The Magnetic and Crystal Structure of MnₓGa (1.15 ≤ x ≤ 1.8) Alloys

D. H. Ryan¹, Ming Yue², C. B. Boyer³, X. B. Liu³, Qingmei Lu², Hongguo Zhang², Chenhui Li², Manli Wang² & Z. Altounian²

Neutron powder diffraction patterns measured above T_c have been used to determine the location of the excess Mn in MnₓGa (1.15 ≤ x ≤ 1.8). This information has then been used to constrain the fits to neutron powder diffraction patterns measured at ambient temperature and so determine unambiguously the Mn moments in this system. We find that Mn randomly occupies the two Ga sites (2a and 2b) in the I₄/mmm structure and propose that it is more appropriate to use a simpler structure based on the P₄/ mmm space group with a reduced unit cell. In this structure the two Ga sites are formally equivalent (they occupy the 1a site while Mn occupies the 1d site). Our experimental observations are supported by DFT calculations. Below T_c we find that the Mn(1d) moment is constant at 2.45(3) μₜ while Mn on the 1a site carries a slightly larger moment (~3 μₜ) that is coupled antiparallel to the Mn(1d) moments, leading to the observed drop in magnetisation with increasing Mn content in MnₓGa.

Manganese-based magnetic compounds are of interest for two main reasons: (1) they avoid the use of rare earths, (2) they offer modest-cost/modest performance alternatives to the two dominant hard magnet technologies: NdₓFeᵧ₁₋ₓB (515 kJ m⁻³) and Ba(Sr)Fe₁₂O₁₉ (45 kJ m⁻³). Mn frequently carries a large moment, has reasonable chemical stability, and comes at a moderate cost. One possible system is Mn-Ga. The predicted saturation magnetisation of stoichiometric MnGa is 116 J/T/kg² and if a reasonably square loop could be achieved, this would yield an energy product in excess of 200 kJ m⁻³. Unfortunately, the Mn-Ga binary phase diagram is extremely complex, lacking a single congruently-melting compound. As a result, sample preparation is complex and quality is often poor. The problem has been compounded by focusing on producing technically interesting materials before the intrinsic properties have been understood.

In a previous paper we described the excellent intrinsic magnetic properties of the MnₓGa system². Here we concentrate on establishing the basic crystal and magnetic structures; determining the location and ordering behaviour of the excess manganese.

Stoichiometric MnGa is reported to adopt the tetragonal P₄/ mmm structure (#123, often denoted as I₄₁₀, shown at the top right of Fig. 1) with a ~3.9 Å and c ~3.8 Å, while MnₓGa adopts a closely related tetragonal I₄/mmm structure (#139, or D₀₁₂, shown at the left of Fig. 1), that is formed by stacking two MnGa cells along the c-axis and redecorating. However, in going from P₄/ mmm to I₄/mmm we pick up an inconvenient selection rule (l = 2n) and the occupation of the 4d site by Mn in the I₄/mmm structure imposes a further constraint on l: l = 2n, ∀ h, k. The result of these constraints is that it is essentially impossible to distinguish the P₄/ mmm and I₄/mmm Mn-Ga structures on the basis of x-ray diffraction data. Indeed, unless there is a severe imbalance in the Mn/Ga occupations of the two Ga sites shown in Fig. 1, the two structures are formally identical: Any packing of a MnₓGa P₄/ mmm cell can be mapped directly onto an I₄/mmm cell yielding the same (doubled cell) crystal structure and precisely the same diffraction pattern. Even if we assume perfect selectivity, the impact on the diffraction pattern is vanishingly small: Taking a composition of Mn₁.₆₆ Ga and placing all of the excess Mn on the Ga(2a) site in the I₄/mmm cell (half filling it) changes the intensity of the (002) peak from ~1% of the (112) peak (the strongest in the x-ray diffraction pattern) to ~1.7%. We adopted the I₄/mmm cell as the starting point for our structural analysis but, as we show below, found that a much simpler structure based on the P₄/ mmm space group with a reduced size unit cell (shown at the bottom right of Fig. 1) provided a consistent fit to our data.

Our interest here is threefold: (1) What is the correct space group and structure for this system? (2) What is the internal packing of the cell? i.e. Where does the excess manganese go as we increase x from 1? (3) What is the origin of the reduction in magnetisation seen on increasing x from 1 in MnₙGa?

