Magnetic short range order in $Tb_xSi_{1-x}$ (0.18<or=x<or=0.87) amorphous alloys



1991 J. Phys.: Condens. Matter 3 2843

(http://iopscience.iop.org/0953-8984/3/17/001)

J. Phys.: Condens. Matter 3 (1991) 2843–2848. Printed in the UK

# Magnetic short range order in $Tb_x Si_{1-x}$ ($0.18 \leq x \leq 0.87$) amorphous alloys

B Boucher†, R Tourbot† and R Bellissent‡

† DPhG, Service de Physique du Solide et de Résonance Magnétique, CEN-Saclay, F-91191 Gif-sur-Yvette Cédex, France

‡ Laboratoire Léon Brillouin (Laboratoire CEA-CNRS), CEN-Saclay, F-91191 Gif-sur-Yvette Cédex, France

Received 19 October 1990, in final form 11 February 1991

**Abstract.** We report the results of neutron diffraction measurements performed at low temperature on $Tb_xSi_{1-x}$ amorphous alloys. We show that for RE-rich alloys the magnetization between first nearest neighbours is large, the dispersion between moments relatively small (35°), and for a volume containing three or four shells of terbium atoms the magnetization is about half the full moment. This asperomagnetic order is practically independent of the terbium concentration. For $x = 0.18$ the intensities are much weaker and the magnetic order cannot be quantitatively determined. Only a speromagnetic character can be suggested.

## 1. Introduction

The physical properties of $Tb_xSi_{1-x}$ amorphous alloys have been extensively studied by Simonnin *et al* (1986) and exhibit very interesting features. Let us recall that for RE-rich alloy (RE = rare earth), evidence for a very general thermal magnetic behaviour accounts for the temperature effect in weak fields, existence of a strong magnetic after-effect, hysteresis loops that are difficult to saturate, and a *metallic* behaviour of the electrical conductivity in contrast to *semiconductor* behaviour for RE-poor alloys.

Thus it is interesting to determine the nuclear and magnetic order of these alloys and its temperature dependence. With this aim we performed small-angle neutron scattering (SANS) and neutron diffraction measurements at room temperature, and the results have been published by Simonnin *et al* (1985, 1986). In this article, we report the results obtained from neutron scattering experiments at low temperature, which allow us to determine the magnetic short-range order and to compare this to results for other amorphous TbCu alloys.

## 2. Experimental details and data analysis

We have proceeded as described by Simonnin *et al* (1987) with the 7C spectrometer at the Laboratoire Léon Brillouin. Two wavelengths were available (0.7 Å; 1.1 Å) and we used the same samples as Simonnin *et al*. The use of a cryostat to

0953-8984/91/172843+06$03.50  

reach low temperatures was the only difference. The data have been treated and normalized in the same manner. The magnetic scattering has been deduced from the difference between low-temperature patterns and high-temperature patterns corrected for paramagnetic and frozen paramagnetic scattering. The calculated form factor of Freeman and Desclaux (1979) for $Tb^{3+}$ was used.

Three samples, $(Tb_{0.87}Si_{0.13})H_{0.16}O_{0.06}A_{0.04}$, $(Tb_{0.59}Si_{0.41})H_{0.15}O_{0.05}A_{0.04}$, $(Tb_{0.18}Si_{0.82})H_{0.07}O_{0.04}A_{0.03}$, prepared by sputtering have been measured. The presence of hydrogen is a consequence of the decomposition of residual water during the preparation. The high content of H is probably due to the affinity of Tb and Si for this gas. A more careful preparation leads to a decrease of hydrogen content ($x = 0.18$). The previous studies show the presence of small composition fluctuations and/or separation of phases of not very different composition for RE-rich alloy and suggest a partial segregation (Si–$TbSi_2$) for $x = 0.18$.

Figure 1 shows the magnetic scattering obtained at 3, 45, 80 and 150 K after the corrections mentioned above for $x = 0.87$. After normalization to a paramagnetic cross section, we can obtain the magnetic structure factor $S_m(q)/f^2$ (figure 2). Fourier transforms of $S_m(q)/f^2$ lead to the pair correlation function $g_m(r)$ (figure 3).

