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Magnetic susceptibility measurements on single crystal $\gamma Mn_{90}Cu_{10}$

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Abstract. The low field magnetic susceptibility of samples cut from two single crystals of $\gamma Mn_{90}Cu_{10}$ has been measured. Both samples show re-entrant spin glass behaviour in the antiferromagnetic state with significant differences between the samples which are related to their metallurgy. Both samples show spin freezing parallel to as well as perpendicular to the magnetic ordering direction, although the amount of spin freezing apparent with an applied field parallel to the ordering direction is less marked.

1. Introduction

The magnetic properties of $\gamma Mn_{1-x}Cu_x$ alloys have proved a fertile field of study for many years. In particular, much of the early information on spin glasses came from studies of this system, and the system is still used as an archetypal example of a metallic spin glass. The γ phase, which is face centred cubic, is stable at high temperatures for all concentrations, is retained at low temperature in copper rich alloys and can be stabilized for manganese rich alloys by rapidly quenching the alloys from high temperature.

For concentrations with more than 72% Mn, the alloy is an itinerant antiferromagnet at low temperatures, and the crystal structure distorts to a centred tetragonal structure with the crystallographic transition coinciding with the Néel temperature (T_N) [1]. A mechanism has been suggested whereby the magnetic transition drives the crystallographic transition [2] consistent with observations of the very sharp drop in the sublattice magnetization close to T_N. The antiferromagnetic spin arrangement is type 1: spins parallel to the [001] direction with the spins aligned ferromagnetically within (001) planes and alternate planes of spins having opposite directions [3]. The antiferromagnetic interactions of this spin structure cannot satisfy simultaneously the ordering arrangement for the face centred cubic structures and thus spin frustration occurs. The Néel temperature for rapidly quenched well annealed polycrystalline $Mn_{90}Cu_{10}$ was found to be 420 K with a moment of 2.4 μ_B per Mn atom calculated for pure Mn [1]. Cu rich alloys show a moment of 4.0 μ_B on the Mn atoms where the moments are more localized.

A spin glass phase exists at low temperatures for all compositions of MnCu. There are no long range ordered crystallographic structures but atomic short range order (ASRO) is

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pronounced for all compositions. The magnetic properties of MnCu alloys have been shown to depend dramatically on the ASRO within the sample, particularly for some concentrations. Varying the ASRO can alter T_N, the spin freezing temperature and, in particular, the magnitude of the magnetic susceptibility. The γ-phase alloys are metastable for Mn rich concentrations and are believed to develop αMn precipitates over time, even at room temperature [4]. On the other hand, in Cu rich γ-alloys the Mn atoms tend to anticluster upon annealing. For Cu rich alloys, where most magnetic work has been concentrated in recent years, it has been noted that composition inhomogeneities cause a smearing of the spin glass transition [5]. It was also noted that compositional variations are hard to avoid in CuMn alloys, especially near the ends of single crystal samples. Only relatively short time (1 h) annealing at high temperature is needed to locally homogenize alloys which have been well mixed and cold worked during manufacture. The magnetic effects of ASRO (an increase in susceptibility for dilute alloys and a decrease in susceptibility for alloys with more than 60% Mn) has been explained [6] on the basis that Mn–Mn nearest neighbour (nn) coupling is antiferromagnetic while next nearest neighbour (nnn) coupling is ferromagnetic. When anticlustering occurs, ferromagnetic interactions increase at the expense of antiferromagnetic interactions, increasing the susceptibility. On the other hand there have been observations of a decrease in the high temperature susceptibility with annealing for dilute alloys [7] and magnetic neutron scattering and other measurements which show a nearest neighbour ferromagnetic correlation [8–10]. Interestingly, compressing the alloys decreases the susceptibility, tensile distortion increases susceptibility [1] and severe plastic distortion can almost destroy the spin glass behaviour [6].

