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Magnetic structure of the high temperature superconductor $Gd_{1-x}Th_xFeAsO$

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The magnetic structure of the high temperature superconductor $Gd_{1-x}Th_xFeAsO$ (x = 0, 0.25) has been determined by neutron powder diffraction. The Gd moments were found to order at $T_N \sim 4$ K and to lie in the basal plane, and form alternating ferromagnetic sheets along the *c*-axis. The orientation of the gadolinium moments in both the doped and undoped compounds has been confirmed using ^{155}Gd Mössbauer spectroscopy. *© 2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4862938]

I. INTRODUCTION

The LnFeAsO (Ln = lanthanide, La-Er) family of materials came under investigation following the discovery of superconductivity at 26 K in $LaFeAsO_{1-x}F_x$.[1] Subsequent studies found that $Gd_{1-x}Th_xFeAsO$ has one of the highest superconducting transition temperatures for this system, with $T_c^{onset} = 54.4(1)$ K for x = 0.16,[2] and $T_c^{onset} = 56$ K for x = 0.2.[3] Lumsden and Christianson[4] provide an excellent review of the LnFeAsO system.

The iron-based oxypnictide superconductors and their parent compounds crystallize at room temperature in the tetragonal ZrCuSiAs-type structure (*P4*/*nmm*, No. 129). Undoped LnFeAsO compounds undergo a transition from the tetragonal structure to an orthorhombic structure (*Cmma*, No. 67) around 150 K.[5–10] Doping has been shown to suppress the transition and to allow the development of superconductivity.[5–9]

In the high temperature tetragonal phase, the Gd site has 4*mm* point symmetry, forcing the principal (*z*–) axis of the electric field gradient (*efg*) tensor to be parallel to the crystallographic *c*-axis and the asymmetry parameter η, to be zero.[11] While these constraints are both relaxed below the structural transition temperature as the point symmetry of the Gd site drops to *mm2*,[7,8] it is unlikely that the *efg* changes in any significant way as the structural distortion is extremely small[10] so we expect $z \parallel c$ and $\eta \sim 0$ in both forms.

As the thermal neutron absorption cross section of natural gadolinium is extremely large (~49 700 b), the only previous attempt to determine the magnetic structure of the Gd sublattice relied on ^{155}Gd Mössbauer spectroscopy.[2] They reported η close to 1, with the Gd moments ~45° away from the *efg* *z*–axis. If *z* remains parallel to the *c*-axis as expected, this places the Gd moments at ~45° off the *c*-axis. All other LnFeAsO compounds exhibit either *c*-axis or basal plane ordering,[6–8,12] so canted ordering of GdFeAsO seems unlikely, especially given the generally low anisotropy of the Gd^{3+} ion.

Here, we present direct measurements of the magnetic ordering of $Gd_{1-x}Th_xFeAsO$ (x = 0, 0.25) by thermal neutron powder diffraction using a large-area flat-plate sample holder.[13] We find that the moments order in the basal plane (90° from the *c*-axis). ^{155}Gd Mössbauer measurements were also performed as an independent verification of the magnetic ordering deduced by neutron diffraction.

II. EXPERIMENTAL METHODS

The polycrystalline samples used in this study were prepared by a solid state reaction in an evacuated quartz tube, with high purity starting materials. The full details of the sample preparation have been presented elsewhere.[3]

The neutron diffraction experiments were carried out at a neutron wavelength of 1.3286(1)Å on the C2 multi-wire diffractometer (DUALSPEC) at the Canadian Neutron Beam Center, Chalk River, Ontario. A large area silicon flat-plate sample holder[13] was used to minimise the effects of absorption by the natural Gd in the sample. Rietveld refinement of the neutron patterns was done using the *Fullprof*/*WinPlotr* suite.[14,15] No absorption correction was applied, however, the neutron data were truncated at $2\theta = 52°$ to minimize the impact of angle-dependent absorption effects.

