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A neutron diffraction study of topological and local magnetic order in the amorphous alloy $Tb_{65}Cu_{35}$

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Abstract. The amorphous alloys $Tb_{65}Cu_{35}$ prepared by sputtering and planar flow casting, in the annealed and as-cast conditions, both unpolished and polished, have been studied by neutron diffraction both above and below the magnetic ordering temperature. The nuclear and magnetic short-range orders are not significantly influenced by mechanical and thermal treatments. The thermal behaviour of the magnetisation is described.

1. Introduction

Owing to their electronic and magnetic properties, amorphous alloys have been the subject of many studies reported recently in the literature (Chappert 1982). Among these alloys, Tb–Cu exhibits peculiar and exciting structural and magnetic properties (Boucher *et al* 1983, 1986, 1988a, b, c, Chieux *et al* 1984). The principal constituents are a large Tb^{3+} ion with a radius of about 1.8 Å, and a much smaller Cu ion with a radius of 1.25 Å which will be assumed to intercalate in a network of Tb-rich alloys. Moreover the Tb^{3+} ion has a large magnetic moment ($9\mu_B$) and strong local anisotropy, leading to the idea of asperomagnetic ordering at low temperatures.

For the samples studied, we used amorphous alloys obtained either by sputtering or by planar flow casting. Thus it was possible to investigate the part played by sample preparation and subsequent thermal treatment on the physical and structural properties of the sample.

Small-angle neutron scattering (SANS) has shown the presence of compositional heterogeneities, which are magnetically ordered at low temperatures, and the influence of sample surface polishing; at low temperatures an anisotropic surface magnetisation linked to an increased volume of magnetic domains at the surface and in the bulk of the samples is evidenced (Boucher *et al* 1988a, b, c) for polished samples.

Therefore we undertook a neutron diffraction investigation of amorphous $Tb_{65}Cu_{35}$ in a temperature range from 4 to 300 K on both sides of the magnetic ordering temperature to determine the roles which the preparation method, annealing and polishing play in the nuclear or magnetic local orders and in the average magnetisations taken over a small volume. Indeed, neutron scattering allows us to determine the temperature at which magnetic order appears.

2. Experimental details

Our measurements were performed on six different samples: the first two samples were prepared by sputtering, one of which was then subsequently annealed; four samples were prepared by the planar flow casting method and were measured in the as-cast condition, the annealed condition, after polishing along the ribbon direction and after polishing perpendicular to the ribbon direction.

X-ray scattering was used to test the amorphous nature of the sample. No Bragg peak was detected for the sputtered samples. However, the quenched samples exhibited some Bragg diffraction corresponding to the $\text{Tb}_{50}\text{Cu}_{50}$ composition, as will be shown from magnetic measurements. The crystallites were shown to be located at the surface of the ribbons which was not in contact with the Cu wheel. However, further polishing succeeded in eliminating most of the crystallites.

Chemical analysis exhibited a slight lack of Tb corresponding to a composition $\text{Tb}_{63.5}\text{Cu}_{36.5}$ for the sputtered samples whereas the quenched samples were found to have the correct composition. The latter were free of impurities except for the 2 at.% O already present in the metallic Tb. However, the sputtered samples contained 9 at.% H, 3 at.% Ar and about 1 at.% C.

A differential scanning calorimetry (DSC) study (Harmelin 1987) has shown structural relaxation between 100 and 190 °C. Thus annealing was performed for 12 h at 110 °C on both types of sample.

Neutron scattering was carried out on the 7C2 spectrometer at the Laboratoire Léon Brillouin at Centre d'Etudes Nucléaires Saclay; the main features of this have already been described elsewhere (Ambroise and Bellissent 1984). It should be noted that a 640-cell position-sensitive detector was used. Two different wavelengths (0.7 and 1.1 Å) were available.

A cylindrical V container, 40 μm thick and 6 mm in diameter has been used for the sputtered samples. These samples were ground to fine powder; their mass was about 4 g.

The quenched samples were measured without any container. The samples consisted of layers made from several ribbons up to about 0.5 mm in total thickness, 10 mm width and 40 mm height with a mass of about 2 g. Sample surfaces were oriented at 45° to the incoming beam in order to minimise the self-absorption correction in a scattering angle range from 0 to 90°.