MnCu alloys lend themselves well to neutron scattering measurements of atomic and magnetic short range order due to the strong contrast between the Mn and Cu scattering lengths for thermal neutrons. There have been many studies of ordering in these alloys. For Cu rich alloys there is a broad $(1\frac{1}{2}0)$ peak [11] which has been interpreted as being mostly due to atomic short range order. Recent theoretical work [12] has shown that this peak is a consequence of a competing mechanism in the electronic structure of the CuMn alloys. For Mn rich alloys there is a very sharp (001) diffuse peak which is purely magnetic. This peak has a magnitude between 2% and 5% of the (110) magnetic Bragg peak and has been attributed to an average 5° canting of spins from the [001] direction [13]. This peak has been shown to increase in intensity with decreasing Mn concentration and increasing temperature (up to T_N) in powder samples [14]. The suggestion that the tails to this peak are partly due to magnons when observed in powder samples has been made, but single crystal data show the existence of a clear gap in the energy spectrum at this point [15]. Certainly the increase in intensity of this peak as T_N is approached can be attributed to magnon scattering as the energy gap decreases. There are no correspondingly intense Bragg peaks (such as $(003) - I_{(003)}/I_{(001)} \simeq 0.07$) in the scattering from this alloy to suggest that this canting is a long range ordered effect and the most plausible current explanation [16] seems to be that when a Mn atom in the lattice is replaced by a Cu atom, the neighbouring spins relax and take up some transverse component [17]. The sharpness of the (001) peak indicates that this transverse magnetic defect is quite long range and it has been called a 'giant staggered moment' [18].

Of particular interest in this alloy system is the existence of a re-entrant spin glass phase in the antiferromagnetic ordered state. An examination of the susceptibility of the re-entrant spin glass compositions in rapidly quenched polycrystalline samples was made by Gibbs and his coworkers [19], although they did not investigate the effect of heat treatments on their samples. For Mn rich alloys the magnetic susceptibility is very small and changes little with temperature and their work was close to the instrumental limits of the Faraday

magnetometer used [20]. They attributed the spin glass behaviour to Mn atoms with nearest neighbour ordering instructions disturbed by a Cu impurity atom. The 'free' Mn spin could then be blocked by nearest neighbour interactions or interact with other 'free' Mn spins to produce a spin glass.

Gabay and Toulouse [21] have attributed re-entrant spin glass behaviour in idealized re-entrant spin glasses in ferromagnets with exchange disorder to freezing of spin components perpendicular to the ordering direction. There is no corresponding model for antiferromagnets. The possibility of testing this idea by directly examining the spin freezing parallel to and perpendicular to the magnetic ordering direction in a re-entrant spin glass phase in an antiferromagnet is the main motivation for the current work. This work is only possible using high quality single domain single crystals. It should be noted that these (real) samples are site disordered spin glasses.

2. Method

Two separate crystals were examined. The first crystal (A) was grown by D A Hukin of the Clarendon Laboratory, Oxford with nominal concentration $Mn_{90}Cu_{10}$ and has been the subject of many studies [14, 18, 22–24]. These studies investigated short range order and the magnons at high temperature and found strong correlations even above T_N. The crystal, with a volume of about 4 cm^3, was grown using a Bridgman technique in an RF furnace in a roughly conical shape. It was then cooled through T_N with a uniaxial compression applied along a [100] direction. A measurement of T_N was made by monitoring the (110) (magnetic) Bragg intensity as a function of temperature and found to be 465 K. The form of this intensity was unusual showing two knees, one at low temperature (of a form consistent with a spin reordering transition) and the other close to T_N where the magnetization drops very sharply. Early measurements showed the sample to be a single crystal but heavily twinned. This is consistent with observations of twinning in a furnace cooled (unquenched) $Mn_{85}Cu_{15}$ crystal [25]. Atomic absorption spectroscopy showed that the sample concentration was uniform at 89.2% Mn.

Later heat treatments prior to 1985 rendered the crystal largely single domain (97%) with no twinning evident. Measurements of the (110) (magnetic) Bragg peak intensity as a function of temperature after these heat treatments showed no sign of the lower temperature knee. A detailed neutron scattering study of the magnetic and atomic short range order for this crystal has since been made [24] and showed that the magnetic order associated with the (001) diffuse peak is static and extends over a range of about 40 Å and the ASRO in this sample was of longer range than could be sensibly modelled using Warren–Cowley parameters. It was clear that both the Mn and the Cu atoms cluster strongly.