¹Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec, H3A 2T8, Canada. ²College of Materials Science and Engineering, Beijing University of Technology, Beijing, 100122, China. ³Canadian Neutron Beam Centre, Chalk River Laboratories, Ontario, K0J J01, Canada. Correspondence and requests for materials should be addressed to M.Y. (email: yueming@bjut.edu.cn)
The poor x-ray contrast between Mn and Ga means that x-ray diffraction cannot be used to study the distribution of Mn within the cell. Indeed, the x-ray diffraction patterns of $\text{Mn}_x\text{Ga}$ are almost indistinguishable from that of a uniform face-centred tetragonal (fct) cell, with the strongest fct-forbidden reflection ($\langle 001 \rangle$ for the $P4/mmm$ cell) being of order 1% of the intensity of the primary (111) reflection. In addition, magnetic order cannot be studied using conventional x-ray diffraction methods. Therefore, we turn to neutron diffraction where there is almost optimal contrast between Mn and Ga (coherent scattering lengths, $b_c$, are: $b_c(\text{Mn}) = -3.75\text{ fm}$ and $b_c(\text{Ga}) = +7.288\text{ fm}$), and we are also sensitive to the magnetic ordering. This latter sensitivity is important as the magnetisation of $\text{Mn}_x\text{Ga}$ decreases with increasing $x$, suggesting that the additional Mn couples antiferromagnetically (AF) to the ferromagnetic (FM) Mn found in the parent $\text{MnGa}$ cell.

Our initial neutron diffraction work on this system confirmed that the moments on Mn atoms that occupied the Ga sites in $\text{Mn}_x\text{Ga}$ ($1.15 \leq x \leq 2.0$) were coupled AF to those on the primary Mn site and that this was the origin of the reduction in magnetisation. However, strong correlations between the cell packing and magnetic contributions to the diffraction patterns made an unambiguous determination of the basic structure impossible. Here we eliminate the correlation problem entirely by analysing neutron diffraction patterns taken above the ordering temperature of each material where the magnetic contribution is absent, and then using the cell packing information derived from these fits to constrain the analysis of the neutron diffraction patterns taken at ambient temperature. This approach is complemented by using density functional theory (DFT) calculations to investigate possible site preferences for the excess Mn in $\text{Mn}_x\text{Ga}$, and to determine the magnitudes and orientations of the Mn moments on the three possible sites in the (initially assumed) $I4/mmm$ cell.

**Experimental Methods**

A series of tetragonal $\text{Mn}_x\text{Ga}$ ($x = 1.15, 1.20, 1.40, 1.50, 1.60$ and $1.80$) alloys were prepared by induction melting high purity gallium (99.9%) and manganese (99.5%) in an argon atmosphere. To compensate for evaporation losses during melting, an extra 3 wt.% Mn was added to the alloys. The as-cast ingots were annealed in a tubular vacuum furnace at temperatures, $T_a$, ranging from 700 K to 900 K for one to seven days and then quenched into ice water. The annealing step is crucial for obtaining single-phase alloys, and the optimal annealing temperature range was found to be quite narrow and depended critically on the composition of the alloy.

Basic structure and phase purity were confirmed using Cu–K$_\alpha$ x-ray diffraction. Magnetic properties were measured using a Quantum Design Physical Properties Measurement System (PPMS) magnetometer with a maximum magnetic field of 14 T. Neutron powder diffraction experiments were carried out at both ambient and elevated temperatures on the C2 800-wire powder diffractometer (DUALSPEC) at the NRU reactor, Chalk River Laboratories, Ontario, Canada, using neutron wavelengths ($\lambda$) of 1.32905(5) Å and 2.37047(8) Å to cover the widest range of scattering vectors ($0.3\text{ Å}^{-1} \leq q \leq 8.0\text{ Å}^{-1}$). The multi-wire detector covers an 80-degree arc of $2\theta$ at one time and the angle ranges used for the two wavelengths were chosen so as to have two strong diffraction peaks in common between the two patterns to facilitate co-refinement (see Fig. 2). For every sample, the patterns at each wavelength were counted so as to have at least 40,000 counts in the strongest diffraction peak.