Absolute differential scattering cross sections for room-temperature measurements were obtained by conventional normalisation to a V sample of similar shape. Absolute normalisation of the scattered intensities at low temperatures, was then obtained by comparison with high-temperature scattering from the same sample.

3. Data reduction

Data reduction was performed as described in a previous paper (Simonnin *et al* 1987). The multiple-scattering contribution was estimated (Blech and Averbach 1965) to represent only 4–7% of the total scattered intensity, and it is assumed to be isotropic, as is usual in amorphous systems. Paramagnetic scattering and incoherent scattering from hydrogen were subcontracted simultaneously. A Placzek-type correction for incoherent inelastic scattering from hydrogen was calculated following Chieux *et al* (1984). We used the paramagnetic form factor f for Tb calculated by Freeman and Desclaux (1979).

Sputtered samples exhibit the presence of about 10 at.% H whereas the quenched samples are hydrogen free. The effective mass used for the Placzek correction is fairly high (about 1.6) which suggests that hydrogen is linked to the Tb or Cu atoms.

Once the high- q limit of the scattered intensity has been normalised using the V scattering and after these corrections have been applied, it compares fairly well with the mean value of the scattering cross section: $4\pi\langle b \rangle^2$, where $\langle b \rangle$ is the coherent scattering length of the samples averaged over all components including impurities. The same procedure has been used on the low-temperature data without the subtraction of any paramagnetic term.

The magnetic scattering was obtained by subtracting the high-temperature intensity from the low-temperature data. The ordered part of the magnetic scattering was assumed to be negligible from room temperature down to 150 K. Such an assumption is supported by the fact that the corresponding total scattered intensities at 150 and 300 K are almost equal. Thus, in order to minimise the thermal diffuse scattering effect, the experiment at 150K was taken as the non-magnetically ordered reference state, although the remains of a magnetic ring are visible.

For high and low temperatures, small-angle scattering ($Q < 1 \text{ \AA}^{-1}$) was subtracted, before Fourier transformation, as being representative of medium-range order only (Chieux *et al* 1984, Boucher *et al* 1986). Moreover, owing to the q -dependence of the integrand in the Fourier transformation

$$g(r) = 1 + \frac{1}{2\pi^2\rho_0r} \int_0^\infty q[S(q) - 1] \sin(qr) dq \quad (1)$$

$g(r)$ is almost unchanged by the way in which we subtract this small-angle term. This point has been checked by applying various corrections. The bulk density has been corrected for the impurities. At low temperatures the magnetic structure factor has been divided by f^2 and truncated at $q > 6 \text{ \AA}^{-1}$ (the magnetic factor being too small to give reasonable accuracy) before performing the Fourier transformation. We checked that the truncation does not change the result appreciably.

4. Experimental results

4.1. Room-temperature data

4.1.1. *Experimental details.* Once the incoherently scattered intensity from hydrogen has been subtracted out, the room-temperature spectra appear to be very similar for all the samples. For the quenched ribbons on which some crystallites were present, subtraction of the Bragg peaks was fairly easy owing to the small amount of crystallites.

The structure factors for the as-cast sputtered and quenched samples are shown in figure 1. They are characterised by an intense first ring, whereas the second ring is strongly damped and exhibits a shoulder on the high- Q side. Much smaller, but well defined, oscillations are present up to 15 \AA^{-1} , indicating a strong local interaction.

The positions of the maxima are similar for all samples. However, from a comparison of the scattered intensities, one should note the following:

- (i) higher intensities for the quenched alloys than for the sputtered alloys (about 20% for the first ring);
- (ii) the small decrease in the first ring after annealing (about 6% for the sputtered sample and 3% for the quenched sample);
- (iii) no difference between the sputtered samples before and after polishing.

