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LETTER TO THE EDITOR

Small-angle neutron scattering above and below the magnetic ordering temperature in amorphous $Tb_{65}Cu_{35}$: a bulk sample origin?

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Abstract. The contrast variation method is applied to the study of small-angle neutron scattering from amorphous $Tb_{65}Cu_{35}$ tapes. The tapes are immersed in a methanol/glycerol solvent mixture, with variable deuteration of the methanol to match the scattering produced by the alloy surface. At 300 K, it is proved that the surface of the tapes plays a negligible role in the scattering. An attempt to apply the method at low temperature, where the system is strongly magnetically ordered, is perturbed by the fracture of the solvent which is then glassy. However, the small-angle magnetic scattering signal is so intense that surface effects are again negligible.

Many amorphous alloys give rise to small-angle neutron scattering (SANS). Depending on the samples, this scattering can be of widely different origin (Lamparter and Steeb 1988). A first question to be answered is to determine whether the scattering comes from the bulk of the sample, or from the interface between the sample and air or vacuum. It is then possible to investigate the characteristics of the bulk of the sample or surface that lead to the scattering: surface roughness, fluctuations of the density and chemical composition in the bulk, segregation . . . . Several authors have tried to quantify the role of the surface in small-angle scattering using the contrast variation method (Roth 1977, Rodmacq *et al* 1985, Janot and Georges 1985). In this method, the sample is immersed in a liquid which has the same scattering length per unit volume as the sample superficial layers. If the surface of the sample is of a homogeneous composition and if the liquid wets it well, the scattering due to the surface roughness is eliminated. In the two latter studies (Rodmacq *et al* 1985, Janot and Georges 1985) it was proved that small-angle scattering was due to the sample surface, polishing treatments being found to increase the microscopic surface roughness, thus increasing the scattering.

Over the last few years, we have studied extensively the amorphous alloys Tb_xCu_{1-x} ($x = 0.18, 0.22, 0.33, 0.50, 0.65$) and Tb_xSi_{1-x} ($x = 0.18, 0.59, 0.87$). We have investigated their magnetic properties, and nuclear and magnetic order at short and medium distances (Boucher *et al* 1983, 1986, 1988a, b, 1989, Simonnin *et al* 1985, 1986, 1987). In particular, we have been able to give a model for short- and medium-range order (nuclear and magnetic) which accounts very well for the microscopic (neutron structure factor and SANS) and macroscopic (density and magnetic properties) measurements. This model consists of nuclear domains of several hundreds or thousands of angströms in

size. The scattering contrast between domains is due to concentration or magnetisation variations. Moreover, small heterogeneities of 10–100 Å in size are dispersed in the alloy. The model accounts quantitatively, in absolute terms, for the q^N ($N = 3$ or 4) and the e^{-aq^2} SANS scattering laws (q being the momentum transfer). The physical parameters (size of domain or heterogeneity, variation in scattering length, magnetic moment . . .) obtained from the fit of the SANS data are in very good agreement with the results of macroscopic measurements of density, magnetisation and magnetic moment. However, analysis of the data is based on the hypothesis of negligible surface effects; this needs to be verified experimentally. This is the object of the present Letter.

