurement made at 4.2 K are shown in fig. 4. The neutron diffraction diagram is composed of diffraction lines due to NiMnSb and of those due to the cryostat. The diffraction patterns were analysed using Rietveld's profile refinement technique [7] together with the description for the exact peak shape as given by Van Laar and Yelon [8]. For the scattering lengths the values 1.030×10^{-12} cm for Ni, -0.373×10^{-12} cm for Mn, 1.060×10^{-12} cm for Ir and 0.564×10^{-12} cm for Sb are used. Form factors were taken from the paper published by Freeman and Watson [9]. First we investigated the occupancy of the four positions of the Cl_b structure type in NiMnSb. Seven different posibilities were considered, indicated by the numbers 1–7 in the first column of table 1. The quality of the fit between experimental and calculated diffractograms is given by the expression $\chi_\gamma^2 = \Sigma_i w_i [y_i(\text{obs}) - y_i(\text{calc})]^2/\gamma$, where $y_i(\text{obs})$ and $y_i(\text{calc})$ are the observed and calculated values of the ith measuring point and w_i is its statistical weight. The number of points minus the number of parameters is indicated by γ. For the investigation of the relative occupancies we used only nuclear neutron intensities. The χ_γ^2 values and the corresponding reliability factors R ($R = \Sigma|I(\text{obs}) - I(\text{calc})|/I(\text{calc})$) obtained after refinement are included in table 1. It is seen that the occupation scheme no. 1 leads to a χ_γ^2 value which is generally an order of magnitude smaller than the other possibilities considered. Furthermore, no lower values for χ_γ^2 and R were
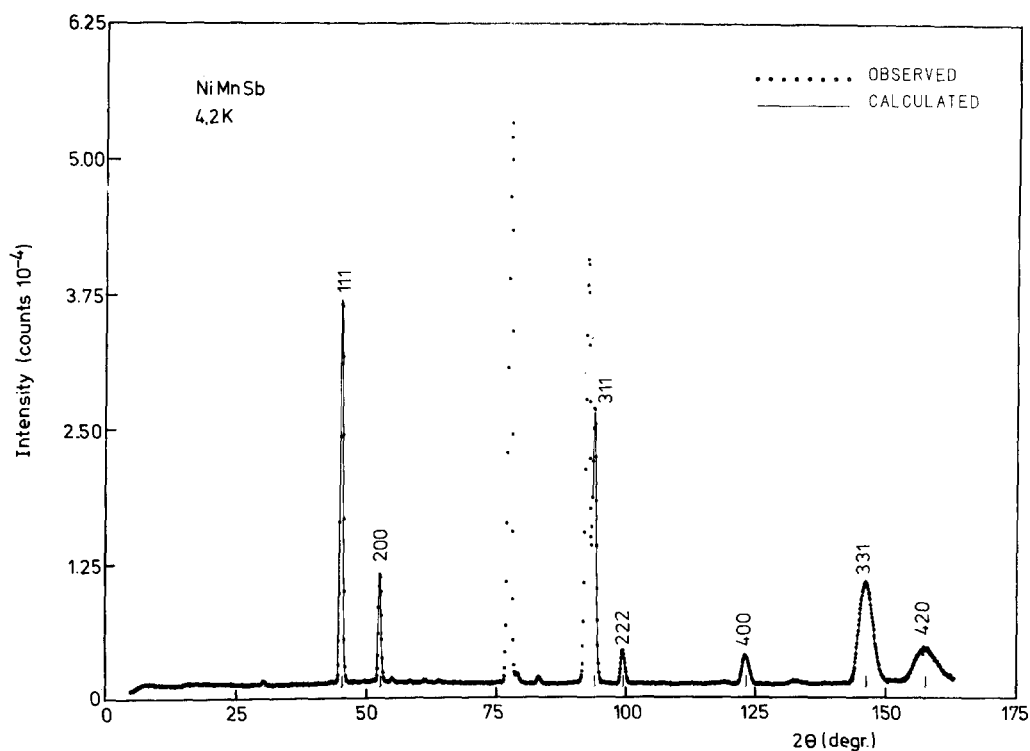
Fig. 4. Neutron diffraction diagram obtained at 4.2 K for NiMnSb. The full line represents a calculated fit to the experimental data points of the neutron diffraction profile. The two large peaks, near the center of the diagram, are due to the cryostat.

obtained when allowing a 10% site interchange between the atoms in the atomic arrangement given by no. 1 in table 1.