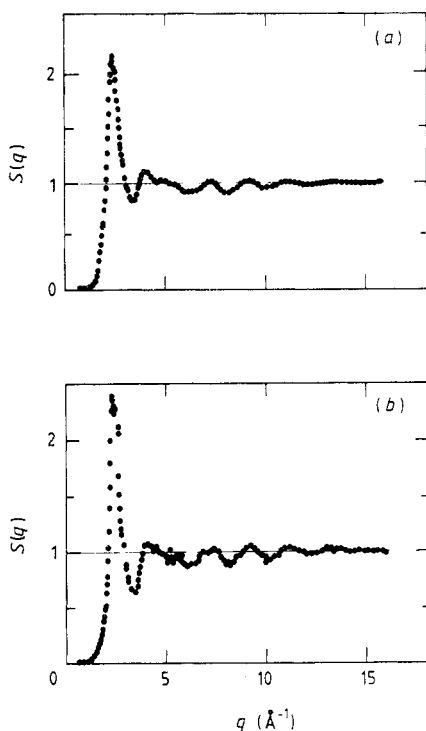


Figure 1. As-cast sample structure factors after correction; (a) sputtered; (b) quenched.

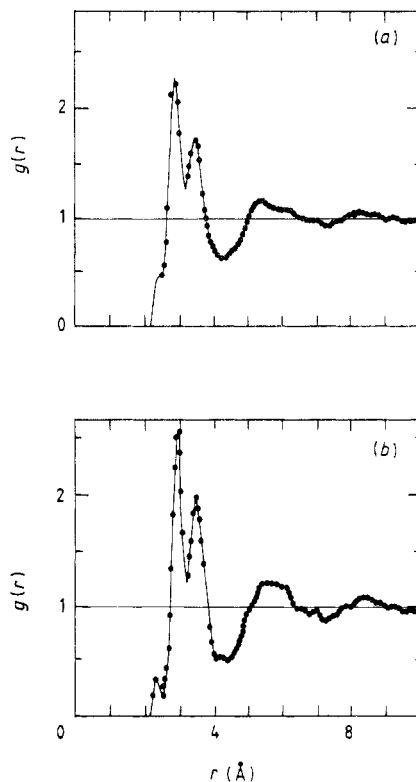


Figure 2. As-cast sample pair correlation functions; (a) sputtered; (b) quenched.

Fourier transformations (figure 2) were calculated using equation (1)

4.1.2. Nuclear short-range order. Several diffusion rings, three of which are fairly well defined, could be observed. By comparison with the ionic radii the distances that we have reported in table 2 (see below) can be attributed respectively to the following pairs:

Cu–Cu	2.55 Å
Cu–Tb	3.04 Å
Tb–Tb	3.52 Å

and the pair correlation function has been taken as a sum of Gaussian peaks; their full width ΔR_1 at half-height (table 1) gives some indication about the dispersion of interatomic distances. The main features of these Fourier transformations are as follows.

- (i) No noticeable difference is seen in the peak position for the various samples.
- (ii) There is a broader distribution for sputtered samples.
- (iii) Sharper peaks occur at distances greater than 4 Å for the quenched sample (which is a reflection of the higher amplitude of the first ring of the structure factor). This could indicate better defined order beyond the first neighbours.

Table 1. Position and FWHM of the peaks of the pair correlation function $g(r)$: S, sputtered; Q, quenched.

Sample	R_1 (Å)	ΔR_1 (Å)	R_2 (Å)	ΔR_2 (Å)	R_3 (Å)	ΔR_3 (Å)
As-cast S	2.44	0.26	2.92	0.46	3.51	0.70
Annealed S	2.44	0.30	2.92	0.47	3.51	0.67
As-cast Q	2.40	0.19	2.94	0.39	3.50	0.53
Annealed Q	2.40	0.20	2.94	0.44	3.50	0.55

(iv) Annealing has almost no influence on the peak positions and produces only small changes in the shape of the distribution of distances. This effect is stronger for the sputtered alloy, which is quite consistent with DSC results (Harmelin 1987).

Coordination numbers (table 2) were determined on the assumption that the first peaks of the partial pair correlation function are sufficiently separated to allow deconvolution of the first peak of the total pair correlation function. This deconvolution was done, using Gaussian peaks, by a minimisation process. Once again, one should note the fairly good agreement between all samples.