For the susceptibility work, two small samples in the shape of rectangular prisms, A1 ($6.0\times4.0\times4.1$ mm^3, 0.678 g) and A2 ($6.0\times4.0\times2.6$ mm^3, 0.427 g), were spark cut from the large end of the much larger conical main crystal. The two pieces were originally adjacent to each other in the large crystal. The faces were (001), (110) and $(1\bar{1}0)$ crystallographic planes with the (110) face being cut within 1.2° of the plane. Electron microprobe studies were made in 1991 and 1997 on a small sample cut from the same region of the crystal as these samples, and show that the concentration varies dramatically between 70% Mn and 96% Mn with, in particular, large regions of about 90% Mn and regions of diameter about 4 μm of 75% Mn. A linear microprobe scan across a small part of the sample is shown in figure 1.

Neutron diffraction measurements on the susceptibility sample A1 showed that the unit cell had $a_0 = 3.774$ Å and $c_0 = 3.595$ Å at room temperature, and that this sample was

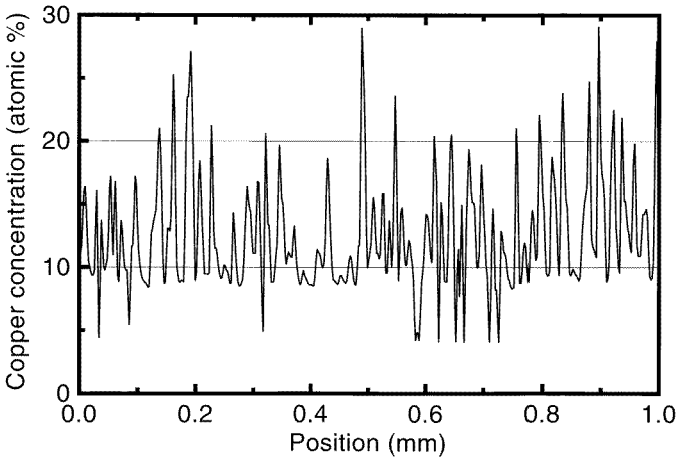

Figure 1. Linear scan by electron microprobe of concentration variation with distance in sample A.

not a single domain but was mixed in a ratio of about 2:1 (figure 2). The location of the misoriented domains was not evenly distributed throughout this sample but localized at one end, which shows that the parent crystal almost certainly has localized small regions of misoriented domains rather than a continuous distribution of mixed domains on a microscopic scale. Measurement of the (110) magnetic Bragg peak intensity as a function of temperature clearly shows the presence of antiferromagnetic long range order at all temperatures from 11–325 K (figure 3). A quadrant scan was performed and showed no sign of any small crystallites. A rocking curve measured to 2.5° either side of the Bragg peak showed no sign of any extra peaks, which is quite remarkable for a transition metal alloy crystal. Measurements of the intensity of the (001) diffuse peak as a function of temperature showed no increase in intensity as the temperature rises, suggesting that the peak is uncontaminated by any magnon scattering.

The second crystal (B) was an offcut of a larger crystal previously used to measure the phonon spectrum in this alloy [26]. The initial alloy was prepared by melting together appropriate quantities of Mn and Cu in an arc furnace. The crystal was then grown in an alumina crucible using the Bridgman technique. It was then annealed at 900 °C and quenched in iced water to retain the γ-phase. To obtain a single domain crystal the specimen was held in a vice while being cooled through T_N, measured to be 465 K for this sample. Sample B is in the form of a rectangular prism of approximate size $6.1 \times 4.2 \times 3.7$ mm^3 with faces parallel to (001), (100) and (010) crystallographic planes. Electron microprobe studies of this crystal showed a much more uniform concentration than for sample A with an average composition of 89 ± 1 at.% Mn. Neutron diffraction measurements of the {002} and {200} peaks for this sample showed that it was a single domain (to better than 98%) single crystal (figure 4). The diffractometer was then set to the Bragg angle for a (111) peak and the sample was rotated in small steps through a quadrant. Only two peaks were detected confirming that no small crystallites were present.