Subsequently the atomic positions according to scheme 1 were used for the refinement of the magnetic structure, considering nuclear as well as magnetic contributions. The values for the collin-

ear Ni and Mn moments were refined separately. All these solutions were, however, contradictory to the experimental value of the saturation moment and thus were left out of consideration. In order to obtain solutions that were able to reproduce the observed saturation moment in a satisfactory way it proved necessary to put the Ni moment equal to

Table 1
Various possibilities of site occupancy in NiMnSb. The values of χ_γ^2 and the corresponding R-factors pertain to refinement procedures in which only nuclear intensities were considered. A statistical distribution of X and Y atoms over two sites is indicated by (X,Y)

No.	0 0 0	$\frac{1}{4} \frac{1}{4} \frac{1}{4}$	$\frac{1}{2} \frac{1}{2} \frac{1}{2}$	$\frac{3}{4} \frac{3}{4} \frac{3}{4}$	χ_γ^2	R-factor
1	Ni	Mn	–	Sb	25	3.1
2	Ni		Mn	Sb	472	25
3	(Ni,Mn)		–	Sb	1201	65
4	Ni	–	(Mn,Sb)		519	43.7
5	(Ni)		Mn	Sb	457	41.4
6	(Ni)		(Mn,Sb)		988	56.4
7	Ni	(Mn,Sb)	–	(Mn,Sb)	95	17.2

Table 2
Results of the final refinement made on the basis of the neutron diffraction profile obtained for NiMnSb and IrMnGa at 4.2 K. The Mn moments M_{Mn} are expressed in μ_B per Mn atom. For the other symbols, see text

Compound	χ_γ^2	R_{nucl} (%)	R_{mag} (%)	M_{Mn}	a(Å)
NiMnSb	18.7	2.1	2.3	4.0(2)	5.9130(1)
IrMnGa	2.9	4.6	3.9	0.6(4)	6.0236(6)

zero. The results of the final refinement made under this restriction are given in table 2. Observed and calculated neutron diffraction profiles for this refinement can be compared in fig. 4. It can be concluded from these results that the Ni atoms in NiMnSb do not carry a magnetic moment. The magnitude of the moments of the Mn atoms is about 4.0 μ_B per atom.

It follows from the results described in section 3.1 that IrMnGa is not magnetically ordered at room temperature. The neutron diffraction profile obtained at 300 K was used to determine the relative distribution of the three atomic species over the four sites available. Results are summarized in table 3, where the R and χ_γ^2 values corresponding to 6 different types of atomic occupancies are compared. The lowest χ_γ^2 value was obtained for 62.6% Ir at 0 0 0 and 37.4% Ir at $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. In view of the fact that the atomic structure of IrMnGa is highly disordered no attempt was made to determine its magnetic structure at temperatures below $T_N = 60$ K. The refinement of the neutron diffraction profile obtained at 4.2 K led to a ferromagnetic component at the Mn site equal to

0.6μ_B/Mn. In view of the high degree of atomic disorder observed this value may not be a very relevant one.

4. Discussion

The neutron diffraction results presented in the preceding section have shown that the atomic positions of Ni, Mn and Sb adopted earlier for the calculation of the energy band structure of the compound NiMnSb are the correct ones, indeed [1]. These atomic positions are different from those proposed on the basis of neutron diffraction results by Szytuła et al. [2]. These latter authors found the lowest R factor (3.7%) for an atomic arrangement where the Ni atoms occupy the 0 0 0 position and the Sb atoms occupy the $\frac{3}{4} \frac{3}{4} \frac{3}{4}$ position but where the Mn atoms reside at the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ position. For the most likely atomic arrangement found by us (case 1 in table 1) Szytuła et al. report an R factor equal to 23.4% compared to the value $R = 3.1\%$ listed in table 1. It is very difficult to reconcile this discrepancy in results. The most plausible explanation seems an erroneous heading of table 1 of Szytuła et al., the symbols B and C being interchanged.

It follows from the analysis of the neutron diffraction data presented in section 3.2 that it is rather unlikely that there is much site interchange of the atoms in the atomically ordered structure of NiMnSb. Shtrikman and Wohlfarth [10] considered fluctuations Δc in the concentration c of the magnetic atoms in binary alloy systems and showed that the following relation holds for the magnetic

Table 3
Comparison of various atomic arrangements for the room temperature neutron diffraction profiles of IrMnGa

No.	0 0 0	$\frac{1}{4} \frac{1}{4} \frac{1}{4}$	$\frac{1}{2} \frac{1}{2} \frac{1}{2}$	$\frac{3}{4} \frac{3}{4} \frac{3}{4}$	χ_γ^2	R
1	Ir	Mn	–	Ga	52	42
2	Ir	–	Mn	Ga	66	51
3	Ga	(IrMn	–	IrMn) [a]	7.2	14.0
4	Ga	(IrMn	–	IrMn) [b]	6.2	10.3
5		(IrMn) [a]	–	Ga	57	48
6		(IrMn) [b]	–	Ga	2.1	3.7

[a] Atoms statistically distributed over both sites.
[b] Occupation factor refined, see main text.

