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SPIN DENSITY DISTRIBUTION IN MnFe<sub>0.09</sub>Sb

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1. Introduction. - In the series of 3d-metal-monoantimonides (TiSb ... NiSb) MnSb has attracted special interest due to its strong ferromagnetism ($T_c = 573$ K (1)). The physical properties of this compound have been interpreted either within the framework of the theory of metallic alloys, which leads to a Mn<sup>3d</sup> configuration (2), or within the framework of ionic band models which leads to a Mn<sup>4d</sup><sup>5s</sup> configuration (3). A polarized neutron diffraction study of nearly stoichiometric MnSb has shown that about four d-electrons are localized on Mn (4). However, physical properties such as magnetic moment magnitude, magnetic ordering and transition temperatures, and lattice parameters are known to be strongly influenced by a T-metal occupation of the interstitial site 2(d) (Fig. 1). In the system Mn<sub>1+δ</sub>Sb, $\delta$ is in the range 0<sub>δ</sub><sub>0.22</sub> (5). A further polarized neutron diffraction study on Mn<sub>1.09</sub>Sb (6) investigated the influence of the interstitial site occupancy on the electronic configuration of the Mn-atoms. Whereas for stoichiometric MnSb the 3d-majority spin bands are nearly fully occupied and the minority spin bands are empty (7) (fig.2), for $\delta$>0 the minority spin bands are occupied by additional

![Fig. 1 - Excess NiAs-type structure.](image-url)
electrons provided by the excess atoms. Consequently the magnetic moment magnitude decreases and the lattice parameter contracts due to the preferred electronic occupation of the low energy level $a_{1g}^t$ which is directed along the Mn-Mn-bond in the [001]-direction. These results will be complemented by information on the interstitial site atoms itself. Since Fe is known to possess a small magnetic moment ($\sigma$) the polarized neutron diffraction technique is a suitable tool to study its magnetic moment and to investigate the effects on the magnetisation density distribution when implanting Fe in the MnSb host lattice. MnSb crystals with 9% Fe concentrated on the interstitial site were grown for this purpose.

fig.2 - Band model for the 3d-electrons in MnSb (4). The 3d-bands are split due to the crystal field $D_{3d}$ at the Mn-atom. The Fermi-level is situated in between the exchange split majority and minority spin bands.

2. Characterization of the sample. - The single crystals were grown by the Bridgman-Stockbarger-method. The main features are described in reference (9). X-ray powder patterns were obtained from material at different heights of the Bridgman-Stockbarger sample; only NiAs-type reflections were found. Two crystals with the dimensions $1.3 \times 2.1 \times 3.1 \text{ mm}^3$ (crystal A) and $1.0 \times 1.2 \times 2.0 \text{ mm}^3$ (crystal B) were prepared. For the X-ray diffraction experiment small crystals with diameters of about 0.1 mm were taken from the direct neighbourhood of crystal A and B. For the determination of the individual Mn and Fe occupations of the sites 2(a) and 2(d) the results of X-ray and unpolarized neutron diffraction experiments were combined. Whereas the refinement with X-ray diffraction data yields the total T-metal occupation of the two sites, the neutron diffraction data allow the distinction between Fe and Mn due to their very different scattering lengths ($b_{Fe} = 9.6 \times 10^{-15} \text{ m}$, $b_{Mn} = -3.7 \times 10^{-15} \text{ m}$ (10)). Using Mo(Kα)-radiation 960 integrated reflection intensities were collected on Philips PW 1100 four-circle diffractometer. All reflections $+h, \pm k, \pm l$ up to $\theta = 30^\circ$ were measured. The neutron diffraction experiments were performed on the four circle diffractometer PI10/FR2, Kernforschungszentrum Karlsruhe (11). Using the wavelength $\lambda = 0.92 \text{ Å}$ the integrated reflection intensities of $+h, k, l$ reflections were measured up to $\sin \theta/\lambda < 0.83 \text{ Å}^{-1}$ by the $\omega$-scan technique. For the determination of the magnetic structures complete data sets were taken at 20 K and 293 K. Since magnetic scattering contributes significantly to low angle reflections only reflections with $\sin \theta/\lambda > 0.5 \text{ Å}^{-1}$ were used for the refinement of the nuclear structure parameters. The results are presented in table 1.
Table 1 - Results of X-ray and unpolarized neutron diffraction experiments on MnFeSb

