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The magnetic structure of β-MnRu

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Abstract

We have performed both conventional and polarized neutron scattering studies of a wide range of β-$Mn_{1-x}Ru_x$ alloy concentrations in the range $0.06 \leqslant x \leqslant 0.23$. We find an incommensurate long-range ordered magnetic structure for Ru concentrations $x \geqslant 0.12$, with a propagation vector of $\mathbf{k} = (u, u, u)$ where $u = 0.278$. The magnetic structure is very complex—showing clear signs of the effect of geometrical frustration. Neutron polarization analysis investigations of the magnetic ground state reveal the persistence of a disordered component of the magnetic structure down to low temperatures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

β-Mn displays a complicated nuclear structure with the simple cubic $P4_132$ space group. Each unit cell contains eight Mn atoms at Wyckoff position 8c (site I), and 12 Mn atoms at position 12d (site II) [1]. NMR spin-lattice relaxation time measurements [2] indicate that only the site II Mn nuclei possess a strong magnetic moment, with $\frac{1}{T1}$ for the site I Mn atoms being 20 times lower than that of site II. However, despite the presence of a large paramagnetic moment on site II, β-Mn remains disordered and rapidly fluctuating at low temperatures [3].

It has long been known that the substitution of dilute quantities of transition metal impurities, as well as non-transition metals such as Al, In and Sn, leads to a static magnetic ground state [4]. This ground state was originally interpreted—mostly on the basis of indirect methods such as NMR and Mössbauer—as being long-range antiferromagnetic. Neutron diffraction measurements [5–7], however, have until recently failed to observe long-range magnetic order in any β-Mn alloy. This issue was first addressed by Shiga and co-workers [5, 8] who pointed out the possibility of topological frustration of antiferromagnetically correlated moments on site II. They drew on the work of Shoemaker *et al* [1] who described the site II sublattice as a distorted network of corner-sharing triangles—termed a 'distorted

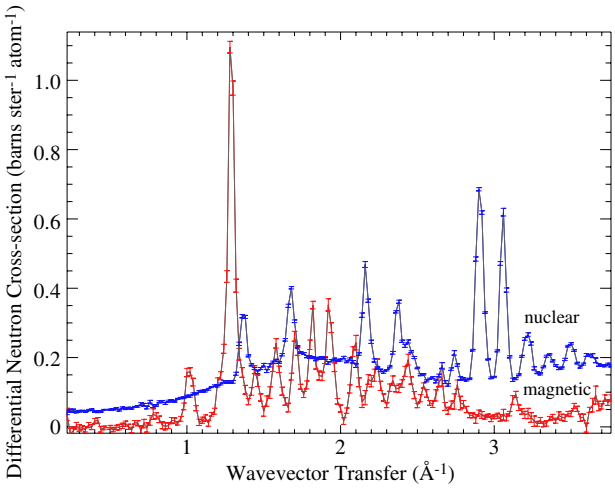

Figure 1. The separated nuclear and magnetic cross-sections of β-$Mn_{1-x}Ru_x$ with $x = 0.19$, measured at 2 K. Considerable diffuse scattering is evident in both the nuclear and the magnetic cross-sections.

windmill'—with the plane of each triangle being normal to local ⟨1 1 1⟩ axes, and each site II Mn atom shared between three triangles.

This 'distorted windmill' structure was later confirmed to be frustrated [9], assuming simple mean-field Heisenberg first near-neighbour exchange between the site II Mn moments and a *perfect* β-Mn lattice; i.e. one in which the triangles of site II Mn atoms are equilateral. If next-nearest neighbour interactions are taken into account, then either $q = 0$ or incommensurate magnetic long-range order is predicted using this model [9].

Long-range order has recently been discovered in alloys of β-Mn with Os and Ru using neutron powder diffraction, although the nature of the ordered magnetic ground state has not yet been elucidated [10, 11]. In this study we present conventional and polarized neutron powder diffraction studies of the ground state magnetic structure of β-MnRu.

2. Neutron polarization analysis

We have performed neutron polarization analysis (NPA) studies of β-$Mn_{1-x}Ru_x$ alloys with $x = 0.6, 0.12, 0.19$ and 0.23 in order to study the transition from short-range to long-range magnetic order as a function of both increasing Ru concentration, x, and decreasing temperature. Neutron polarization analysis is a valuable tool for the investigation of magnetic short-range order since it enables the magnetic contribution to be separated from the nuclear and spin-incoherent contributions to the neutron scattering [12]. Previous NPA studies of β-MnAl have proved invaluable in the characterization of both the nuclear and magnetic short-range order in that system [13]. These experiments were performed on the D7 diffuse scattering polarization analysis spectrometer at the Institut Laue-Langevin (ILL) in Grenoble, using an incident neutron wavelength of 3.1 Å.