isotherms

$$a\left[1 - \frac{\alpha^2}{\left(a + 3b\langle\sigma\rangle^2\right)^2}\right] - b\langle\sigma\rangle^2 = \frac{H}{\langle\sigma\rangle},$$

where a and b are constants and where α^2 is proportional to $\langle\Delta c^2\rangle$. Application of this formalism to NiMnSb seems justified since we have found by means of neutron diffraction that the magnetism is exclusively due to a single type of atoms. The quantity Δc can therefore be taken to reflect the fluctuations of the Mn concentration, present if site exchange of the different atoms in NiMnSb were non-negligible. Inspection of the results contained in fig. 1 shows that straight lines are obtained when σ^2 is plotted versus H/σ, meaning that α is very small or zero. This can be regarded as further evidence for the absence of large atomic disorder in NiMnSb.

In order to investigate the effect of site interchange in more detail we performed ASW calculations for three distinct atomic arrangements, possible in the Heusler Cl_b structure. For these calculations we used the same procedures and approximations as described in ref. [1]. The results of the calculations are summarized in table 4. Structure 1 was considered by us already in a previous report [1]. Structure 2 can be derived by interchanging the nickel and manganese atoms. Structure 3 was proposed by Szytula et al. [2]. It is found that structures 2 and 3 are less stable than structure 1 by 420 and 503 kcal/mol, respectively (which is about twice the heat of evaporation of the compound).

The magnetic moment of a half-metallic ferromagnet is an integer number. This is reflected in table 4 by the M value corresponding to structure

Table 4
Various possibilities of site occupancy in NiMnSb. The ΔE values represent total energies calculated with respect to the most stable structure (no. 1) in kcal/mol. The theoretically derived values of the magnetic moments are listed under M

No.	0 0 0	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$\frac{3}{4}\frac{3}{4}\frac{3}{4}$	ΔE	M
1	Ni	Mn	–	Sb	0	4.00
2	Mn	Ni	–	Sb	420	3.32
3	Ni	–	Mn	Sb	503	3.11

1 ($4.00\mu_B$), which is virtually the same as the experimental value (see section 3). The magnetic moment values corresponding to structures 2 and 3 ($3.32\mu_B$ and $3.11\mu_B$, respectively) differ significantly from the experimental value.

A relatively high atomic disorder was observed by means of neutron diffraction to occur in IrMnGa. This feature is reflected in the unsharp magnetic ordering transition. It implies that this material does not qualify for consideration as half-metallic antiferromagnet. It was shown in ref. [1] that the basic requirement for the occurrence of an energy gap near E_F in the band of minority spin electrons is the broken symmetry at the Mn site in the Cl_b structure with respect to the normal Heusler alloys of $L2_1$ structure. This broken symmetry is caused by the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ sites being unoccupied. Inspection of the site occupation presented in table 3 (no. 6) for IrMnGa shows that this feature has remained preserved. However, only a fraction of the Mn atoms resides at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, and from these Mn atoms only a fraction will have an undisturbed neighbour atom coordination consisting of two interpenetrating tetrahedrons of Ir atoms and empty sites, respectively. Moreover, part of the Mn atoms occupy the 0 0 0 positions, meaning that the band structure of IrMnGa will differ considerably from that of, for instance, PtMnSb. A more promising candidate for qualifying as half-magnetic antiferromagnet seems CuMnSb. From the electronic point of view it is more like NiMnSb than IrMnGa. Neutron diffraction showed that the magnetic structure corresponds to $\pi\ \pi\ \pi$ at 4.2 K [11]. This means that the magnetic unit cell edge is twice as large as the chemical unit cell edge below T_N. Above T_N the doubling of the unit cell needs not to be considered, the Mn atoms still being magnetic. This latter fact follows from the observation of Curie–Weiss behaviour with a sizable effective moment. The results of neutron diffraction measurements showed that atomic disorder is relatively unimportant in CuMnSb. Also the results of the magnetic measurement point into this direction. The paramagnetic–antiferromagnetic transition is relatively sharp while deviations from linear χ^{-1} versus T behaviour are unimportant and are restricted to the immediate vicinity of T_N. This means that short range magnetic

ordering that would be associated with atomic site interchange is relatively unimportant.

Concluding, the Heusler compounds NiMnSb and CuMnSb crystallize in the cubic Cl_b structure with little or no deviations from the ideal site occupancy. In these materials the Mn atoms occupy the B type atomic site with T_d symmetry which is a prerequisite for the formation of an energy gap in the minority spin band. From the results of magnetic measurements and neutron diffraction measurements we derived that Ni has no magnetic moment or only a very small magnetic moment in NiMnSb. The Mn atoms carry a moment equal to $4.0\mu_B$, which is in excellent agreement with the results of band-structure calculations. The compound IrMnGa has a crystal structure similar to the Cl_b type but shows a considerable atomic disorder between the Ir and Mn atoms.

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