For the high temperature (non-magnetic) data, shown in Fig. 2, the long and short wavelength diffraction patterns were co-refined to a single structural model for each composition using GSAS/EXPGUI. For each composition, several structural models were tried starting from the $I4/mmm$ space group and the final selection was...
constrained by demanding agreement with the nominal alloy composition. As described below, an evaluation of these fits led us to reject the I4/mmm cell as the basis for describing the structure of Mn$_x$Ga and adopt a simpler reduced-cell P4/mmm-based crystal structure for both the structural and magnetic fits.

With the cell symmetry and packing established from the analysis of the high temperature patterns, the ambient temperature patterns (taken at both wavelengths and recorded to the same quality as the high temperature patterns) were then co-refined to determine the Mn moments, subject to the structural constraints derived from the high temperature fits.

Figure 2. Neutron diffraction patterns for Mn$_{1.60}$Ga taken at 500 °C (i.e. above $T_c$). The top panel shows the pattern measured using 2.37047(8) Å neutrons and fitted assuming the I4/mmm cell. The position of the (101) peak that would be present if the I4/mmm cell were the correct choice and there was an imbalance in the Mn occupations of the two Ga sites is also shown (see text for more details). The middle and bottom panels show the data taken with 2.37047(8) Å and (bottom) 1.32905(5) Å neutrons respectively and fitted assuming the small P4/mmm cell. The region between $2\theta = 52^\circ$ and $2\theta = 82^\circ$ has been rescaled by a factor of 20 in the centre panel so that the (111) peak from the 0.25(5) wt.% MnO impurity can bee seen. There is also a small peak from an unidentified impurity at $2\theta = 67.2^\circ$. The solid line in each case is a fit. Bragg markers and a plot of the residuals are also shown. Several Mn$_{1.60}$Ga peaks in the 2.37047(8) Å patterns are indexed, as are the first two in the 1.32905(5) Å pattern (to establish the overlap between the two data sets).
To understand the site distribution of the excess Mn at the 2\(a\) and 2\(b\) sites in the I4/mmm cell, the total energy for Mn\(_x\)Ga (1.0 \(\leq x \leq 2.0\)) with different occupancy configurations of Mn were calculated by a DFT (density functional theory) method. We set the super-cell with a nominal composition of Mn\(_4\)(Mn\(_2\)Ga\(_2\)) with the four Mn atoms at the 4\(d\) site and the two Ga atoms at either the 2\(a\) or the 2\(b\) site. The remaining two Mn atoms were then placed on the vacant 2\(b\) or 2\(a\) site. The QUANTUM ESPRESSO package\(^8\), in the projected augmented wave (PAW) framework\(^9\), was employed to perform DFT calculations using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof\(^10,11\) for the exchange correlation functional. The atomic PAW potentials were adopted from the PS library.\(^1\) generated by A. Dal Corso.\(^12\) The wave functions were expanded in plane-wave basis sets truncated at a cutoff energy of 60 Ry. Brillouin zone integrations were performed on a 8\(\times\)8\(\times\)8 \(k\)-point grid, and Marzari-Vanderbilt broadening\(^13\) was applied with a smearing width of 5 mRy. The structural degrees of freedom were fully relaxed to obtain optimized structural parameters. In addition, the magnetic moments in Mn\(_x\)Ga have been calculated using a linear muffin-tin orbital method with coherent potential approximation (LMTO-CPA)\(^14,15,16\).

**High Temperature Results–Cell Symmetry and Packing**

Our starting point for the fits to the high temperature neutron diffraction patterns was the body-centred tetragonal I4/mmm cell with Mn atoms on the 4\(d\) site and Ga on both the 2\(a\) and 2\(b\) sites giving an initial stoichiometry of MnGa. The two patterns for each composition were fitted by permitting vacancies on the 2\(a\) and 2\(b\) sites, partial filling of each site with Mn, or no vacancies with a mix of Mn and Ga on the 2\(a\) and 2\(b\) sites. In each case, statistically equivalent quality fits could be obtained, but only the model with the 2\(a\) and 2\(b\) sites filled (no vacancies) returned the expected stoichiometry. The other models were therefore rejected.

