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Citation for published version (APA):

Vennix, C. W. H. M., Frikkee, E., Swagten, H. J. M., Kopinga, K., & Jonge, de, W. J. M. (1991). Neutron diffraction on the diluted magnetic semiconductor tin manganese telluride. *Journal of Applied Physics*, 69(8), 6025-6027. <https://doi.org/10.1063/1.347805>

DOI:

[10.1063/1.347805](https://doi.org/10.1063/1.347805)

Document status and date:

Published: 01/01/1991

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Neutron diffraction on the diluted magnetic semiconductor $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$

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In the diluted magnetic semiconductor $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$, magnetic ordering occurs at low temperature when the charge carrier density p exceeds a critical value. By means of single-crystal neutron diffraction on samples with $x = 0.03$, $p = 7 \times 10^{20} \text{ cm}^{-3}$ and $x = 0.06$, $p = 11 \times 10^{20} \text{ cm}^{-3}$, we have shown that this ordered phase is ferromagnetic. For the 6% Mn crystal indications were found for magnetic fluctuations just below the ordering temperature. The experimental results rule out the existence of a (reentrant) spin-glass phase at these Mn concentrations and charge carrier densities.

INTRODUCTION

The compound $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ is a member of the IV-VI group of diluted magnetic semiconductors (DMS). DMS are ternary or quaternary alloys in which a part of the nonmagnetic cations of the host material has been substituted by magnetic ones, in this case Mn^{2+} ions. There is a close relationship between the magnetic and electronic properties of DMS. In the magnetic phase diagram of the IV-VI group alloys $\text{Pb}_{1-x-y}\text{Sn}_y\text{Mn}_x\text{Te}$, the charge carrier density p , originating from slight deviations from stoichiometry, has to be introduced as a parameter besides the temperature T and the Mn content x . For $\text{Pb}_{0.25}\text{Sn}_{0.72}\text{Mn}_{0.03}\text{Te}$, Story *et al.*¹ established the existence of a critical charge carrier density p_c ($\sim 3 \times 10^{20} \text{ cm}^{-3}$), above which ferromagnetic ordering was observed below 5 K. For $p < p_c$ paramagnetic behavior was observed. Swagten *et al.*² were able to explain this behavior on the basis of a modified (RKKY) interaction mechanism, in which contributions from charge carriers in different regions of the Brillouin zone are taken into account. When p exceeds the critical density p_c , the Fermi level enters a set of heavy hole valence bands, located along the Σ axis, which brings about the step-like increase of the ferromagnetic interactions.

Recently a similar charge carrier density induced transition to a "ferromagnetic-like" state was reported by De Jonge *et al.*³ for $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ with $x = 0.03$ and $x = 0.06$, again with $p_c = 3 \times 10^{20} \text{ cm}^{-3}$. However, their measurements of the ac susceptibility, the magnetic specific heat, and the magnetization did not supply evidence on the nature of the low-temperature phase for high charge carrier densities, which had previously been reported as ferromagnetic^{4,5} as well as (reentrant) spin-glass-like.⁶

We started single-crystal neutron diffraction experiments to determine the actual nature of the magnetic ordering in this low T , high p regime. These experiments are combined with measurements of the Hall effect, the ac susceptibility, and the magnetic specific heat on the same crystal. In the diffraction experiments ferromagnetic order-

ing will result in magnetic Bragg scattering superimposed on the nuclear Bragg reflections below the transition temperature T_c . In the case of a common spin-glass state no intensity increase will be observed below the freezing temperature T_f . For a reentrant spin glass the ferromagnetic transition will result in increasing Bragg scattering with decreasing temperature, until the transition temperature to the spin-glass state is reached, below which the intensity will fall off again.⁷

As the additional intensity in the case of ferromagnetic order will be small for the actual Mn concentrations, it is necessary to select weak nuclear Bragg reflections to allow a distinction between the two cases. Fortunately, the rock-salt crystal structure of $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ and the scattering lengths of Sn, Mn, and Te ($b_{\text{Sn}} = 6.228 \text{ fm}$, $b_{\text{Mn}} = -3.73 \text{ fm}$, and $b_{\text{Te}} = 5.80 \text{ fm}$) offer this possibility. In the rock-salt structure only the Bragg reflections with indices $h, k, l = 2n$ and $h, k, l = 2n + 1$ are allowed. For the latter subset the nuclear intensity can be reduced to zero by choosing $x = 0.043$. There is no composition for which the other subset of reflections is suppressed. Obviously the reflections with odd indices are the most favorable ones for magnetic studies and, because of the magnetic form factor, especially the (111) reflection.