The ^{155}Gd Mössbauer samples were mounted in a vertical helium flow cryostat[16] and the spectra were fitted using an exact solution to the full Hamiltonian.[17]

III. NEUTRON DIFFRACTION

Long-duration powder neutron diffraction patterns were obtained at 1.75 K and 6 K, and short-duration patterns at temperatures in between. Fitting the temperature dependence of the (001) magnetic peak intensity (Fig. 1) with a squared $J = \frac{7}{2}$ Brillouin function yields transition temperatures of 4.2(1) K and 3.7(1) K for the Gd sublattices in the undoped and doped samples, respectively.

A LeBail refinement with multiple excluded regions was performed on the 6 K patterns to obtain the lattice parameters necessary for indexing the magnetic peaks. The excluded regions were chosen by looking at the pattern calculated by

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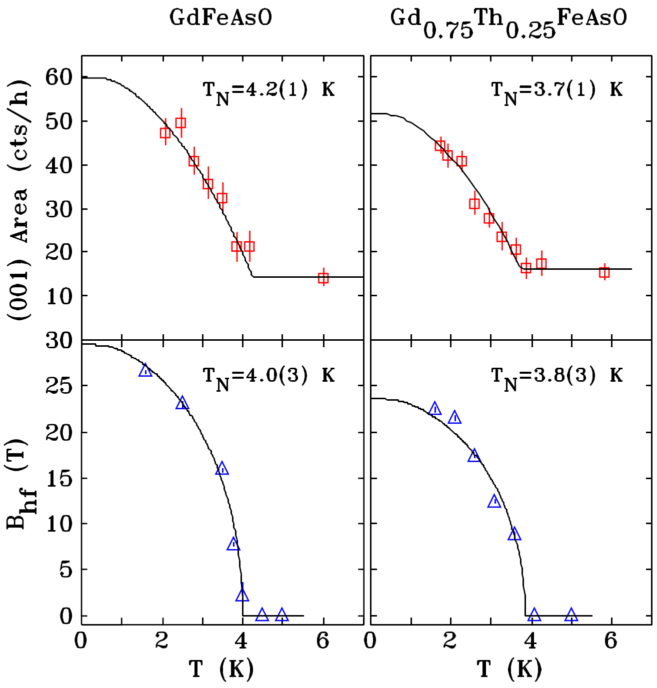

FIG. 1. Temperature dependence of the area of the (001) magnetic peak and of the ^{155}Gd hyperfine field. The solid lines are fits to a squared $J=\frac{7}{2}$ Brillouin function in the case of the area, and to a $J=\frac{7}{2}$ Brillouin function in the case of the hyperfine field.

