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Magnetic ground states and spin dynamics of β-$Mn_{1-x}Ru_x$ alloys

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Abstract
The geometrical frustration of the β-Mn lattice suppresses moment formation, leading to a spin-liquid ground state. Alloying β-Mn to expand the unit cell results in moment localization, but the resulting ground state is normally a spin glass. However, alloys of β-Mn with Ru and Os were found to exhibit long-range order. This paper reports a study of the low-frequency spin dynamics in β-MnRu alloys using muon spin relaxation, supported by susceptibility, heat capacity and neutron diffraction data. For Ru concentrations $\leqslant$9 at.%, spin-glass ground states are found. Antiferromagnetism is found at higher concentrations, but at low temperatures there is evidence for a coexistent spin-glass state.

1. Introduction

The β-Mn crystal structure is a well documented example of a geometrically frustrated system. The cubic unit cell contains 20 atoms, which crystallize in the $P4_132$ structure. Eight atoms occupy site I with a near-neighbour separation of 2.37 Å, while the 12 site II atoms have an interatomic distance of 2.52 Å. The site II atoms form a corner-sharing triangular arrangement constituting a distorted Kagomé sublattice. NMR and NQR studies [1] indicate that while site I atoms are weakly magnetic, the site II atoms display large-amplitude spin fluctuations with characteristic $\sqrt{T}$ temperature dependence of the NMR spin–lattice relaxation rate, $1/T_1$. The development of local atomic moments and stabilization of long-range magnetic order is suppressed by the geometric frustration. Canals and Lacroix [2] have shown that a Heisenberg antiferromagnet with site II connectivity is orientationally degenerate along $\langle 111\rangle$-type lines in reciprocal space. Inelastic neutron scattering studies reveal a very broad spectrum of spin fluctuations [3]. The wavevector-dependent susceptibility $\chi(Q)$, obtained by integrating the dynamical susceptibility over the energy, has the form of a liquid structure factor with a peak at 1.5 Å^{-1}, consistent with the picture of a spin-liquid ground state for β-Mn [4].

There have been many studies of the effect of alloying β-Mn with transition and non-transition metals. In almost every case alloying leads to a reduction of the Sommerfeld constant from its large value $\gamma \sim 80$ mJ/mol^{-1} K^{-2} in the pure material [5]. Expansion of the unit cell would be expected to aid the formation of local moments. However, different solutes display different site preference: for example in β-Mn$_{1-x}$Al$_x$ alloys the Al shows a strong preference for site II. In this case muon spin relaxation (μSR) measurements and neutron polarization analysis [6, 7] show a crossover from a spin-liquid to a spin-glass ground state at a concentration of 9% Al. It would appear that the site II substitution, while lifting the configurational degeneracy, leads to a disordered ground state. In β-Mn$_{1-x}$Co$_x$ alloys, where the Co shows a strong preference for site I, there is no long-range order up to 20% Co, but the range of the spin correlations is much longer than that found in β-Mn$_{1-x}$Al$_x$.

Recent studies have found long-range antiferromagnetism in β-Mn alloys for the first time: heat capacity measurements show clear cooperative anomalies in β-Mn$_{1-x}$Ru$_x$ alloys for $x \geqslant 0.18$ [8]. Neutron diffraction shows well defined magnetic Bragg peaks for $x \geqslant 0.12$ in this series [9]. Clear evidence of antiferromagnetic (AF) phase transitions are also found in β-Mn$_{1-x}$Os$_x$ [10] and β-Mn$_{1-x}$Ir$_x$ alloys [11]. X-ray and neutron diffraction measurements show that Ru, Os and Ir atoms have a strong preference to occupy site I.

This paper presents part of an extensive investigation of the development of the magnetism of β-Mn$_{1-x}$Ru$_x$ alloys with Ru composition. Here we present results of a muon spin relaxation study, supported by susceptibility and specific heat measurements. We have also relied on detailed neutron diffraction and polarization analysis measurements of the magnetic structure that are reported elsewhere in these proceedings [9].