The Tb–Tb coordination number is high (close to 10) whereas the Cu–Cu number is very small (about 1). The total nearest-neighbour number around a Tb atom of 12.6 ($=9.8 + 2.8$) is even higher than that of a close-packed system. There are only 5.3 Tb atoms around a central Cu atom whereas the prediction of Schutte and Van der Waerden (1951), based on a mixture of hard spheres of different diameters, leads to 7.5 Tb atoms. Thus, around Cu atoms, our system is much less compact than a hard-sphere mixture and chemical order is very important.

In conclusion, we would like to emphasise that the preparation method (sputtering or quenching), the annealing and the polishing do not lead to marked differences in local order. We find that the quenched samples are slightly better ordered than the sputtered samples. In both cases, the surroundings of the Tb atom are compact and those of a Cu atom are loose.

4.2. Low-temperature data

4.2.1. Experimental details. We show in figure 3 the difference spectra reported by subtracting the high-temperature (150 K) intensity from that measured at 5, 60 and 100 K. In figure 4, we report a magnetic structure factor obtained by dividing the result of this last operation by the square of the magnetic form factor.

Table 2. Coordination number: S, sputtered; Q, quenched.

Sample	$N_{\text{Cu-Cu}}$	$N_{\text{Cu-Tb}}$	$N_{\text{Tb-Cu}}$	$N_{\text{Tb-Tb}}$
As-cast S	≈ 1	5.2	2.8	9.8
Annealed S	≈ 1	5.2	2.7	9.8
As-cast Q	≈ 1	5.4	3	9.7
Annealed Q	≈ 1	5.3	3.1	9.7

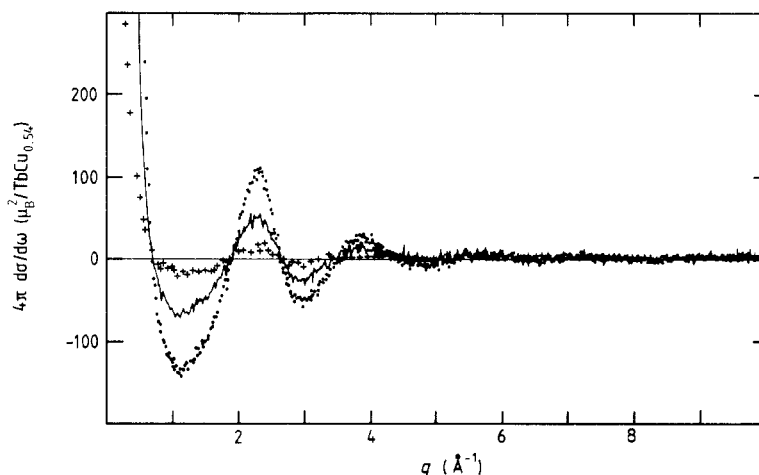


Figure 3. Magnetic scattering obtained as the difference between low- and high-temperature (150 K) spectra (uncorrected for paramagnetic scattering): \cdots , 5 K; —, 60 K; +, 100 K.

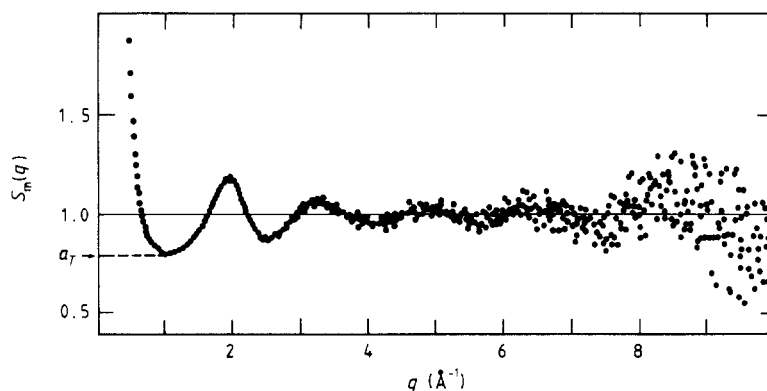


Figure 4. As-cast sputtered sample magnetic structure factor (at 5 K), after dividing by the square of the magnetic form factor of Tb. ($a(T)$ is the square of the disordered part of magnetic moments.)