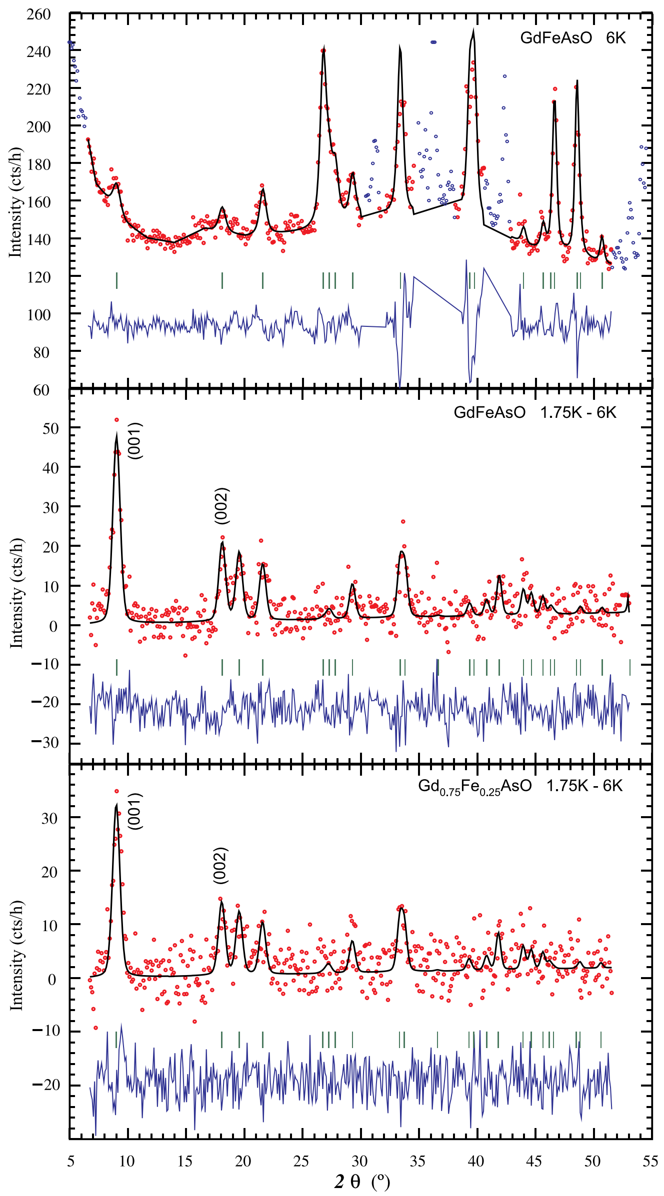

FIG. 2. LeBail refinement of the 6 K neutron diffraction pattern of GdFeAsO (top panel), and Rietveld refinements of the difference patterns for GdFeAsO (middle panel) and $Gd_{0.75}Th_{0.25}FeAsO$ (bottom panel). Blue dots show the excluded regions, the solid line is the result of the refinements, and the residuals are plotted at the bottom of each panel. The Bragg markers for the difference patterns are only for the magnetic contribution. The vertical scale is shown in counts/hour so that the signal strengths of the nuclear and magnetic scattering for GdFeAsO can be compared.

Powder Cell[18] and excluding regions containing unexpected features. Possible impurity phases include GdAs, FeAs, and As_2O_3. Due to the small size of the structural distortion, the refinements were carried out with the *a* and *b* lattice parameters constrained to be equal. Rietveld analysis was then used to set the nuclear scale factor so that gadolinium moments could be determined from the difference patterns. Simulations showed that any magnetic peaks from the iron ordering in GdFeAsO would be less than 1% of the intensity of the nuclear peaks and so it was not included in our analysis.

As we were primarily interested in the magnetic structure of the Gd sublattice, we took the difference between the 1.75 K and 6 K patterns. The Fe sublattice orders at 128 K,[19] GdAs orders at ∼19 K,[20] and FeAs orders at 69.6(1) K.[21] These ordering temperatures are well above the transition temperature of the Gd sublattice determined above. The resulting patterns (middle and bottom panels of Fig. 2) thus contain little or no contribution from impurity phases or from the Fe sublattice.

All magnetic peaks can be indexed with the commensurate propagation vector k = [0, 0, 0]. In order to consider all possible magnetic structures allowed for GdFeAsO, we carried out Representational Analysis for the Gd site using BasIreps.[14,15] Ferromagnetic arrangements were discarded on the basis of previous susceptibility measurements that clearly show antiferromagnetic behaviour.[2,3] The remaining three irreducible representations align the moments with the three crystallographic axes.

The (001) and (002) magnetic peaks are the strongest contribution to the difference patterns in the middle and bottom panels of Fig. 2 so that *c*-axis ordering can be ruled out. As we cannot resolve the orthorhombic distortion here, *a* and *b* remain equivalent and we are limited to describing the magnetic ordering as “basal plane.” Final refinements are shown by the solid line in the middle and bottom panels of Fig. 2.

The Gd moments lie in the basal plane and form alternating ferromagnetic planes along the *c*-axis. Basal ordering is also observed in CeFeAsO and NdFeAsO but the alternating ferromagnetic planes are not observed in other members of the LnFeAsO system. In GdFeAsO, the moments are $\mu_{Gd} = 6.0(1)\ \mu_B$ at 1.75 K, which extrapolates to $6.7(1)\ \mu_B$ at $T = 0$ K, close to the expected value of 7 μ_B. For $Gd_{0.75}Th_{0.25}$ FeAsO, the moments are $\mu_{Gd} = 5.45(8)\ \mu_B$ at 1.75 K, which extrapolates to $6.1(1)\ \mu_B$ at $T = 0$ K.