2. Sample preparation and characterization

Polycrystalline β-Mn$_{1-x}$Ru$_x$ samples covering the concentration range $0.03 \leqslant x \leqslant 0.23$ were produced by arc melting the constituent materials in an argon atmosphere. The samples were annealed for 24 h at 900 °C before undergoing a rapid quench. The compositions were subsequently confirmed by Rietveld refinement of neutron powder diffraction data: this is particularly sensitive because of the large scattering length contrast between Mn and Ru.

Neutron polarization analysis measurements, using the D7 instrument at ILL, Grenoble, were carried out on samples with 6%, 12%, 19% and 23% Ru. This technique allows an isothermal separation of magnetic and non-magnetic scattering. While the 19% and 23% samples showed strong antiferromagnetic Bragg peaks, the 12% sample showed very weak magnetic Bragg intensities that disappeared just above 80 K. Only magnetic diffuse scattering was found for the 6% Ru alloy, arising from short-range magnetic correlations. The curve of the ordering temperatures versus composition, deduced from susceptibility peaks [8], shows a change of slope near 12% Ru. It would appear that the susceptibility peaks below 12% Ru correspond to a transition to spin-glass order, and that the crossover from spin glass to antiferromagnetism occurs slightly below 12% Ru. Interestingly, while the heat capacity of the 19% Ru sample shows a clear cooperative anomaly consistent with a Néel temperature of 137 K, the 12% Ru sample shows only a cusp-like feature at 80 K (figure 1). This is consistent with this sample being close to the critical concentration for long-range AF order.

3. Muon spin relaxation experiments

Muon spin relaxation measurements were made using the MUSR instrument at the ISIS pulsed muon facility, Rutherford Appleton Laboratory (RAL). Three ruthenium concentrations, 6%, 9% and 19 at.%, were studied in detail, using both zero-field (ZF) and longitudinal-field (LF) techniques. For all three samples at high temperature (>150 K) the ZF muon relaxation data were best fitted to a Gaussian Kubo–Toyabe (GKT) form multiplied by an exponential function.

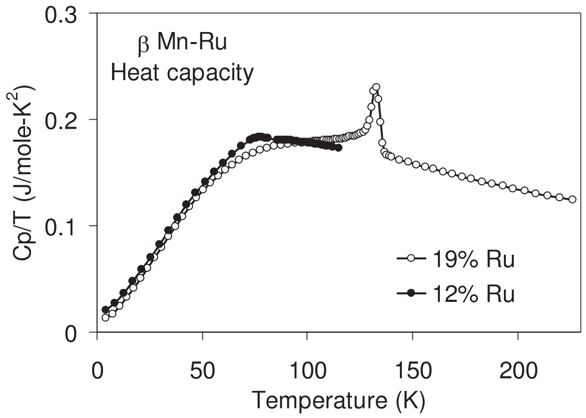

Figure 1. Molar heat capacity data plotted as C/T versus T for β-$Mn_{0.88}Ru_{0.12}$ (filled circles) and β-$Mn_{0.81}Ru_{0.19}$ (open circles). While the 19% sample shows a clear cooperative anomaly at $T_N = 137$ K, the 12% sample exhibits only a weak cusp at $T_N \sim 80$ K.

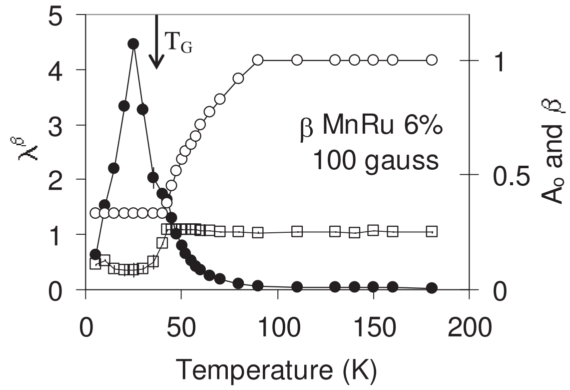

Figure 2. Temperature dependence of μSR parameters for the β-$Mn_{0.94}Ru_{0.06}$ sample, measured with 100 G longitudinal field. Solid circles: relaxation rate parameter λ^β (left-hand scale); open circles: exponent β of the stretched exponential; open squares: initial asymmetry parameter A_0. The values of β and A_0 refer to the right-hand scale. The arrow indicates T_G, the spin-glass temperature deduced from susceptibility data.