We see strong small-angle scattering as previously observed (Boucher *et al* 1988a, b, c), fast damping of the oscillations with momentum transfer and even stronger damping with increasing temperature; at a larger q -value, some scattering rings, whose positions are very similar to those corresponding to nuclear order, are visible at room temperature.

There is no large quantitative difference between spectra obtained for different samples, apart from the presence for the quenched samples of intense magnetic Bragg peaks which disappear at 115 K (figure 5). These peaks allow us to determine accurately the nature and percentage of parasitic crystallites (Cable *et al* 1964). We have 1.5–3% of Tb atoms engaged in crystallites of $\text{Tb}_{50}\text{Cu}_{50}$ in annealed samples and half this amount in as-cast samples. The polishing was observed to have no influence on the amorphous part of scattering for $q > 1 \text{ \AA}^{-1}$ for both types (quenched and sputtered) of sample, whereas it did for $q < 1 \text{ \AA}^{-1}$ by SANS.

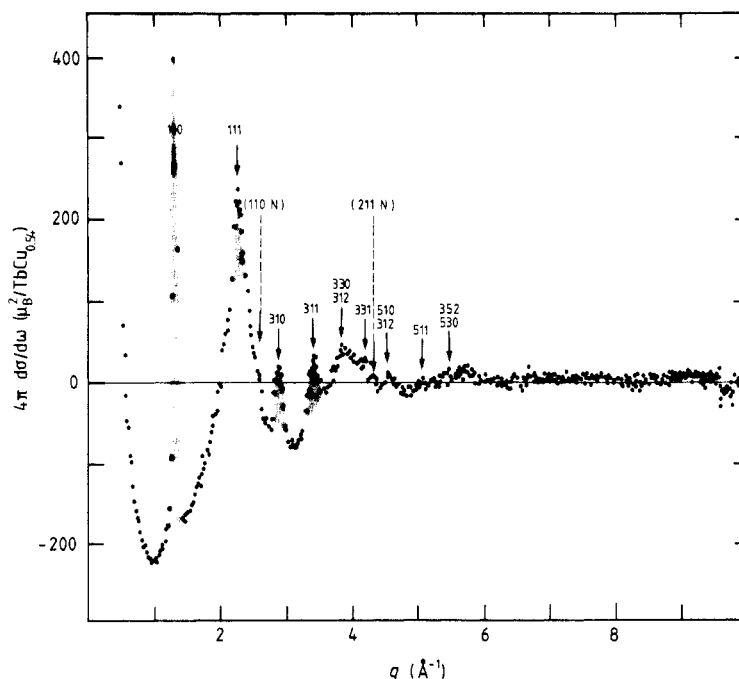


Figure 5. Annealed quenched alloy cross section (5 K). Both nuclear and magnetic Bragg peaks have been indicated. The darker areas indicate the crystallite contribution to the total scattered intensity. The magnetic Bragg peaks are well defined whereas the nuclear peaks are very weak (and their number very limited). Indices are given in the $2a, 2a, a$ cell for magnetic reflections and in the a, a, a cell for nuclear scattering (in this case the indices are followed by an N).

The Fourier transformation calculated as indicated in § 3 is reported in figure 6.

4.2.2. Magnetic short-range order. In an amorphous alloy which presents asperomagnetic order, we can define a local magnetisation $S_v(M_i)$ where the summation of magnetic moments is taken over a volume v . The average value of magnetisation of course depends on the volume v . Thus, to describe the local order, it is necessary to define the volume over which the magnetisation calculation will be performed.

(i) The magnetic structure factor exhibits a high background which is mainly due to spin disorder. The limiting value of the scattered intensity, for the higher values of the momentum transfer q , corresponds to a completely random system of spins whereas the background is limited in the low- q range (q of the order of 1 \AA^{-1}). The intensity $a(T)$ of this background at this minimum of $S(q)$ for a given temperature (figure 4) corresponds to the maximum disordered part of the spins in a volume of typical size $2\pi/q$ (about 6 \AA). Thus a minimum value of the ordered part of the magnetic moments (corresponding to about three inter-atomic spacings) should be defined as $1 - a(T)$ and will be proportional to the square of the magnetisation of the corresponding moments.