As the top panel of Fig. 3 shows, we appeared to observe a slight systematic preference for Mn to occupy the 2\(a\) site over the 2\(b\) site. However, if we reversed the starting point for the fits by exchanging the occupations of the 2\(a\) and 2\(b\) sites, we could obtain a fit with the same \(\chi^2\) and precisely the same occupations (to four digits) but with Mn favouring the 2\(b\) site over the 2\(a\) site. Examination of simulated diffraction patterns with a stronger 2\(a\):2\(b\) bias revealed that an occupation imbalance led to appearance of the (101) peak (near \(2\theta = 40^\circ\) in the long wavelength pattern – see upper panel of Fig. 2) and some minor changes in the intensity of the (002) and (110) peaks to the left and right of the (101) peak respectively. The (101) peak was absent from all of our measured patterns and it therefore appears that the 2\(a\):2\(b\) imbalance was an artefact of the fitting program chasing noise.

Constraining the occupations of the 2\(a\) and 2\(b\) sites to be the same had no impact on the quality of the final fit and still returned the expected stoichiometry. This observation led us to consider the possibility that the 2\(a\) and 2\(b\) sites were not actually distinct: i.e. that the space group was incorrect. A search for possible alternative space groups led us back to the simple tetragonal P4/mmm space group (#123) but with the reduced-size unit cell.

![Figure 3](image-url). (top) Fitted Mn occupations of the 2\(a\) and 2\(b\) sites (assuming an I4/mmm cell) compared with the Mn occupation of the 1\(a\) site assuming the simpler P4/mmm cell). (bottom) Stoichiometry derived from the two models. The dashed line has a slope of one and indicates the expected correspondence between the nominal and fitted compositions.
**Figure 4.** The basal planes for the small (bottom left) and large (top right) P4/mmm cells showing the relationship between the \(a\)-axes in the two cases. The smaller-cell P4/mmm basal plane is rotated by 45° and reduced in size by a factor of \(\sqrt{2}\) with respect to the large-cell P4/mmm basal plane. See Fig. 1 for views perpendicular to the \(c\)-axis.

**Figure 5.** Neutron diffraction patterns for Mn\(_{1.60}\)Ga taken at ambient temperature (i.e. below \(T_c\)) using (top) 2.37047(8) Å and (bottom) 1.32905(5) Å. The solid line in each case is a fit to the P4/mmm magnetic and structural model described in the text. Bragg markers and a plot of the residuals are also shown. The two strongest magnetic contributions at (011) and (110) are identified on the 2.37047(8) Å pattern.
originally proposed by Bither and Cloud. Figure 4 shows the relationship between the basal planes of the large and small cell P4/mmm structures. Placing the Mn atoms in the 1d site (located at 1/2 1/2 1/2) and the Ga atoms in the 1a site (located at 0 0 0) yields precisely the same packing as our I4/mmm starting point, and the same calculated diffraction pattern. The (101) peak (in the I4/mmm cell) that could have signalled a difference in Mn occupation between the “two” Ga sites is forbidden, consistent with the sites now being equivalent. Refinements from this starting point yield fits that were fully equivalent to those obtained using the I4/mmm cell and returned the expected stoichiometry, but required fewer fitting parameters. Fitted patterns for the Mn 1.60Ga sample taken at 500 °C and using the smaller P4/mmm cell are shown in Fig. 2.

To further investigate whether the 2a and 2b sites in the I4/mmm cell were indeed equivalent, we carried out DFT calculations looking at the energy associated with placing Mn on either the 2a or the 2b site. Our calculations showed that the binding energy for the excess Mn at the 2a site is precisely the same as that for Mn at the 2b site (−4.08 eV/atom). We therefore conclude that the two sites are indeed fully equivalent and that the P4/mmm space group is the correct one to use for Mn0.60Ga. As a final check, we confirmed that the energies associated with substituting Mn at each of the two Ga sites in the large-cell P4/mmm structure were also the same. The revised structural description is simpler (only two crystallographic sites are occupied) and the stoichiometry for the end-member (MnGa) is obtained directly.

The Mn occupation of the 1a site and the resulting stoichiometry are plotted in Fig. 3. These results form the starting point for our analysis of the magnetic ordering in the ambient temperature patterns.