<table>
<thead>
<tr>
<th>space group : P6$_3$/mmc</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice parameters (T = 293 K) :</td>
</tr>
<tr>
<td>MnFe$_{0.09}$Sb</td>
</tr>
<tr>
<td>a in Å</td>
</tr>
<tr>
<td>c in Å</td>
</tr>
<tr>
<td>population parameters : MnFe$_{0.09}$Sb</td>
</tr>
<tr>
<td>site 2(a)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>site 2(d)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Neutron thermal vibration tensors (units of 10$^{-2}$ Å$^2$) : MnFe$_{0.09}$Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb : $U_{11}$</td>
</tr>
<tr>
<td>$U_{33}$</td>
</tr>
<tr>
<td>Mn : $U_{11}$</td>
</tr>
<tr>
<td>$U_{33}$</td>
</tr>
<tr>
<td>Fe : $U_{11}$</td>
</tr>
</tbody>
</table>

| Reliability factors R = Σ| |F| - |F| |Σ|F| |
|--------------------------|
| X-ray diffraction | neutron diffraction |
| R = 0.042 | R(T=293 K) = 0.026 |
| R(T=20 K) = 0.054 |

Within the error limits the crystal can be described as MnSb with 9% Fe well separated on the interstitial site 2(d).

The magnetic ordering and transition temperatures of the crystal were determined by following selected reflections as a function of temperature. Ferromagnetism sets in at 496(8)K. The spins are aligned $\parallel c$ and after an intermediate temperature region (77(4)K < T < 207(7)K), where the spins are inclined to c, they turn in the hexagonal basal plane. Magnetic measurements, performed on crystal A, yielded $\mu = 3.31(4) \mu_B/\text{Mn-atom}$ at 4.2 K, calculated assuming a magnetic moment of $\mu_B/\text{Fe-atom}$ for which the moment direction is antiparallel to the magnetisation of the Mn-matrix.

3. Spin density distribution in MnFe$_{0.09}$Sb :

3.1. Experimental : The polarized neutron diffraction experiments were carried out on the instrument D3 at the Institut Laue-Langevin (HFR Grenoble). The neutron beam was polarised by a CoFe monochromator giving a wavelength of $\lambda = 0.993$ Å. The polarization analysis with a CoFe test-crystal showed $P = 0.965(2)$. The MnFe$_{0.09}$Sb sample (crystal A) was oriented with its [110]-direction parallel to the $\omega$-axis of the instrument. The precise orientation of the sample was determined by centering 10 high angle reflections. The measurements were performed at 4.2 K in
an applied magnetic field of 13.5 KOe, which is sufficient to saturate the ferromagnetic moment and to turn the spins into the magnetic field direction. All reflections of the type hhl, h-l, h-2 l were measured up to a limit of sin θ/λ < 0.8 Å⁻¹. In the course of the experiment, the statistical error of the magnetic structure factors could be lowered to 0.01 µB for 49 out of 58 independent reflections. 8 reflections had to be rejected because their nuclear structure factors were too small. In order to improve the flipping-ratios of the reflections h01 in the zero-layer crystal B was mounted with its [100]-direction parallel to H. In this way four magnetic structure factors were obtained more precisely.

3.2. Evaluation and results: The experimental flipping ratios were corrected for depolarisation P and spin-flipper efficiency P' according to (1):

\[ f.r. = \frac{1 + 2\gamma/(1 + \gamma^2)}{1 - 2P'(2P-1)\gamma/(1+\gamma^2)} \]  

(1)