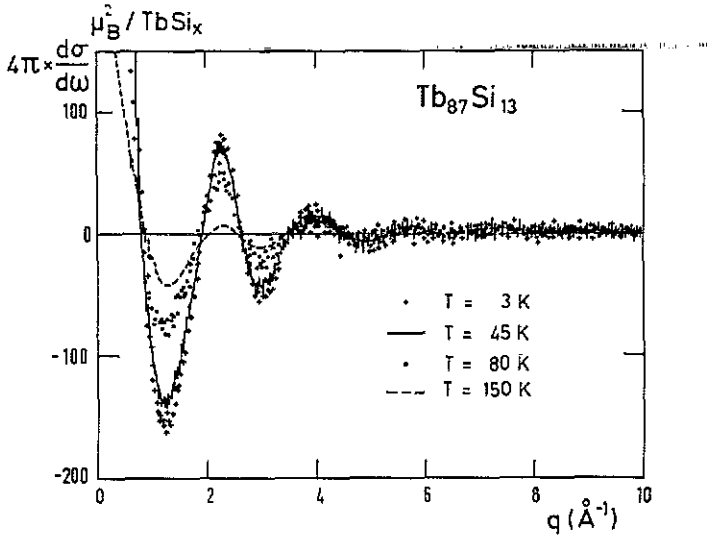


**Figure 1.** Magnetic cross section ($4\pi\ d\sigma/d\omega$) (in $\mu_B^2$/Tb atom) for $x = 0.87$ obtained from the difference between the low- and high-temperature patterns. The spectra are corrected for the 'frozen paramagnetic scattering'.

Following Blech and Averbach (1964), the Fourier transforms (FT) of a magnetic structure factor introduces an extra term due to the directional properties of moments, and varying both as $1/q^2r^2$ and $1/q^3r^3$. Wright (1980) demonstrates that this term is zero when there is no correlation between the radius vector and the moment directions. In our case the large distance between first Tb–Tb neighbours (3.6 Å) leads to a small extra term and the observation of the absence of correlations between the radius vector and the local order allow us to neglect this term for RE-rich alloys. However, it is necessary to be more prudent for $x = 0.18$, Simonnin *et al* having shown that the existence of a silicon matrix introducing semiconductor behaviour could induce order between the tetrahedra of silicon and, in consequence, correlations between the

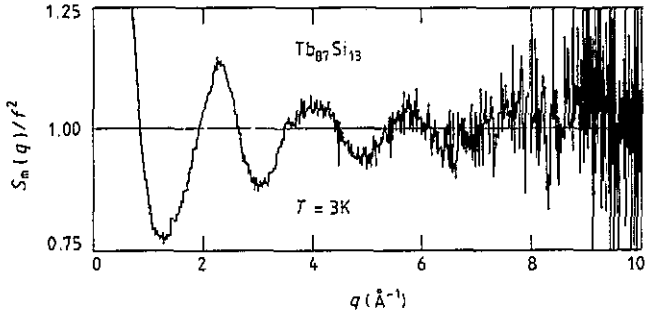


**Figure 2.** Magnetic structure factor corrected for squared form factor for $x = 0.87$. The large oscillations are due to the correction for $f^2$.

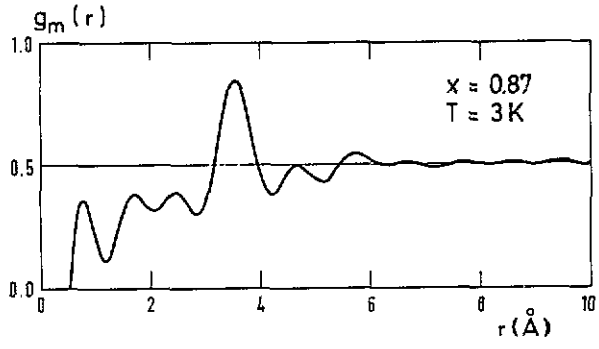


**Figure 3.** Magnetic pair function $g_m(r)$ obtained by Fourier transform of the magnetic structure factor $(S_m(q)/f^2)$ for $x = 0.87$.

easy directions of magnetizations. Moreover, the small coordination number of Tb–Tb pairs ($\sim 1$) deduced from room temperature measurements suggests the existence of small clusters.

## 3. Results

For $x = 0.87$ and 0.59, we observe intense SANS increasing with decreasing temperature. This scattering indicates a magnetic medium-range order which will be described in detail elsewhere.