The magnetic susceptibility was measured using a commercial SQUID magnetometer (Quantum Design MPMS-7) in applied fields between 50 Oe and 1000 Oe at temperatures between 1.8 and 300 K. Over this range of fields no significant variation in the magnitude or form of the susceptibility of each sample were observed. Data, particularly those taken

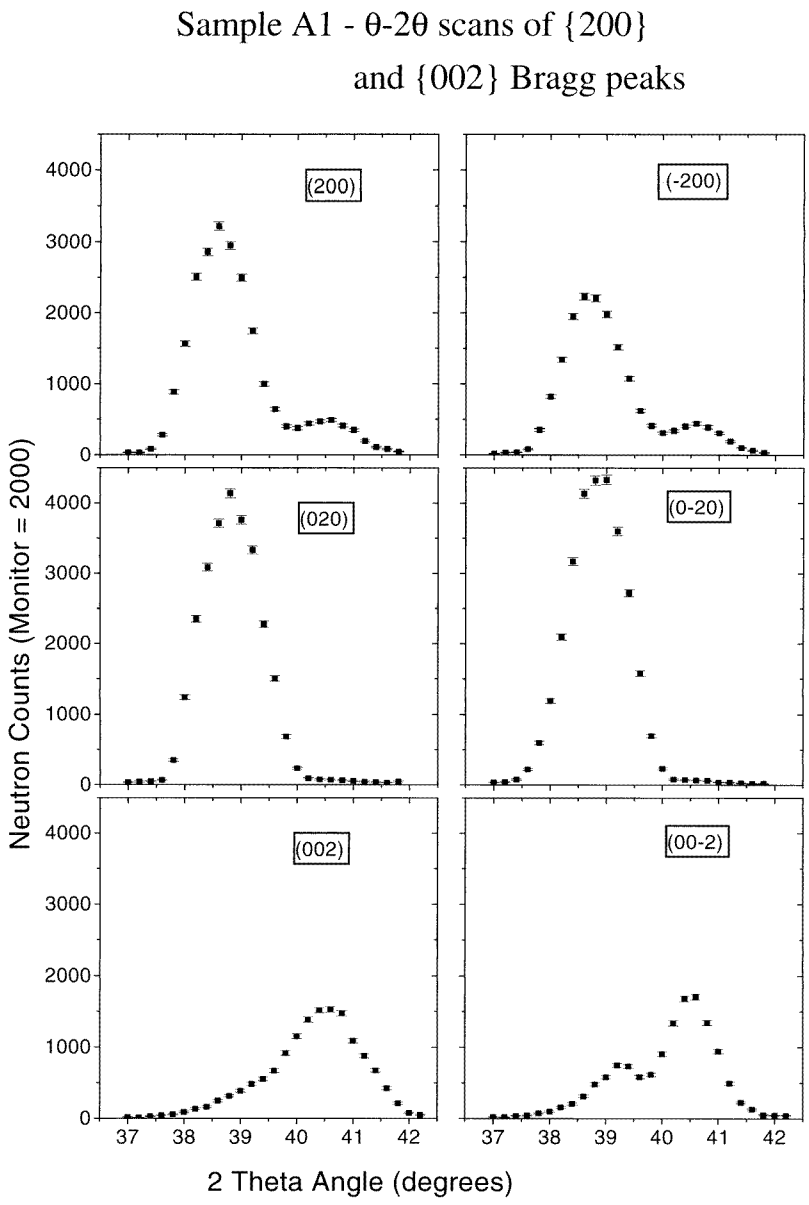

Figure 2. Longitudinal (θ-2θ) scans of the structural Bragg peaks for sample A1 showing the existence of mixed orientation of the tetragonal domains in the crystal.

in fields below 100 Oe, were occasionally subject to instrumental errors due to remanent flux of the order of a few Gauss trapped in the superconducting magnet. This made the measurements difficult, particularly those of the thermo-remanent moment (TRM). The effect of trapped flux is to shift the entire curve along the susceptibility axis. Data compared between runs where this effect occurred and did not occur gave us confidence in the nature of its origin and enabled its correction. The TRM is known to decay to zero above the freezing temperature which can be independently determined from a comparison of the