Figure 1 shows the separated nuclear and magnetic cross-sections for the $x = 0.19$ sample. Both the nuclear and the magnetic data show considerable diffuse scattering, indicating, in the magnetic case, magnetic disorder co-existent with the long-range magnetic order, and, in the nuclear case, the presence of non-random Ru concentration fluctuations (anti-clustering Ru atoms).

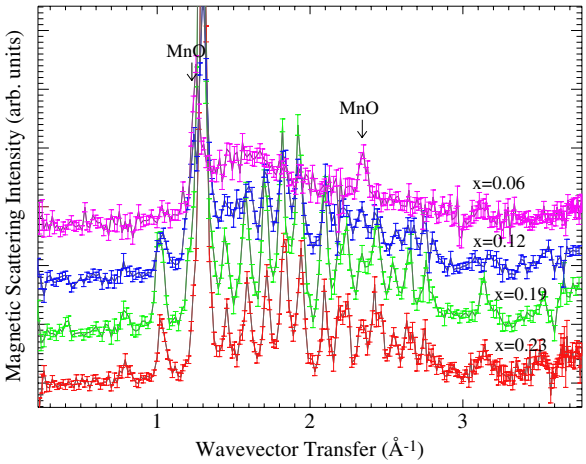

Figure 2. The magnetic cross-sections of β-$Mn_{1-x}Ru_x$ with (top to bottom) $x = 0.06, 0.12, 0.19$ and 0.23 measured on D7.

Figure 2 shows the magnetic cross-sections of all the samples studied, measured at 2 K. Magnetic Bragg peaks appear for $x \geqslant 0.12$ but a residual disordered component (similar to that seen in the $x = 0.06$ sample) remains. The Bragg peak positions are seen to be *independent* of x. Temperature-dependent measurements of the magnetic scattering show a gradual transition from short-range order in the paramagnetic regime to long-range order at low temperatures. The position of the Bragg peaks does not change with temperature. All attempts to index the magnetic peaks based on a commensurate propagation vector proved unsuccessful, suggesting that the observed magnetic structure is incommensurate.

3. Unpolarized neutron powder diffraction

In order to further examine the long-range ordered magnetic structure of β-MnRu we have performed a high-resolution neutron powder diffraction experiment on the $x = 0.23$ sample, using the D1A neutron powder diffractometer at the ILL, with an incident wavelength of 1.91 Å.

The projection of a three-dimensional reciprocal lattice onto a one-dimensional powder diffraction spectrum greatly hinders the determination of incommensurate wavevectors as many different wavevectors will allow magnetic scattering at the same angular positions, limiting the usefulness of searches based only on the observed scattering angles and those permitted for the different wavevectors. For this work the wavevectors trialled were limited to the points, lines and planes of symmetry given in table 1 with values of any free reciprocal lattice coordinate being chosen randomly. For each trial, the magnetic structure factors for equal moments on the magnetic Mn positions were refined for 20 reverse Monte Carlo cycles with the χ^2 for the refinement as the figure-of-merit parameter. Using this technique it was found that the magnetic scattering of β-$Mn_{0.77}Ru_{0.23}$ could only be well described using a propagation vector along the $\mathbf{k}_9 = \Lambda$ line with $u = 0.278$. Rietveld refinement of the diffraction data was carried out using SARA*h* [14] together with FullProf [15] and the final fit is shown in figure 3.

Symmetry analysis of the ordered magnetic structures for site I and site II reveals that there is insufficient symmetry in the unitary little group of the propagation vector G_k^{unit} to relate all of the equivalent positions associated with these two crystallographic sites: those of site I are split into four distinct groups or 'orbits' (see table 2). Extension to include anti-unitary