We shall now describe the procedure used in the experiments. Since the scattering characteristics of the TbCu system are quite independent of composition, we chose $Tb_{65}Cu_{35}$ for our study. Tapes (1 cm) of amorphous $Tb_{65}Cu_{35}$ alloy were obtained by planar flow casting. The tapes could be polished with fine sandpaper if so desired. Polishing causes supplementary nuclear (q^{-3} law) and very intense supplementary magnetic scattering (q^{-4} law plus diffraction peaks) (Boucher *et al* 1988a, b). Two samples were studied: one as cast, the other polished. They were immersed in a solution of 80% methanol and 20% glycerol, glycerol being added to lower the point at which the glassy solvent fractures at low temperature. The scattering length per unit volume of the solvent was varied by changing the degree of deuteration of the methanol. Since hydrogen and deuterium have neutron scattering lengths of opposite signs, a solvent with zero overall scattering length (like a vacuum) can be obtained (this is achieved for 5.5% deuteration of the methanol). For a methanol deuteration of 60%, the scattering length per unit volume of the solvent is calculated to be roughly equal to the nuclear scattering length per unit volume of the amorphous sample at room temperature. At low temperatures it was probable that the strong magnetic scattering of the sample would no longer be matched by the solvent. For those measurements we used 100% deuterated methanol, which would match the nuclear scattering of the sample plus an average magnetic scattering of about 1.8 Bohr magnetons per terbium atom. The measurements were performed on the D11 spectrometer at the Institut Laue–Langevin (ILL), Grenoble. The range of momentum transfer investigated was from 2.6×10^{-3} to 2.3×10^{-2} Å^{-1}. All runs were performed in an ILL orange cryostat with quartz windows.

The sample consisted of about twelve pieces of amorphous alloy tape of width 12 mm and thickness about 50 μm piled up in a cell with two quartz windows, mounted perpendicular to the neutron beam. The optical path of the cell was 2 mm. The $\Phi = 10$ mm neutron beam area at the cell was defined by using cadmium masks. The overall thickness of the sample was then about 0.6 mm and the thickness of the solvent 1.4 mm.

Measurements were performed at 300 K on the empty cryostat (CR), empty cryostat plus empty cell (CRC), CRC plus solvent, CRC plus alloy and finally CRC plus alloy plus solvent. The measurements were made for different degrees of solvent deuteration. Transition measurements were made in each case. The detector cells were calibrated and normalised with a known scatterer. After corrections for cryostat plus cell, the sample scattering in a vacuum could be compared to the sample scattering in the presence of a solvent (the scattering due to the (1.4 mm thick) solvent being correctly subtracted).

A low-temperature experiment was first performed at 130 K, i.e. at a temperature where some magnetic ordering effects are detectable but remain very weak (Boucher *et al* 1988a). Then a scan was performed at 20 K where the magnetic ordering is strongly noticeable.

At 300 K the observed SANS is isotropic. The comparison of the sample scattering in a vacuum and the sample scattering in the presence of a solvent mixture with zero
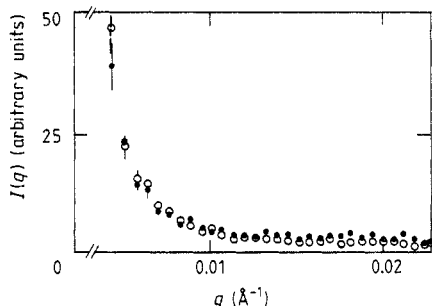
Figure 1. Intensity at 300 K for a polished sample in vacuum (●), and for the same sample measured in the presence of an 80% methanol (50% deuterated)/20% glycerol solvent mixture after subtraction of the solvent scattering (○).

Table 1. Results of low-temperature SANS experiments, showing effect of the solvent (80% methanol (100% deuterated)/20% glycerol). Intensity measured at momentum transfer $q_1 = 5.7 \times 10^{-3}$ Å^{-1}; all values corrected for background and empty cell. Data for the sample immersed in solvent are corrected for solvent scattering.

Sample	Intensity (arbitrary units)	
	130 K	20 K
Solvent	18	70
$Tb_{65}Cu_{35}$ in a vacuum	15	324
$Tb_{65}Cu_{35}$ in solvent	15	1782

scattering length per unit volume shows that the two corrected patterns are identical within experimental error.

In figure 1 we compare the scattering at 300 K of a polished $Tb_{65}Cu_{35}$ sample in a vacuum to that of the same sample in the presence of a (50% deuterated methanol) solvent mixture after subtraction of the solvent scattering. At the lowest q-values the two sets of data are identical. At larger q-values there is a reduction in intensity of about 15% in the presence of the solvent. This is the largest effect we could observe out of six trials (with the as-cast sample nearly nothing could be detected) with varying deuteration ratio (which changed the scattering length per unit volume of the solvent mixture from zero to 1.5 times the sample scattering length). We conclude that over the range of q investigated most of the scattering is due to the bulk of the sample.