**Ambient Temperature Results – Magnetic Ordering**

The most striking feature of the ambient temperature patterns for Mn0.60Ga shown in Fig. 5 is how little they change in comparison with the 500 °C patterns shown in Fig. 2. The most visible changes are the increase in the intensity of the (010) reflection relative to the (001) and some very small increases in intensity at the (011) and (110) positions. This immediately serves to underline the critical need both for high quality patterns and to establish the locations of the excess Mn atoms within the cell before proceeding to a determination of the magnetic structure. The magnetic and crystallographic cells are the same size (no cell doubling occurs when the magnetic order develops) so the magnetic scattering appears only at nuclear-allowed positions. There is significant cross-talk between the scattering contributions from the cell packing and the magnetic ordering, and there are many different ways to play off these contributions. However, by determining the Mn locations above Tc we sidestep this problem entirely, and can proceed to determining the magnetic moments free of ambiguity.

Figure 6. (top) The open symbols show the fitted Mn moments for the two sites in the P4/mmm Mn0.60Ga structure. The moment of the manganese on the 1d site is essentially constant at 2.45(3) μB/Mn while a slightly larger antiparallel moment of ~3 μB/Mn appears on Mn atoms that occupy the 1a site. Also shown as solid points are the corresponding moments calculated using DFT. (bottom) Net magnetisation derived from the neutron scattering fits (neutron) compared with values obtained from bulk magnetisation data (PPMS).
The magnetic structure used as a starting point was based on the P4/mmm magnetic space group that allows for c-axis FM ordering of the Mn moments on the 1d site. This magnetic group also permits c-axis ordering at the 1a site where we have shown that the excess Mn substitutes for Ga. Only collinear magnetic structures were considered here. The magnetic space group adopted for the analysis here is essentially equivalent to the I4/mmm magnetic space group used previously when the I4/mmm structure was being considered.

For all compositions we find that the Mn atoms that replace Ga atoms on the 1a site have moments that couple antiparallel to those on the primary 1d site, broadly consistent with our earlier analysis. In addition, we find that the size of the Mn(1d) moment is essentially independent of composition at 2.45(3) μB/Mn. The situation at the 1a site is somewhat less clear as the Mn occupation of this site never exceeds 0.25 and for the two lowest excess Mn samples ($x = 1.15$ and $1.20$) the Mn occupation of the 1a site is only ~0.1. This leads to rather large uncertainties on the fitted moment, however it appears to be broadly constant, and at 3.0(1) μB/Mn, it is clearly larger than that on the 1d site. These results are plotted on the upper panel of Fig. 6. Comparison of the derived magnetisation with that measured by bulk magnetometry (lower panel of Fig. 6) shows that the neutron results track well with the bulk data but appear to be about 10% higher. The origin of this offset is not understood, and it may reflect some incomplete saturation in the bulk data. We can however rule out canting of the moments. Strictly speaking, occupation of the 1d and 1a sites in the P4/mmm space group is only compatible with purely c-axis ordering, but leaving this issue of principle aside, any planar (ab-) component to the magnetic order would almost certainly lead to a severe mis-fit to the intensity of the (002) peak, especially given the significant magnetic contribution to the (110) peak. Any long-period modulation of the order (spirals, cones etc.) would be expected to contribute both magnetic satellites and a low-angle peak from the new periodicity. Neither are seen (see Fig. 2 of Rejali et al. for data down to 0.3 Å$^{-1}$). It is clear from our fits to the magnetic structure that the decline in bulk magnetisation with increasing Mn in Mn$_x$Ga is the result of antiparallel Mn moments on the 1a (Ga) sites (shown in Fig. 7).

Calculated moments for the two sites derived from our DTF work are shown for comparison as solid symbols on the upper panel of Fig 6. The agreement is remarkably close. For the Mn on the 1d site we observe a slight (~2.5%) decline over the studied range, with an average value of 2.40(2) μB/Mn, while for the Mn on the 1a site we observe a similar, ~3%, decline with increasing Mn content and an average value of −3.24(3) μB/Mn. The former
moment is in perfect agreement with the experimental value, while the latter value is only slightly outside experimental error for the average value and well within the experimental scatter (Fig. 6).