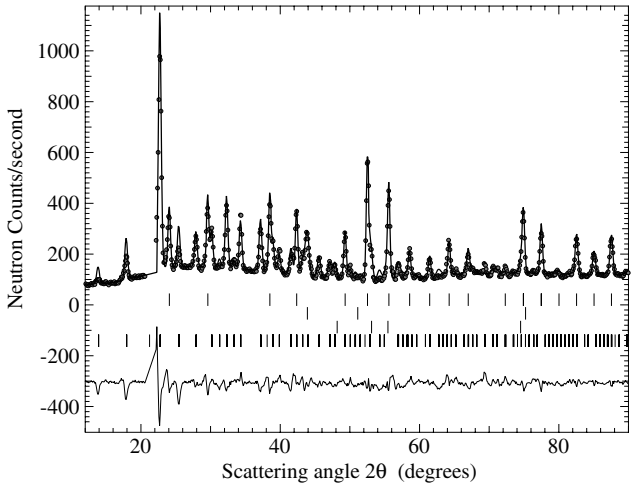

Figure 3. The experimental (○) and refined (−) low temperature diffraction pattern of β-$Mn_{0.77}Ru_{0.23}$. From the top, the tick marks indicate the locations of the magnetic reflections that are due to the nuclear scattering from β-$Mn_{0.77}Ru_{0.23}$, a small amount of MnO and Ru impurities, and the magnetic ordering of β-$Mn_{0.77}Ru_{0.23}$. The final value of R_{Bragg} for the magnetic phase was 18.9 with 22 variables.

Table 1. Points, lines and planes of symmetry for the Brillouin zone of primitive cubic space group $P4_132$. The observed magnetic ordering wavevector corresponds to the line of symmetry $\mathbf{k}_9 = \Lambda = (0.278,\ 0.278,\ 0.278)$, defined with respect to the conventional nuclear cell. The labelling schemes used are those of Kovalev [16] and Bradley and Cracknell [17].

Point [16]	Point [17]	Coordinates
$\mathbf{k}_1$	A	$u, v, 0$
$\mathbf{k}_2 h_5$	B	$u, v, \frac{1}{2}$
$\mathbf{k}_3$	C	u, u, v
$\mathbf{k}_4$	Σ	$u, u, 0$
$\mathbf{k}_5 h_5$	S	$u, u, \frac{1}{2}$
$\mathbf{k}_6 h_9$	Z	$\frac{1}{2}, 0, u$
$\mathbf{k}_7$	T	$\frac{1}{2}, \frac{1}{2}, u$
$\mathbf{k}_8 h_5$	Δ	$0, 0, u$
$\mathbf{k}_9$	Λ	u, u, u
$\mathbf{k}_{10} h_5$	X	$0, 0, \frac{1}{2}$
$\mathbf{k}_{11}$	M	$\frac{1}{2}, \frac{1}{2}, 0$
$\mathbf{k}_{12}$	Γ	$0, 0, 0$
$\mathbf{k}_{13}$	R	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

symmetry [17] links some of these orbits together: site I, $1 \oplus 4$; site II, $2 \oplus 3$. As all of the co-representations associated with the anti-unitary group of the propagation vector G_k^{anti} are of type 'A' [17], the linking of the orbits requires that their basis vector mixing coefficients be the same. This must not, however, be taken as a complete homogenization of the magnetic order as there is an arbitrary phase factor that relates the otherwise disjoint groups that should be refined. The decomposition of the magnetic representation and co-representation are given in table 2.

Although the structure is an extremely complex helix, it corresponds to the most symmetric co-representation of the little group generated from the space group $P4_132$ and the propagation

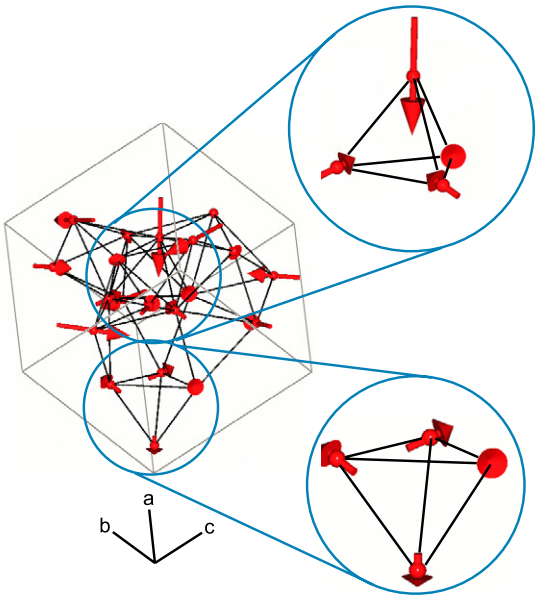

Figure 4. The refined magnetic structure of β-$Mn_{0.77}Ru_{0.23}$ with the propagation vector $\mathbf{k} = (0.278, 0.278, 0.278)$.