At large angles we obtain very similar patterns for both concentrations. We observe intense modulations superimposed on the nuclear modulation (table 1, figure 1) which persist up to 200 K, which is considerably above the asymptotic Curie temperature ($\theta \simeq 66$ and 57 K respectively). A numerical treatment is possible and the Fourier transforms exhibit a peak at 3.55 Å, due to the magnetic resultant of first-neighbour moments (figure 3). By integration of this peak, we obtain an effective magnetic coordination number $N_m$ defined, following normalization to scattering by one Tb atom moment, as the number of atoms carrying a full moment ($9\mu_B$) and aligned in the same direction. The $N_m$ values are reported in table 2. Knowing the nuclear coordination number from neutron measurements at 300 K (Simonin *et al* 1987) we

can deduce the mean value of moments carried by a first-neighbour Tb. Thus we have $N_m/N_n = \cos^2\varphi$ where $\varphi$ is the mean angle of next-neighbour moments with the local magnetization direction (weighted sum of first neighbour moments). We find that the moments are roughly at a mean angle of 35° and that the local magnetization is $M_l = M_s\cos\varphi$—about $7\mu_B$ per terbium atom as against 9 ($M_s$) for the full moment when the moments are perfectly aligned.

**Table 1.** $q$ values of nuclear ($q_n$) and magnetic ($q_m$) scattering ring positions. The alloy with $x = 0.18$ gives markedly different values.

| $x$ | $q_n$ (Å$^{-1}$) | | | | $q_m$ (Å$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| 0.87 | 2.18 | 3.81 | 5.18 | | 2.23 | 3.90 | 5.70 |
| 0.59 | 2.48 | 3.75 | 4.62 | | 2.30 | 3.80 | 5.70 |
| 0.18 | 2.38 | 3.58 | 4 | 0.76 | 1.95 | 2.95 | 3.95 |

**Table 2.** Nuclear ($N_n$) and magnetic ($N_m$) coordination numbers, mean angle ($\varphi$) and mean magnetization ($M_l$) of nearest-neighbour moments and magnetization $M_2$ of small linear size ($\simeq 10$ Å).

| $x$ | $N_n$ | $N_m$ | $\varphi°$ | $M_l$ ($\mu_B$/Tb) | $\alpha$ | $M_2$ ($\mu_B$/Tb) |
|---|---|---|---|---|---|---|
| 0.87 | 8.7 | 7.1 | 38 | 7.1 | 0.76 | 4.40 |
| 0.59 | 6.9 | 4.6 | 35 | 7.3 | 0.81 | 3.92 |
| 0.18 | $\sim 1$ | | | | 0.84 | |

The patterns yield further information. For $q_{min} \simeq 1.25$ Å$^{-1}$ we observe a minimum of the magnetic scattering. The minimum $\alpha$ of $S_m(q)$ corresponds to scattering of which the larger part is due to the disordered part of the moment and the rest due to SANS and diffraction. The SANS contribution is negligible (Boucher *et al* 1991) while the diffraction part can only be expected to be very small. Then $\alpha$ can be considered as the maximum value of the scattering due to the mean disordered moment, and its complementary part $(1-\alpha)$ as a mimimum of the scattering due to the ordered moment. Then $(1-\alpha)M_2^2$ is the mean square magnetization taken over a size of radius of about $2\pi/q_{min} \simeq 5$ Å, either three or four shells of atoms. Thus table 2 indicates that inside a 10 Å linear size the mean magnetization ($M_2$) is of the order of $4\mu_B$/Tb, i.e. a little more than half the magnetization due to the first neigbhours; the magnetization decreases sharply with distance.

We must emphasize that the observed magnetization values are of the same order of magnitude as these obtained for $Tb_xCu_{1-x}$ (Boucher *et al* 1991) and are fairly independent of the RE concentration. The first nearest moments are relatively undispersed and the magnetization is close to the value of the full moment; inside a 10 Å linear size the magnetization is of the order of half the full moment. This similarity between the two alloys is in agreement with the metallic behaviour of silicon for the RE-rich concentration (Simonnin *et al* 1986) and indicates that the ratio between the anisotropy and exchange is of the same order whatever the alloy.

When the temperature increases, the amplitude of the $S_m(q)$ ring decreases and allows us to describe the temperature dependence of the magnetization of a small, volume containing the nearest neighbours (figure 4).

For $x = 0.18$, the results are more difficult to interpret. We observe a weak magnetic scattering at large angles at 2.5 K (figure 5) and it is impossible to compute the Fourier transform numerically, the $S_m(q)$ variation being too weak and the dispersion too large. But we emphasize the existence of four magnetic rings of which the first is at a low $q$-value ($q_1 \simeq 0.76$ Å$^{-1}$) and at least two are at positions that do not correspond to these of nuclear rings (indicated by the letter N on the magnetic pattern representation, figure 5; table 1). We also note, in contrast to the case for Tb-rich alloys, the absence of noticeable nuclear or magnetic small-angle scattering for $q \geqslant 0.3$ Å$-1$. If SANS were detectable it would be at lower $q$-values as shown by Simonnin *et al* (1985) for nuclear scattering.