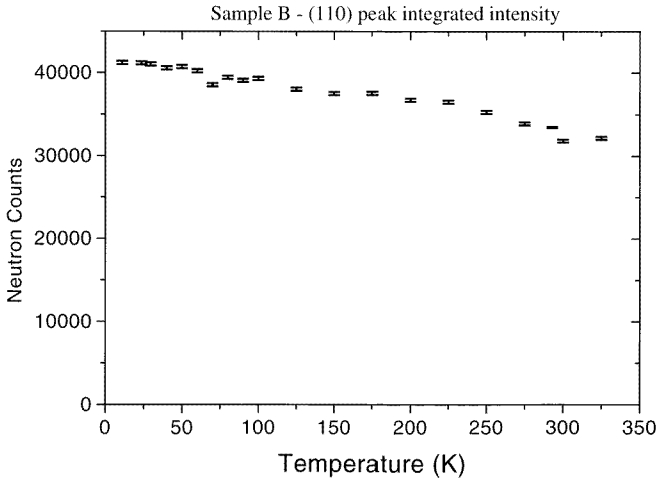

Figure 3. Integrated intensity of the (110) magnetic Bragg peak for sample B measured by neutron diffraction over a range of temperatures. Note that the intensity remains down to base temperature, confirming the existence of antiferromagnetic order and that there are no anomalies at 50 K, the spin glass freezing temperature.

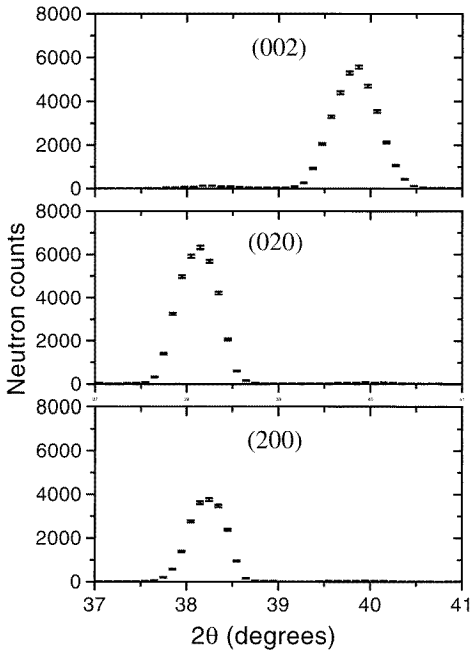

Figure 4. Longitudinal (θ-2θ) scans of the structural Bragg peaks for sample B showing that there is an insignificant proportion (<2%) of mixed orientation of the tetragonal domains in the crystal.

field cooled (FC) and zero field cooled (ZFC) measurements. This information was used to correct the measured data for the effects of trapped flux where necessary.

The crystals were mounted within 2° of the [001] direction and within 5° of the [100] and [110] directions, although in each of the latter cases the field was perpendicular to [001] to within 2°.

Measurements close to T_N were avoided at this stage because T_N for these alloys coincides with a tetragonal crystallographic distortion. Passage through T_N may introduce irreversible changes in the samples.