EXPERIMENTAL RESULTS

Experiments have been performed on single crystals of $\text{Sn}_{0.97}\text{Mn}_{0.03}\text{Te}$ [$p = (7 \pm 1) \times 10^{20} \text{ cm}^{-3}$] and $\text{Sn}_{0.94}\text{Mn}_{0.06}\text{Te}$ [$p = (11 \pm 1) \times 10^{20} \text{ cm}^{-3}$]. These compositions are close enough to $x = 0.043$ to reduce the nuclear (111) intensity almost to zero. The samples were cut from as-grown Bridgman batches. The carrier densities were measured using a Van der Pauw method. The neutron diffraction experiments were performed on the HB3 triple-axis spectrometer at the HFR Petten. The wavelength of the incident neutrons was 0.142 86 nm. Two 30' Soller collimators were placed between the reactor and the C(002) monochromator and between the sample and the C(002) analyzer. For both compositions the profile of the

FIG. 1. $\text{Sn}_{0.94}\text{Mn}_{0.06}\text{Te}$, $p = 11 \times 10^{20} \text{ cm}^{-3}$. (a) Integrated (111) intensity vs temperature, triple-axis mode. Full curve: mean-field approximation for $S = 5/2$ and $T_c = 9.3 \text{ K}$. (b) ac susceptibility vs temperature. (c) Magnetic specific heat vs temperature.

(111) reflection along the [001] direction was studied as a function of temperature, both with and without the analyzer. To check whether intensity variations in the (111) reflection are indeed of magnetic origin, the (222) reflection, for which the magnetic contribution is negligible compared to the nuclear scattering, was also measured at a few temperatures. The measured profiles were fitted with a Gaussian peak shape and a constant background. In Fig. 1(a) the integrated intensity of the Gauss fits to the (111) profile, observed in triple-axis configuration, is presented as a function of temperature for the $\text{Sn}_{0.94}\text{Mn}_{0.06}\text{Te}$, $p = 11 \times 10^{20} \text{ cm}^{-3}$ crystal. The behavior in double-axis mode was qualitatively similar. Just like the measurements of the ac susceptibility and the magnetic specific heat, presented in Figs. 1(b) and 1(c), respectively, the data in Fig. 1(a) indicate a transition to an ordered magnetic phase with a transition temperature $T_c = 9.3 \pm 0.2 \text{ K}$. Below T_c the magnetic intensity, which is proportional to the square of the magnetization, is superimposed on the temperature independent nuclear (111) and $\lambda/2$ (222) inten-

FIG. 2. $\text{Sn}_{0.94}\text{Mn}_{0.06}\text{Te}$, $p = 11 \times 10^{20} \text{ cm}^{-3}$, full width at half-maximum of Gauss fits to the magnetic (111) peak vs temperature. Open circles: triple-axis mode; filled circles: double-axis mode. Dashed lines: experimental resolution in triple- (lower) and double-axis mode (upper).

sities. The curve in Fig. 1(a) is the result of a mean-field calculation for a 3D ferromagnet with $S = 5/2$ and $T_c = 9.3 \text{ K}$. The excellent agreement between the data and this curve suggests a perfect mean-field-like behavior of the magnetization. Mean-field characteristics are also observed for the magnetic specific heat [as shown in Fig. 1(c)]. These features may be related to the long-range nature of the RKKY interaction suggested by Swagten *et al.*²

On the basis of the measured (002), (220), and (222) intensities, a “theoretical” value for the maximum magnetic (111) intensity can be calculated. Assuming a multidomain single crystal with the nominal Mn concentration, the observed maximum magnetic (111) intensity is $\sim 0.57 \pm 0.02$ of the calculated value, corresponding with a magnetization of 0.75 ± 0.02 of the theoretical value. This implies that the alignment of the Mn spins is not perfect even at very low temperatures, which is in agreement with high-field magnetization measurements by Escorne *et al.*⁸