The GKT form arises from the fluctuation of the Mn nuclear spins, while the exponential term indicates a component of relaxation by the electronic spins. This was confirmed by the application of a small longitudinal field of 100 G, which completely suppressed the GKT component by decoupling the muon spin from the fluctuating field of the nuclei. The lower-temperature ZF data showed the muon relaxation developing into a dynamical Kubo–Toyabe form as the spin fluctuation response of the Mn slowed down. To avoid the complication of modelling the form of the response in this limit, we have chosen to present here data measured with a longitudinal field of 100 G, so effects from the nuclear spins are decoupled.

For the 6% and 9% Ru samples the LF muon response could be simply modelled using Lorentzian relaxation above 100 K and a stretched exponential form at lower temperatures:

$$P_z(t) = A_0 \exp\left[-(\lambda t)^\beta\right] + B, \quad (1)$$

where B is a small constant background term. The temperature dependences of the fitted parameters are shown in figure 2 for the 6% Ru sample and figure 3 for the 9% Ru sample.

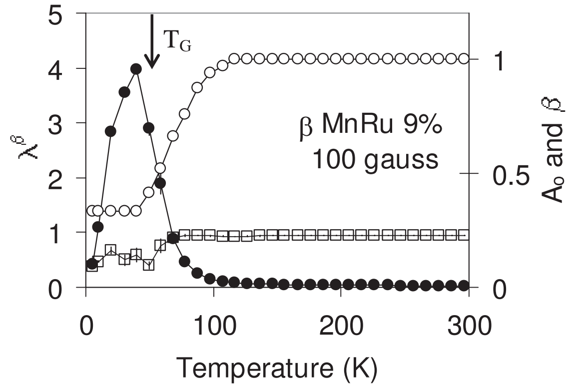

Figure 3. Temperature dependence of μSR parameters for the β-$Mn_{0.91}Ru_{0.09}$ sample, measured with 100 G longitudinal field. The key to the symbols is the same as in the caption of figure 2.

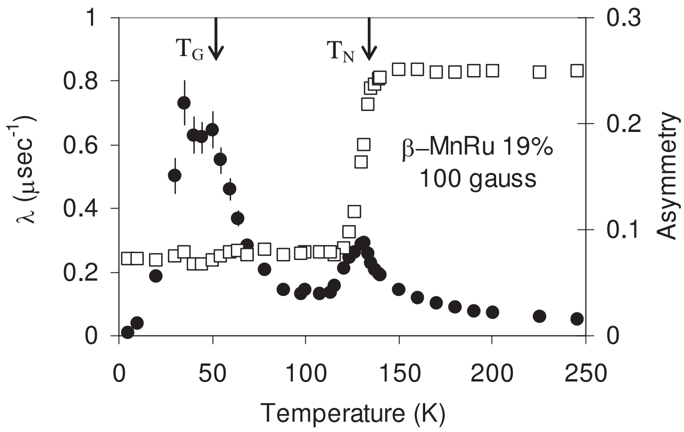

Figure 4. Temperature dependence of muon relaxation rate λ (filled circles) and initial asymmetry A_0 (open squares) for β-$Mn_{0.82}Ru_{0.18}$ alloy, measured in 100 G longitudinal field.

In both the 6% and 9% Ru samples the exponent of the stretched exponential drops smoothly from 1 at high temperature to a value close to one third at a temperature where the initial asymmetry has fallen to about half its high-temperature value. These temperatures agree well with the temperature T_G determined from peaks in the zero-field-cooled (ZFC) susceptibility, indicated by arrows in figures 2 and 3. The relaxation rate parameter λ^β shows a sharp peak at a slightly lower temperature than T_G. This overall behaviour is very similar to that found in many spin-glass systems, in particular β-$Mn_{1-x}Al_x$ alloys [6].

For the 19% Ru sample the muon response is distinctly different. The fitted parameters are shown in figure 4. Simple Lorentzian relaxation ($\beta = 1$) is found down to the Néel temperature $T_N = 137$ K. The initial asymmetry A_0 begins to drop suddenly at T_N and there is a peak in the relaxation rate λ at a slightly lower temperature. Below T_N the form of the relaxation has a stretched exponential form, but the exponent β falls quite slowly to a value of 0.6 at low temperature. Roughly one third of the asymmetry remains below T_N and this component displays a second peak in the relaxation rate near 50 K.