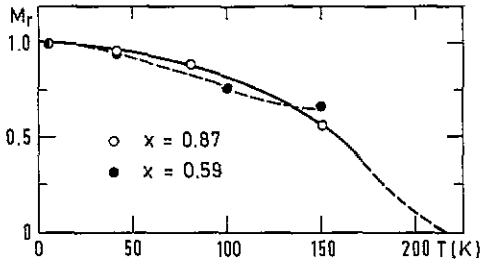


**Figure 4.** Temperature dependence of the reduced magnetization per terbium atom of small size deduced from the amplitude of the first scattering ring normalized to the amplitude at 3 K. The magnetic short-range order sets in at about 200 K while the asymptotic Curie temperature (long-range order) is very low ($\simeq$ 60 K). The latter does not seem to disturb strongly the variation of magnetization measured in this way.

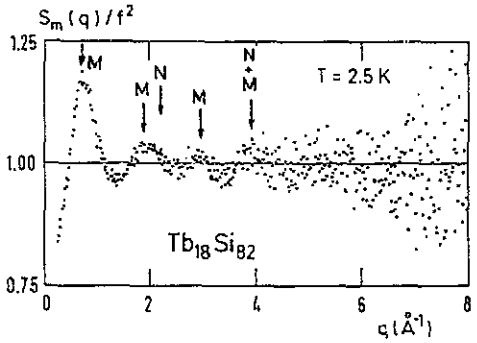


**Figure 5.** Magnetic structure factor corrected for $f^2$ for $x = 0.18$ at 2.5 K. The magnetic scattering appears between nuclear scatterings. N indicates the position of a nuclear ring and M the position of an observed magnetic ring.

So we can say that the magnetic correlations exist out to distance of $2\pi/q_1 \simeq$ 8.3 Å. The negative value of the asymptotic Curie temperature ($\theta \sim -10$ K) (indicating dominant negative magnetic interactions), the positions of the magnetic rings between the nuclear ones, the absence or at best the weakness of SANS (i.e. of the magnetization) at $q \simeq 0.3$ Å$^{-1}$ and the low Tb–Tb coordination (leading to a diminishing of the frustration) all seem to lead to a type of antiferromagnetic order in the sense that neighbour moments would be approximatively aligned in opposite directions. More experimental measurements, especially at small angles, are needed to elucidate the magnetic order for this composition.

## 4. Conclusion

The RE-rich alloys show an important magnetic order between both first nearest and next-nearest neighbours which exists up to about 200 K, i.e. much higher than the asymptotic Curie temperatures ($\simeq$ 60 K). The magnetic short-range order behaviours

of TbCu and TbSi alloys are very similar and the values of the magnetization for a small volume are not significantly different. Thus the substitution of a metallic element such as copper and silicon does not affect the magnetic order. The important difference is the difficulty of saturating the hysteresis loops of TbSi alloy, but on this point the neutron diffraction measurements do not shed any light.

It is not possible to describe the role played by hydrogen since we lacked a hydrogen free sample. We can only draw assumptions from the analogy with $Tb_{65}Cu_{35}$ (Boucher *et al* 1989). In that case the presence of hydrogen decreases the ordering temperature, diminishes the local anisotropy and the energy connected to the hysteresis loop, all of which leads to a smoother magnetic behaviour.

For $x = 0.18$, the experimental results do not allow us to determine the magnetic order in detail. Only the covalent character of silicon appears, the antiferromagnetic interactions become more significant and the scattering seems to indicate the existence of small magnetic clusters with antiferromagnetic and ferromagnetic Tb pairs.

## References

Blech I A and Averbach B L 1964 *Physics* **1** 31

Boucher B, El Gadi M, Sanquer M, Tourbot R and Bellissent R 1989 *J. Phys.: Condens. Matter* **1** 2057

Boucher B, Sanquer M, Tourbot R and Bellissent R 1991 *J. Phys.: Condens. Matter* **3** 1985

Freeman A J and Desclaux J P 1979 *J. Magn. Magn. Mater.* **12** 11

Simonnin P, Tourbot R, Boucher B and Bellissent R 1987 *J. Phys. F: Met. Phys.* **17** 559

Simonnin P, Tourbot R, Boucher B, Perrin M and Vanhaute J 1986 *Phys. Status Solidi* a **98** 551

Simonnin P, Tourbot R, Tournarie M and Boucher B 1985 *J. Phys. F: Met. Phys.* **15** L189

Wright A C 1980 *J. Non-Cryst. Solids* **40** 325–46