Besides the analysis of the composite (111) profile as measured, we also performed a detailed study of the separated magnetic (111) reflection, obtained by subtracting a profile measured above T_c from the ones measured below T_c . These difference profiles were again fitted with a Gaussian. In Fig. 2 the full width at half-maximum (FWHM) from these fits is displayed vs temperature for both triple- and double-axis measurements. In the first case the line-width remains constant within the accuracy at a value equal to the experimental resolution up to 9 K. In double-axis mode the FWHM starts to deviate significantly from the resolution width for $T > 7 \text{ K}$. The difference between the measurements with and those without an analyzer is an indication that just below T_c part of the spins is fluctuating and not yet long-range correlated. Below 7 K the fluctuations have disappeared and the magnetic order has become overall long range.

The continuously increasing intensity with decreasing temperature, together with the behavior of the FWHM of the magnetic reflection below 7 K, leads to the conclusion that the low T , high p phase of $\text{Sn}_{0.94}\text{Mn}_{0.06}\text{Te}$ is ferromagnetic. No indications are found for (reentrant) spin-glass behavior in the temperature range covered in the diffraction experiments.

FIG. 3. $\text{Sn}_{0.97}\text{Mn}_{0.03}\text{Te}$, $p = 7 \times 10^{20} \text{ cm}^{-3}$, integrated (111) intensity vs temperature, triple-axis mode. Full curve: mean-field approximation for $S = 5/2$ and $T_c = 4.9 \text{ K}$.

For the $\text{Sn}_{0.97}\text{Mn}_{0.03}\text{Te}$, $p = 7 \times 10^{20} \text{ cm}^{-3}$ sample the integrated intensity of the Gauss fits to the (111) reflection as a function of temperature is shown in Fig. 3 for the measurements in the triple-axis mode. The behavior in the double-axis mode was similar. Like in the 6% Mn case, on cooling down the intensity remains constant until the transition temperature is reached. In this case, $T_c = 4.9 \pm 0.2 \text{ K}$, in agreement with the value from ac susceptibility, magnetization, and magnetic specific heat measurements.³ The curve in Fig. 3 represents the mean-field approximation for an $S = 5/2$, 3D ferromagnet with $T_c = 4.9 \text{ K}$ and is in good agreement with the data. The observed maximum magnetic (111) intensity amounts to $\sim 0.95 \pm 0.27$ of the value calculated by scaling on the nuclear reflections, corresponding with a magnetization of 0.98 ± 0.14 of the theoretical value. This leads to the conclusion that the $\text{Sn}_{0.97}\text{Mn}_{0.03}\text{Te}$, $p = 7 \times 10^{20} \text{ cm}^{-3}$ crystal is a normal ferromagnet. Within the experimental accuracy the spins are completely aligned at low temperature, in contrast to the $x = 0.06$ sample.

Because of the lower Mn concentration, the analysis of the separated magnetic peaks is less accurate than for the 6% Mn crystal. However, within the error limits the fits did not yield a systematic difference between the double- and triple-axis mode measurements. In both cases the FWHM is equal to the experimental resolution immediately below T_c .

CONCLUSIONS

The main conclusion from the present work is that the low-temperature, high charge carrier density phase in $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$, with $x = 0.03$ and $x = 0.06$, is ferromagnetic. The experimental results rule out the existence of a (reentrant) spin-glass phase. For the 6% Mn sample magnetic fluctuations are found just below T_c . Additional experiments, e.g., a search for critical scattering just above T_c or energy analysis of the scattering below T_c , are necessary to elucidate the nature of these fluctuations.

To complete the (T, x, p) magnetic phase diagram of $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$, experiments on samples with other compositions and other charge carrier densities must be performed. Very recently⁹ the existence of a second critical carrier density was conjectured, above which the ferromagnetic state turns back into a spin-glass phase. It was argued that an increase of p at constant x gives rise to a competition between ferromagnetic and antiferromagnetic interactions due to the oscillatory character of the RKKY interaction, whereas at smaller p the ferromagnetic interactions are dominating. In view of this conjecture, experiments on crystals with higher charge carrier densities might be interesting.

ACKNOWLEDGMENTS

We would like to thank H. H. A. Plas, M. L. Broekmans, and C. van der Steen for their experimental assistance.

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