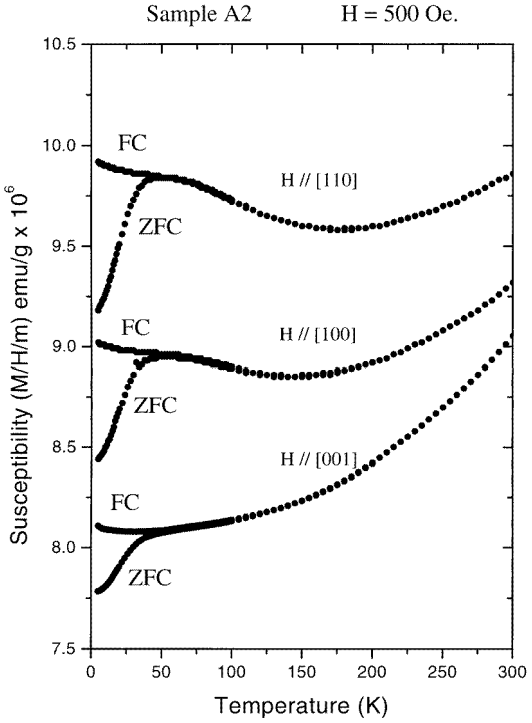

Figure 5. Magnetic susceptibility (g^{-1}) for sample A2 measured in a magnetic field of 500 Oe applied parallel to all principal crystal axes. FC and ZFC scans are shown. The TRM was separately measured and found to be equal to the difference between the FC and ZFC measurements.

3. Results and discussion

The magnetic susceptibility for samples A2 and B measured parallel to all principal crystallographic directions is presented in figures 5 and 6. The data for sample A2 show a large frozen moment below 50 ± 1 K with a smaller component up to 130 ± 5 K. In sample A1 the component with a higher freezing temperature was even more pronounced. This is illustrated by a representative data set shown in figure 7. Sample B, the better sample, only shows the component up to 52 ± 1 K. The difference between the field cooled and zero field cooled runs was compared to the thermo-remanent moment measurements and found to be identical as explained by Gray and Hicks [27]. The higher temperature component for samples A1 and A2 is attributed to the concentration variations in crystal A and it is noted that a freezing temperature of 130 K is consistent with a concentration of $Mn_{72}Cu_{28}$ in accordance with the microprobe data. Note that the freezing temperature of about 50 K

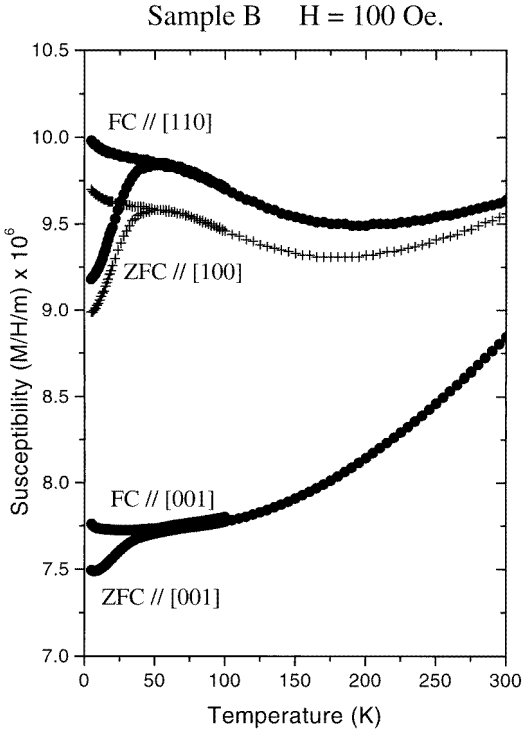

Figure 6. Magnetic susceptibility (g^{-1}) for sample B measured in a magnetic field of 100 Oe applied parallel to all principal crystal axes. FC and ZFC scans are shown.

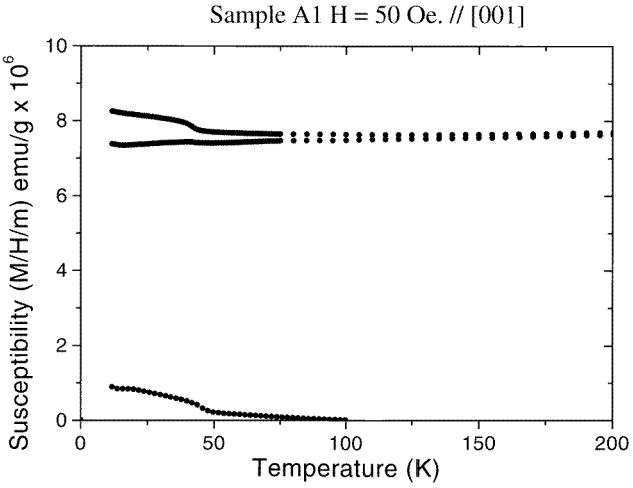

Figure 7. Magnetic susceptibility (g^{-1}) of sample A1 measured in a magnetic field of 50 Oe applied parallel to the [001] crystal axis. FC, ZFC and TRM scans are shown. Note the sharp knee in the curves near the lower freezing temperature (50 K) and the existence of a frozen moment up to 130 K.