(ii) The Fourier transformation $g_m(r)$ of the magnetic structure factor exhibits a maximum at 3.4 \AA , a distance very similar to that found at room temperature for Tb-Tb pairs (figure 6). By integrating the distribution function $P_m(r) = 4\pi\rho_0 r^2 g_m(r)$, we

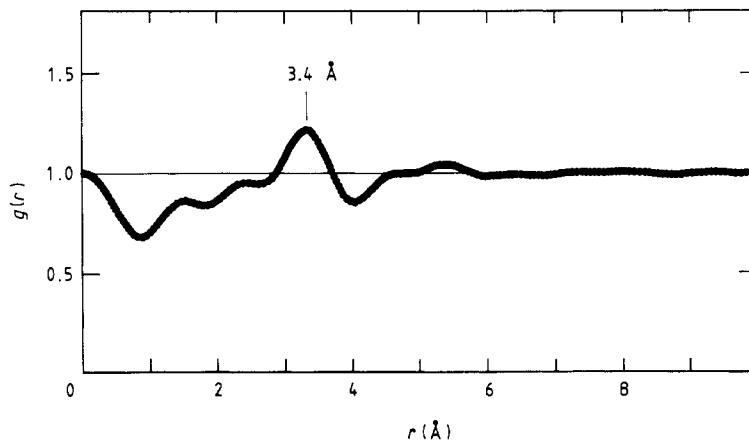


Figure 6. As-cast sputtered sample Fourier transformation. Cut-off effects give rise to spurious oscillations below the first maximum at about 3.4 Å. Integration of the first peak of the radial distribution function $P_m(r) = 4\pi\rho_0g_m(r)$ provides a fairly good order of magnitude for the first-neighbour magnetisation.

calculated the corresponding coordination number N_m . This number should be compared with the coordination number ($N_{\text{Tb-Tb}} = 9.8$) previously calculated from room-temperature data. The ratio $N_m/N = \cos \varphi$ provides us with the mean angle between the two nearest-neighbour magnetic moments of $9\mu_B$.

Data are reported in table 3. Owing to the impossibility of assigning well defined limits for the $P_m(r)$ integration, the N_m value is only known with a large uncertainty. However, it must be noted that sputtered alloys exhibit a nearest-neighbour magnetisation of about $5\mu_B$ per Tb atom at 5 K whereas this value is about $6\mu_B$ for the quenched samples (mean dispersions of first-neighbour moments are 56° and 48° , respectively). The magnetisations over three inter-atomic spacings as deduced from the $1 - a(T)$ calculated above are $4\mu_B$ per Tb atom and $5\mu_B$ per Tb atom in quenched and

Table 3. Mean value of magnetisation: S, sputtered; Q, quenched; P_{\parallel} , polished parallel to the tape axis; P_{\perp} , polished perpendicular to the tape axis. The mean values of the magnetisation have been deduced as follows: M_{max} from the first-neighbour magnetisation obtained from the ratio N_m/N calculated from the integrated area under the first maximum of the nuclear of magnetic radial distribution function; M_{min} from the minimum of the structure factor taken to be at about 1 \AA^{-1} which corresponds to about three shell sizes in real space.

Sample	M_{max} , first neighbours (μ_B per Tb atom)	M_{min} , three shells (μ_B per Tb atom)
As-cast S	4.9	4.2
Annealed S	4.9	3.8
As-cast Q	6.3	5.3
Annealed Q	6.3	5.2
P_{\parallel}	6.1	5.0
P_{\perp}	6.3	5.5