It is informative to compare these data with susceptibility measurements made on the same sample using a vibrating sample magnetometer with an applied field of 1000 G. These data are

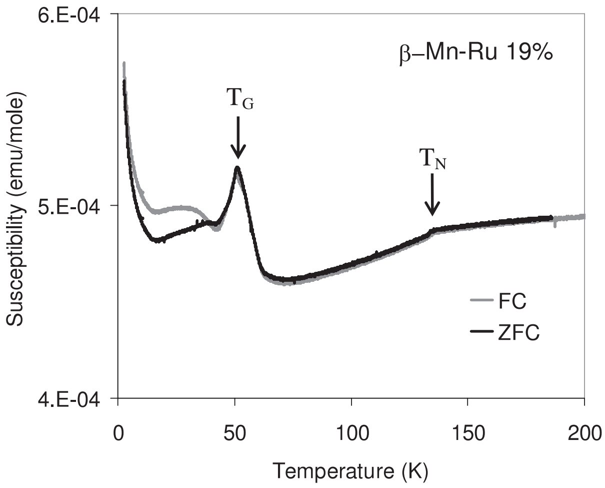

Figure 5. Zero-field-cooled (ZFC) (black curve) and field-cooled (FC) (grey curve) susceptibility of β-$Mn_{0.81}Ru_{0.19}$ sample measured in a field of 1000 G.

shown in figure 5. The onset of antiferromagnetism is signalled by a discontinuity in the slope of $\chi(T)$ at 137 K. However, in addition there is a distinct peak in both the ZFC and field-cooled (FC) susceptibility at 51.7 K, close to the temperature where the muon relaxation rate shows its second maximum. We attribute this peak to the onset of a spin-glass transition within the antiferromagnetic phase. The two arrows in figure 4 correspond to the temperatures of the two features seen in the susceptibility data. There is no clear sign of the spin-glass transition in the temperature dependence of the magnetic Bragg intensities of this sample, so we infer that it has no effect on the AF order parameter. In this case we must regard the spin-glass order as coexistent with the AF phase: this is not an example of a 're-entrant' spin-glass phase, where freezing of the transverse components of the moments leads to finite correlation lengths and the breakdown of long-range magnetic order.

4. Discussion

The nature of the coexistence of spin-glass and long-range AF order in the 19% Ru sample needs further investigation. Since the AF order parameter is not affected by the spin-glass freezing, it is likely that anomalies seen in both the susceptibility and the muon relaxation rate arise from changes in the low-frequency spin dynamics. We have studied the dynamical magnetic response of these alloys by inelastic neutron scattering, using the HET time-of-flight spectrometer at the ISIS pulsed neutron source, RAL. A full analysis of these data will be presented elsewhere; however; there are some qualitative features that bear on the present discussion. All the alloys display a very broad response with a linewidth (HWHM) of order 30 meV, strongly peaked near $|Q| = 1.5$ Å^{-1}. In the 19% Ru sample, for temperatures down to 100 K, the magnetic scattering is peaked at zero energy transfer. Below 100 K the character of the dynamics changes dramatically. At 50 K the response has two components: an inelastic peak near 15 meV and a narrow quasielastic response. The width of the quasielastic response decreases down to 5 K, with extra weight appearing within the elastic line. These measurements were carried out with modest energy resolution (2.5 meV FWHM), so it was not possible to chart the quasielastic width as a function of temperature, nor to distinguish between a very narrow quasielastic line and a truly elastic component. However, it is likely that the spin-glass freezing seen in the susceptibility and the muon relaxation rate are associated with the low-frequency dynamics of this quasielastic component. Further neutron scattering work with high-energy resolution is planned to explore this scenario further.

Systems with a high degree of magnetic frustration are expected to have a high density of low-frequency modes, associated with the degeneracies in the excitation spectra in the Brillouin zone [2]. It is not apparent how this spectral weight becomes distributed in the case of long-range AF order emerging from a frustrated ground state. Taken together, the present observations on β-$Mn_{0.81}Ru_{0.19}$ suggest that a significant weight persists in the low-frequency excitation spectrum of antiferromagnetically ordered β-Mn alloys.

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