The magnetic structure factors F_N(hkl) are then calculated by F_N(hkl) = γ . F_N(hkl), where the F_N(hkl) are the nuclear structure factors known from the refinement of the crystal structure. Using the resolution curve of the four-circle diffractometer P110/FR2, the mosaic spread of the sample was calculated to ΔM = 0.4°. Because of this value extinction effects seemed to be negligible and no correction was applied. The experimental form factors are shown in fig.3. As in the case of Mn₀.₉⁹Sb they fit, to first approximation, quite well to the theoretical Mn²⁺ form factor curve calculated by Watson and Freeman (12). Fourier transformation of the observed magnetic structure factors yields the magnetisation density distribution which corresponds to the spin density distribution for g = 2. With g = 1.978(2) (13) in the case of MnSb the orbital contribution can be neglected. When calculating spin density sections the series termination error was kept small by averaging the density at x,y,z over a cube of edge length δ = 0.30 Å. Spin density Fourier and difference Fourier-sections through the Mn-atoms revealed small deviations from the spherical symmetry. In particular the spin density is expanded in the [100]-direction and compressed in [001]; the latter finding is indicated by negative contour lines. The results are reproduced in the quantified electronic configuration of Mn given below. Fig.4 shows that a small magnetic moment is localized on the interstitial Fe-atom; in contrast to the information given by Yamaguchi and Watanabe (8) the Fe magnetic moment is polarized antiparallel to the magnetic matrix of Mn. The magnetisation
The small positive spin density accumulation in between the Mn-atoms at \( z = 0.25 \) and \( z = 0.75 \), since this seems to be an artifact.

Although a band structure calculation of Sandratskii et al. (7) on MnAs showed strong p-d hybridisation of the majority spin states it was found for Mn\(_{1.09}\)Sb that the anisotropy of the spin density distribution can be reproduced using 3d-orbital wave functions for the calculation of the magnetic structure factors (6). Using the formula given by Yamaguchi et al. (4) the magnetic structure factors for Mn can be written as follows:

\[
\begin{align*}
\text{hkl,1} & = 2n : F_M(hkl) = 2(\mu_{xo} + \mu_{xt} + \mu_{ut})<j_0> + \frac{10}{7}(\mu_{xo} - \frac{1}{2} \mu_{xt})(1 - 3\cos^2\beta)<j_2> \\
& + \frac{9}{14}(\mu_{xo} - \frac{1}{9} \mu_{xt} - \frac{7}{18} \mu_{ut})(3 - 30\cos^2\beta - 35\cos^4\beta)<j_4> \\
\text{hkl,1} & = 2n+1: F_M(hkl) = -\frac{10}{\sqrt{2}} (\mu_{xt} - \mu_{ut}) \sin 3\cos 3\cos \chi <j_4>
\end{align*}
\]

(2)

(3)

\( \mu_{xo} \) - magnetic moment per Mn atom in the \( t_{2g} \)-level

\( \mu_{xt} \) - magnetic moment per Mn atom in the \( e_{g} \)-level

\( \mu_{ut} \) - magnetic moment per Mn atom in the \( e_{g} \)-level

\( <j_n> \) - \( \int_0^{\infty} R^{2}_{32}(r) j_n(Kr) \) dr with \( j_n(Kr) \) as Bessel function of the n-th order.

\( \beta \) - angle between scattering vector and c-axis

\( \chi \) - angle between scattering vector and x-axis.

According to (3) the reflection group \( \text{hkl,1} = 2n+1 \) was used to refine the magnetic moment difference \( \mu_{xt} - \mu_{ut} \). In the same run the magnetic moment magnitude of the interstitial Fe was included as a free parameter. Because of the small scattering contribution of Fe its spin density distribution was approximated as a sphere; the Fe\(^{1+}\) form factor curve (12) was used for the calculation of the \( F_M(hkl) \). The best
agreement was obtained for \( \mu_{x^\pm} - \mu_{u^\pm} = 0.21(4)\mu_B \) and \( \mu(\text{Fe}) = -1.0(2)\mu_B/\text{Fe atom} \) (Table 2).

Table 2 - Comparison of calculated and observed magnetic structure factors for reflections with \( hkl, l = 2n+1, \sin \theta/\lambda > 0.5 \text{ Å}^{-1} \).