Table 2. The orbits of the different Mn lattice positions, and the decomposition of the magnetic representation according to the unitary little group G_k^{unit}. Anti-unitary symmetry links the orbits and decompositions of site I, $1 \oplus 4$, and site II, $2 \oplus 3$.

Site I orbit	Decomposition	Site II orbit	Decomposition
1	$1\Gamma_1 + 1\Gamma_2 + 1\Gamma_3$	1	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
2	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$	1	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
2	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$	1	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
2	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$	2	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
3	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$	2	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
3	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$	2	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
3	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$	3	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
4	$1\Gamma_1 + 1\Gamma_2 + 1\Gamma_3$	3	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
		3	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
		4	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
		4	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$
		4	$3\Gamma_1 + 3\Gamma_2 + 3\Gamma_3$

vector **k**, and is symmetric with respect to the E, C_{31}^{-} and C_{31}^{+} symmetry operations. The high frustration of the magnetic system is evidenced by the canting of the moments and the formation of tetrahedra with $\sum_i S_i \sim 0$, as highlighted in figure 4.

4. Conclusions

We have performed neutron diffraction studies of a number of β-$Mn_{1-x}Ru_x$ concentrations. For $x \geqslant 0.12$ incommensurate long-range magnetic order is established with a propagation vector of $\mathbf{k} = (0.278, 0.278, 0.278)$. The magnetic order is extremely complex with moment

formation on both Mn lattice sites. A candidate structure based on one magnetic site (on the site II β-Mn sublattice) was tried, and was found to fit the data well, but there is no *prima facie* evidence for the absence of a magnetic moment on site I from the data presented in this study. Single crystal studies would certainly shed more light on this issue—if single crystal samples of β-MnRu were available. It is remarkable that the incommensurate wavevector **k** is extremely stable with respect to both temperature and Ru concentration. The polarization analysis data show that this long-range ordered ground state co-exists with a disordered magnetic component. This is consistent with the results of a muon spin relaxation and ac susceptibility study published elsewhere [18] which find a low-temperature spin-glass-like transition in β-$Mn_{1-x}Ru_x$ with $x = 0.19$.

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References

[1] Shoemaker C B, Shoemaker D P, Hopkins T E and Yindepit S 1978 *Acta Crystallogr.* B **34** 3573
[2] Kohori Y, Noguchi Y and Kohara T 1993 *J. Phys. Soc. Japan* **62** 447
[3] Stewart J R, Rainford B D, Eccleston R S and Cywinski R 2002 *Phys. Rev. Lett.* **89** 186403
[4] Kohara T and Asayama A 1974 *J. Phys. Soc. Japan* **37** 401
[5] Shiga M, Nakamura H, Nishi M and Kakurai K 1994 *J. Phys. Soc. Japan* **63** 1656
[6] Funahashi S and Kohara T 1984 *J. Appl. Phys.* **55** 2048
[7] Nakai Y 1994 *J. Phys. Soc. Japan* **63** 775
[8] Nakamura H, Yoshimoto K, Shiga M, Nishi M and Kakurai K 1997 *J. Phys.: Condens. Matter* **9** 4071
[9] Canals B and Lacroix C 2000 *Phys. Rev.* B **61** 11251
[10] Sasao K, Umetsu R Y and Fukamichi K 2001 *J. Alloys Compounds* **325** 24
[11] Miyakawa M, Umestu R Y, Ohta M, Fujita A, Fukamichi K and Hori T 2005 *Phys. Rev.* B **72** 054420
[12] Stewart J R, Andersen K H, Cywinski R and Murani A 2000 *J. Appl. Phys.* **87** 5425
[13] Stewart J R and Cywinski R 2004 *J. Magn. Magn. Mater.* **272–276** 676
[14] Wills A S 2000 *Physica* B **276** 680 (program available from ftp.ill.fr/pub/dif/sarah/)
[15] Rodriguez-Carvajal J 1993 *Physica* B **192** 55
[16] Kovalev O V 1993 *Representations of the Crystallographic Space Groups* 2nd edn (London: Gordon and Breach Science Publishers)
[17] Bradley C J and Cracknell A P 1972 *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon)
[18] Leavey C J, Stewart J R, Rainford B D and Hillier A D 2006 *J. Phys.: Condens. Matter* **18** at press