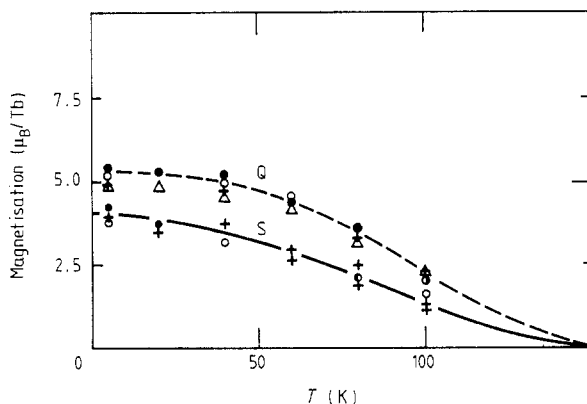


Figure 7. Thermal variation in the magnetisation deduced from the background intensity ($q = 1 \text{ \AA}^{-1}$) and from the amplitude of the first scattering ring: S, sputtered sample (\circ , as-cast samples; \bullet , +, annealed samples); Q, quenched sample (\circ , as-cast samples; \bullet , annealed samples; +, samples polished parallel to the tape axis; \triangle , sample polished perpendicular to the tape axis). The same variation is observed for both samples.

sputtered as-cast samples, respectively and $1.6\mu_{\text{B}}$ per Tb atom and $3.8\mu_{\text{B}}$ per Tb atom in polished and field-cooled samples, respectively (Boucher *et al* 1988a,c).

On the contrary, the amplitude of the oscillation of the magnetic structure factor $S_{\text{m}}(q)$ is proportional to the square of the ordered local magnetic moment. Such a measurement cannot provide quantitative data directly in the range of such magnetic order. However, the thermal variation in the amplitude of these oscillations exhibits a corresponding variation in local magnetisation which varies as $1 - a(T)$ (figure 7). Moreover, these data do not depend on the sample preparation method. The magnetic order temperature is clearly higher than 100 or even 120 K.

5. Discussion

The neutron scattering shows that the neighbours of a Tb atom (the larger atom) are densely packed while the surroundings of a Cu atom (the smaller atom) are much less so. The preparation method introduces a weak difference in the order between the first coordination shells—order which is impossible to determine in detail; we can say that the quenched samples are better ordered, in agreement with the DSC measurements. At low temperatures the first magnetic moments are slightly more correlated in quenched samples, but the local order is not fundamentally changed by the preparation or treatment (annealing or polishing).

Thus neither the preparation method nor the treatment (annealing or polishing) of the surface leads to a drastic variation in the nuclear or magnetic local order, while differences are observed in the medium-range order; this shows that annealing increases the size of the heterogeneities (amorphous or crystallised such as TbCu) and of the magnetic domains and their magnetisations. The polishing influences preferentially the surface and bulk magnetic properties rather than local order (Boucher *et al* 1988b,c).

The fact that the polishing does not introduce any perceptible modification in the magnetic local order while it introduces a preferred direction for the surface magnetisation in a sheet of thickness 1200 \AA and increases the domain size indicates that the

average dispersion between first neighbours is not changed and that the average direction of the magnetisation tends to be preserved for larger distances. Thus the domain magnetisation is increased (and the SANS is more intense) while the local magnetisation is almost unchanged.

It is worth noting that we are able to determine the magnetisation on three different scales: for first coordination shell, for third coordination shell and for domain dimensions (typically a few thousand ångströms). For example at 4 K for the as-cast quenched sample we have respectively $6.3\mu_B$ per Tb atom, $5.3\mu_B$ per Tb atom and $0.5\mu_B$ per Tb atom. For polished or cooled-field samples, the first two values do not change within the limit of experimental accuracy but the domain magnetisation tends to $1.6\mu_B$ per Tb atom (Boucher *et al* 1988b) or $3.8\mu_B$ per Tb atom (Boucher *et al* 1988a) in the bulk. So the local order seems to be much less sensitive to thermal or mechanical treatment than is the medium-range order.

It is interesting to recall that magnetic order between first shells, third shells or at few tens of ångströms exists below 200 or 150 K and can be observed by neutron scattering or SANS at intermediate q -values. At the asymptotic Curie temperature θ of about 80 K SANS at low q -values indicates the appearance of magnetic long-range order (a few thousand ångströms) (Boucher *et al* 1988b). At this temperature, no change occurs in the neutron scattering patterns at large q . This confirms that the short-range order does not appreciably change when the long-range order appears.

The different sample treatments slightly modify the θ_C value, θ_C increasing with increasing order (Boucher *et al* 1988b). It is likely that impurities play a more important role in governing the asymptotic Curie temperatures than does the preparation method.

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