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>( F_c )</th>
<th>( F_o )</th>
<th>( \sigma(F_o) )</th>
<th>( hkl )</th>
<th>( F_c )</th>
<th>( F_o )</th>
<th>( \sigma(F_o) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>311</td>
<td>-0.0075</td>
<td>-0.0094</td>
<td>0.0059</td>
<td>315</td>
<td>0.0219</td>
<td>0.0287</td>
<td>0.0080</td>
</tr>
<tr>
<td>321</td>
<td>0.0178</td>
<td>0.0165</td>
<td>0.0097</td>
<td>325</td>
<td>0.0151</td>
<td>0.0060</td>
<td>0.0077</td>
</tr>
<tr>
<td>421</td>
<td>0.0058</td>
<td>0.0144</td>
<td>0.0098</td>
<td>107</td>
<td>-0.0083</td>
<td>-0.0150</td>
<td>0.0055</td>
</tr>
<tr>
<td>313</td>
<td>0.0503</td>
<td>0.0546</td>
<td>0.0060</td>
<td>207</td>
<td>0.0134</td>
<td>0.0184</td>
<td>0.0047</td>
</tr>
<tr>
<td>323</td>
<td>0.0055</td>
<td>0.0060</td>
<td>0.0077</td>
<td>217</td>
<td>0.0044</td>
<td>0.0090</td>
<td>0.0098</td>
</tr>
<tr>
<td>205</td>
<td>-0.0079</td>
<td>0.0051</td>
<td>0.0043</td>
<td>317</td>
<td>0.0193</td>
<td>0.0106</td>
<td>0.0089</td>
</tr>
<tr>
<td>215</td>
<td>0.0300</td>
<td>0.0309</td>
<td>0.0063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to cut off delocalized magnetic electrons only magnetic structure factors with \( \sin \theta/\lambda > 0.5 \text{ Å}^{-1} \) were included in the refinement. The same argument is valid for the reflection group \( hkl, l = 2n \). Here the observed data were corrected for the magnetic scattering contribution of Fe and then \( \mu_{x^\pm} - \mu_{u^\pm} \) could be refined using (2).

Comparing the results for \( \text{Mn}_{1.09}\text{Sb} \) and \( \text{MnFe}_{0.09}\text{Sb} \), no significant changes are found in the unpaired electron numbers for the 3d-energy levels. The saturation magnetization of Mn refined from the neutron data is slightly different from the value obtained by the magnetic measurements. The difference amounts to \( 0.09(5)\mu_B/\text{formula-unit} \) and may be due to delocalized electrons.

4. Discussion.- Implanting Fe instead of Mn in the MnSb host lattice seems not to affect the Mn-Mn interaction parallel to \( c \) as can be seen from the comparison of the ferromagnetic ordering temperatures \( T_c(\text{Mn}_{1.09}\text{Sb}) = 510(10) \text{ K} \) and the \( a_{1g}^t \) unpaired electron numbers. Also the 3d interactions between interstitial and regular atoms seem not to be influenced as it is indicated by the values found for \( \mu_{u^\pm} \) in both studies. However, in \( \text{MnFe}_{0.09}\text{Sb} \), \( c \) is contracted by about 1% (Table 1); This suggests that important hybridization between interstitial 3d orbitals and 5s, 5p functions of the neighbouring Sb atoms has to be taken into account. This should be reflected in a larger energy width \( \Delta \) of the 3d state for the interstitial Fe. Following the interpretation for the magnetic behaviour of impurities in MnSb given by Yamaguchi and Watanabe (8), this effect has to be compensated by an increased energy difference.
between the Fermi-energy and the energy of the 3d spin-up level in order to support
the magnetic moment found on Fe. Since there is no experimental evidence for an
important difference of the Fermi-energy in \( \text{Mn}_{1.09}\text{Sb} \) and \( \text{MnFe}_{0.09}\text{Sb} \), the magnetic
moment of Fe is mainly explained by a lower energy of the Fe spin-up band.
As the kind of interstitial atoms (Fe or Mn) affects neither the unpaired electron
distribution of the regular Mn atoms nor the magnetic ordering temperature, it may
be concluded that the interstitial atoms are not directly involved in the magnetism
of the compound. Their influence on the magnetic properties of the sample consists
of their contribution to the electronic configuration of the regular Mn atoms.

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