Conclusions
Neutron powder diffraction patterns measured above and below Tc have been used to determine the site occupancies and magnetic properties of a series of MnGa (1.15 ≤ x ≤ 1.8) alloys. Both our high temperature diffraction patterns and DFT calculations show that there is no difference between the the 2a and 2b sites in the commonly used I4/mmm–based (D022) structure, or equivalently, 1a and 1c sites in the large-cell P4/mmm (L12) structure. We therefore propose a much simpler crystal structure based on the I4/mmm space group with a reduced unit cell, originally suggested by Bither and Cloud17. We find that the excess Mn in MnGa replaces some of the Ga on the 1a site, and with the crystal structure as a constraint we are able to make an unambiguous determination of the magnetic structure and Mn moments. Antiparallel ordering between the 2.45(3) μB Mn moments on the 1d site and the 3.0(1) μB moments associated with the excess Mn on the 1a site leads to the observed decline in bulk magnetisation. These results are in full, quantitative agreement with both DFT calculations and bulk magnetisation measurements.

If hard magnets are to be developed based on the MnGa system, it will be necessary to find something that will substitute for Ga on the 1a site but that either carries a much smaller moment than the Mn (without causing a loss of anisotropy) or couples parallel to the Mn moments on the 1d site. Given the remarkable agreement between our experimental data and the DFT calculations, it would appear that a preliminary search using DFT calculations could reliably identify promising candidates and so greatly reduce the synthetic effort associated with the development of new materials in this system.

References
1. Coey, J. M. D. New permanent magnets: manganese compounds. Journal of Physics: Condensed Matter 26, 064211 (2014).
2. Sakuma, A. Electronic structures and magnetism of CaAu-type MnNi and MnGa. J. Magn. Magn. Mater. 187, 105 (1998).
3. Lu, Q. et al. Intrinsic magnetic properties of single-phase Mn0.4xGa0.58(0 < x < 1) alloys. Scientific Reports 5, 17086 (2015).
4. Mix, T., Müller, K.-H., Schultz, L. & Woodcock, T. G. Formation and magnetic properties of the L12 phase in bulk, powder and hot compacted Mn-Ga alloys. J. Magn. Magn. Mater. 391, 89 (2015).
5. Beaulieu, R. et al. Crystal structure and magnetism of the Mn0.5Ga (1.15 ≤ x ≤ 2.0) rare-earth-free permanent magnet system. AIP Advances 6, 056003 (2016).
6. Larson, A. C. & Von Dreele, R. B. General structure analysis system (GSAS). Los Alamos National Laboratory Report LAUR 86–748 (2000).
7. Toby, B. H. Expgui, a graphical user interface for GSAS. J. Appl. Cryst. 34, 210–213 (2001).
8. Giannozzi, P. et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter 21, 395502 (2009).
9. Blochl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).
10. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
11. Perdew, J. P. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. Phys. Rev. Lett. 100, 136406 (2008).
12. Del Corso, A. Pseudopotentials periodic table: From H to Pu. Computational Materials Science 95, 337–350 (2014).
13. Marzari, N., Vanderbilt, D., De Vita, A. & Payne, M. C. Thermal contraction and disordering of the Al(110) surface. Phys. Rev. Lett. 82, 1296–1299 (1999).
14. Andersen, O. K. Linear methods in band theory. Phys. Rev. B 12, 3060–3083 (1975).
15. Kresse, G., Joubert, D. Quantum Monte Carlo Methods. Surfaces and Interfaces (Kluwer, Boston, 1997).
16. Ke, L., Belashchenko, K. D., van Schilfgaarde, M., Kotani, T. & Antropov, V. P. Effects of alloying and strain on the magnetic properties of Fe5N3. Phys. Rev. B 88, 024404 (2013).
17. Bither, T. A. & Cloud, W. H. Magnetic tetragonal δ phase in the Mn–Ga binary. Journal of Applied Physics 36, 1501–1502 (1965).

Acknowledgements
Financial support for this work was provided by: the Natural Sciences and Engineering Research Council of Canada, the Fonds Québécois de la Recherche sur la Nature et les Technologies, the National Natural Science Foundation of China (51331003, 51401002).

Author Contributions
D.H.R. carried out the neutron diffraction measurements (working with C.D.B.), analysed the data and drafted the manuscript. Z.A. developed the structural model and assisted with the drafting of the manuscript. X.B.L. carried out the DFT calculations. M.L. Wang prepared samples and measured XRD. C.H. Li measured magnetic properties. M. Yue contributed to the concept. Q.M. Lu analysed the XRD results. H.G. Zhang analysed the magnetic results.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2017