for these crystals is much higher than that for a rapidly quenched polycrystalline sample, which has a freezing temperature of 21 K [19]. However, the freezing temperature is almost

identical to that measured recently in a single crystal of $Mn_{86}Cu_{14}$ [28] and the form of that susceptibility curve is close to that noted in the present work for sample A1 with a distinct knee in the field cooled susceptibility and a small kink in the zero field cooled susceptibility near the freezing temperature.

The spin freezing temperature is the same in all principal directions suggesting that it is the same spins and mechanism involved in the frozen susceptibility in each direction. The frozen component of the moment is of broadly comparable magnitude in each direction.

The existence of a frozen magnetization parallel to the [001] crystallographic direction (the ordering direction) is the most interesting feature of the data. This magnetization is larger than can be attributed to domain misorientation (at least in the case of crystal B) or to misorientation of the crystals within the magnetometer. Thus there is a freezing of random components of the moments parallel to the ordering direction. The amount of freezing is also too large to attribute to a 5° canting of spins from the ordering direction unless these canted spins contribute more than proportionally to the frozen moment. It is possible that the frozen moment can be associated with the giant staggered moment postulated to explain the (001) diffuse peak, but if this is the case the susceptibility of the frozen moment is only a small fraction of the total moment involved in the clusters implying that the coupling within these clusters is largely antiferromagnetic.

The susceptibility measured with the field applied perpendicular to the spin axis is larger as in a normal antiferromagnet. The susceptibility measured with the field perpendicular to the spin axis shows a rise towards low temperatures which is not evident in the susceptibility with the field parallel to the spin axis. This means that there are fluctuations in the moment along the perpendicular direction, most probably due to moment components perpendicular to both the field and the spin axis. These components freeze at 50 K.

A diluted antiferromagnet is also subject to random fields. The lower critical dimension for stability of the antiferromagnetic phase subject to random fields is three. It is therefore interesting that $Mn_{90}Cu_{10}$ shows history dependent effects only below about 50 K which is well below the Néel temperature. In contrast, $Mn_{0.75}Mg_{0.2}S$ has divergent ZFC and FC susceptibilities for all temperatures below its Néel temperature of 120 K in a field of 1100 Oe [29]. It may be that the greater range of the exchange interactions in metals has a role to play here.

4. Conclusions

Measurements of the magnetic susceptibility in two single crystal samples of $\gamma Mn_{90}Cu_{10}$ show spin freezing parallel to the ordering direction beyond that which can be attributed to instrumental or measurement technique effects. There is clearly freezing of moment in the re-entrant spin glass phase parallel to the ordering direction as well as perpendicular to it, and probably more frozen moment in the parallel direction. It is possible that this frozen moment can be associated with the transverse moments already suggested to exist in this material, and the susceptibility measurements suggest that these 'transverse moments' have a larger component parallel to [001] than perpendicular to it. The freezing temperature is much higher than for rapidly quenched polycrystalline samples and this is tentatively ascribed to the slower quench for the crystals.

One of the samples, crystal A, is not of uniform composition and the crystal directions are not completely unique within the sample. Its magnetic properties differ from those of crystal B, which is of uniform composition in a way consistent with it being a mixture of phases. It would require a very detailed study of many aspects of this sample to firmly associate particular effects with particular aspects of the variations in this sample

and unfortunately further conclusions are impossible at this stage. The data presented for this sample should be useful in considering the previous work performed on this sample. Despite the well known dependence of many properties of MnCu alloys on their thermal history, some properties are relatively insensitive to the detailed state of the sample.

These measurements highlight the difficulty of comparing theory and experiment for real spin glasses. In general real metallic spin glasses are complex site disordered alloys with defects. It would be valuable if a theoretical study of the mechanisms for re-entrant spin glass phases in antiferromagnets could be made and especially if such a study could incorporate some description of the effects of site disorder.

Acknowledgments

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