The results are summarised at low temperature in table 1, where we give for $q_1 = 5.7 \times 10^{-3}$ Å^{-1} the corrected intensity scattered by the solvent mixture, by the sample in a vacuum and by the sample in the presence of the solvent mixture. The sample tapes are as cast, and the methanol is 100% deuterated. At 130 K the corrected sample scattering does not vary when the sample is immersed in the solvent, confirming the 300 K result. At 20 K there is a strong increase of the solvent scattering due to the fracture of the then glassy mixture (figure 2), but there is also such a strong increase of sample scattering due to magnetic ordering that the immersion method could, in principle, still be applied. However, at 20 K we observed a considerable increase of the apparent sample scattering in the presence of the solvent (figure 3) which we interpret as a strong enhancement of the solvent fracture produced by stresses at the metal–solvent interface. Therefore it becomes impossible to use the contrast variation method until such time as the problem of fracture is fully mastered or ways are found to prevent it (this has been investigated on a system such as $LiCl \cdot nD_2O$ by Carmona (1989)).

In conclusion, the SANS measurements at 300 K on polished or as-cast $Tb_{65}Cu_{35}$ amorphous tapes, immersed in a solvent mixture, show that the scattering is essentially a property of the sample bulk. It thus validates experimentally the hypothesis of negligible surface effects used in the model description of this system, which allowed us to correlate
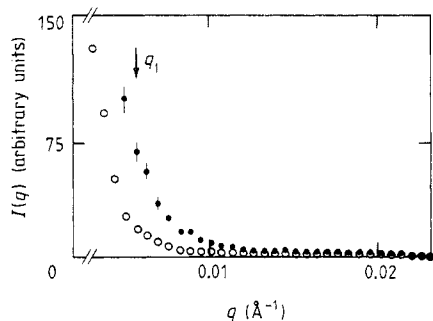
Figure 2. Scattering intensity of the 80% methanol (100% deuterated)/20% glycerol solvent mixture, at 20 K (●) and at 130 K (○). $q_1 =$ 5.7×10^{-3} Å^{-1}.
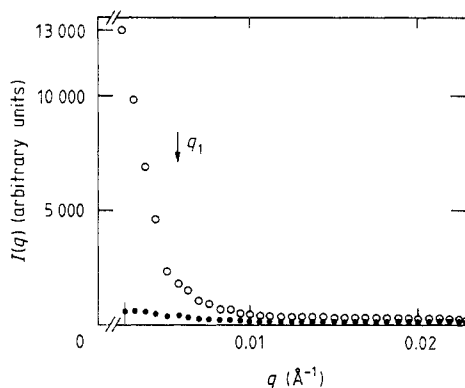
Figure 3. Scattering intensities at 20 K reported for the same thickness of sample for an as-cast $Tb_{65}Cu_{35}$ sample in a vacuum (●), compared with the intensity for the same sample measured in an 80% methanol (100% deuterated)/20% glycerol solvent mixture (○). $q_1 = 5.7 \times 10^{-3}$ Å^{-1}.

quantitatively the bulk local- and medium-range order with the measured macroscopic properties. Comparable results showing that the SANS is caused mainly by the bulk (in contrast to the other systems quoted in the first paragraph of this Letter) have been found for the $Ni_{33}Y_{67}$ amorphous alloy (Maret *et al* 1988). Systematic investigations of the surface–bulk scattering should therefore be undertaken for every type of binary alloy and over the complete q-range of the SANS study. We have not yet found a satisfactory solution to the experimental use of the immersion method at low temperatures, since all glassy solvents that we have tested fracture. Also, the signal seems to be considerably enhanced by the alloy–solvent interface. However, the intensity of the magnetic SANS obtained with the polished sample at 20 K and expressed in Bohr magneton squared per molecule (Boucher *et al* 1988a, b) is so intense that it must come mostly from the bulk and one is therefore justified in continuing to neglect the surface scattering effects.

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