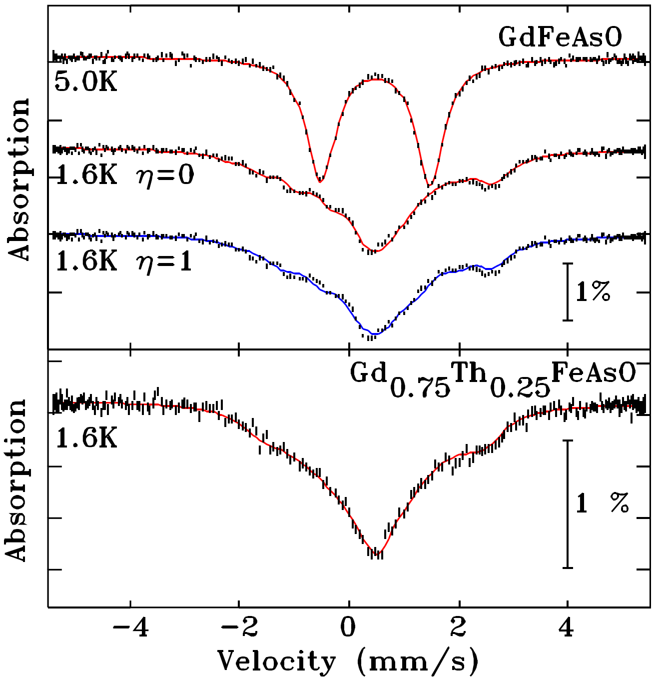

FIG. 3. ^{155}Gd Mössbauer spectra of GdFeAsO (top panel) and $Gd_{0.75}Th_{0.25}FeAsO$ (bottom panel). The refinements are shown by the solid line through the data, with red representing $\eta = 0$ and blue representing $\eta = 1$.

IV. ^{155}Gd MÖSSBAUER SPECTROSCOPY

The neutron diffraction results allow us to exclude the $\eta = 1$, $\theta = 45°$ set of hyperfine parameters, but for completeness, a refinement of the 1.6 K ^{155}Gd Mössbauer spectrum of GdFeAsO using the parameters from Wang *et al.*[2] as a starting point was attempted. The result of the refinement is shown in Fig. 3. A second refinement was made starting with $\eta = 0$, $\theta = 90°$, and $eQV_{zz} = 4.202(9)$ mm/s (taken from the 5 K paramagnetic pattern). In an unconstrained fit, η drops below zero, thus it was not refined. The angle between the principal *efg* axis and the magnetic moments was found to be $\theta = 90(3)°$, consistent with the results of powder neutron diffraction. The resulting pattern, shown in the top panel of Fig. 3, is clearly a better fit to the data and has $\chi^2 = 1.70$ compared to $\chi^2 = 2.25$ for $\eta = 1$. The peak structure at velocities < 0 is correctly reproduced with $\eta = 0$ but not with $\eta = 1$.

Refinement of the ^{155}Gd Mössbauer spectrum of the doped sample gave similar results (bottom panel of Fig. 3), with $\eta = 0$, $\theta = 90(6)°$, and $eQV_{zz} = 3.82(2)$ mm/s.

Fitting the temperature dependence of the hyperfine field in GdFeAsO with a $J = \frac{7}{2}$ Brillouin function (appropriate for a Gd^{3+} ion) gave a transition temperature of $T_N = 4.0(3)$ K, in excellent agreement with both the previously reported value 4.1(1) K,[2] and the 4.2(1) K found by neutron diffraction (Fig. 1). Similarly, for $Gd_{0.75}Th_{0.25}FeAsO$, we found a transition temperature of 3.8(3) K, in agreement with the neutron diffraction results.

V. CONCLUSION

Both neutron powder diffraction and ^{155}Gd Mössbauer spectroscopy measurements show that the Gd moments in $Gd_{1-x}Th_xFeAsO$ ($x = 0, 0.25$) order in the basal plane.

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