

# Magnetic structure of the high temperature superconductor $\text{Gd}_{1-x}\text{Th}_x\text{FeAsO}$

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The iron-based oxypnictide superconductors and their parent compounds crystallize at room temperature in the tetragonal  $\text{ZrCuSiAs}$ -type structure ( $P4/nmm$ , No. 129). Undoped  $\text{LnFeAsO}$  ( $\text{Ln} = \text{Lanthanides}$ ) compounds undergo a transition from the tetragonal structure to an orthorhombic structure ( $Cmma$ , No. 67) around 150 K.<sup>1-6</sup> Doping has been shown to suppress the transition and allow the development of superconductivity.<sup>1-5</sup>  $\text{Gd}_{1-x}\text{Th}_x\text{FeAsO}$  has one of the highest superconducting transition temperatures for this system, with  $T_c^{\text{onset}} = 54.4(1)$  K for  $x = 0.16$ ,<sup>7</sup> and  $T_c^{\text{onset}} = 56$  K for  $x = 0.2$ .<sup>8</sup>

In the high temperature tetragonal phase, the Gd atoms occupy a crystallographic site that has  $4mm$  point symmetry, forcing the principal ( $z$ -) axis of the electric field gradient ( $efg$ ) tensor to align with the crystallographic  $c$ -axis and the  $efg$  asymmetry parameter,  $\eta$ , to be zero.<sup>9</sup> These constraints are both relaxed in the low temperature orthorhombic structure as the point symmetry of the Gd site drops to  $mm2$ .<sup>3,4</sup> The structural distortion is extremely small<sup>6</sup> so, despite the lower symmetry of the Gd site, it is unlikely that the  $efg$  changes in any significant way. We therefore expect  $z \parallel c$  and  $\eta \sim 0$  in both tetragonal and orthorhombic phases.

A previous <sup>155</sup>Gd Mössbauer study of GdFeAsO reported  $\eta$  close to 1, with the Gd moments  $\sim 45^\circ$  away from the  $efg$   $z$ -axis.<sup>7</sup> If  $z$  remains parallel to the  $c$ -axis as expected, this places the Gd moments at  $\sim 45^\circ$  away from the  $c$ -axis. This magnetic arrangement is unlikely due to the constraints mentioned above. In addition, all other  $\text{LnFeAsO}$  compounds exhibit either  $c$ -axis or basal plane ordering,<sup>2-4,10</sup> so canted ordering of GdFeAsO seems unlikely, especially given the low anisotropy of the  $\text{Gd}^{3+}$  ion.

Our aim was to make a direct measurement of the ordering direction of the Gd moments in  $\text{Gd}_{1-x}\text{Th}_x\text{FeAsO}$  using neutron powder diffraction and <sup>155</sup>Gd Mössbauer spectroscopy. As natural gadolinium is the most powerful neutron absorbing element we used a large-area flat-plate sample holder to perform the neutron powder diffraction measurements. We have successfully used this technique several times to obtain good quality thermal neutron diffraction patterns of Gd-containing compounds. A full description of the flat-plate sample holder has been published in the Journal of Applied Crystallography.<sup>11</sup>

In the top panel of Figure 1 we show the neutron powder diffraction pattern of GdFeAsO at 6 K. As 6 K is above  $T_N \sim 4$  K, this pattern shows only nuclear peaks. The middle and bottom panels show the difference between the 1.75 K and 6 K patterns for both GdFeAsO and  $\text{Gd}_{0.75}\text{Th}_{0.25}\text{FeAsO}$ . As the Fe sublattice orders at

128 K,<sup>12</sup> GdAs orders at  $\sim 19$  K,<sup>13</sup> and FeAs orders at 69.6(1) K,<sup>14</sup> these difference patterns contain little or no contribution from impurity phases or from the magnetic order of the Fe sublattice. The peaks in the difference patterns are therefore all from the Gd magnetic moment order.

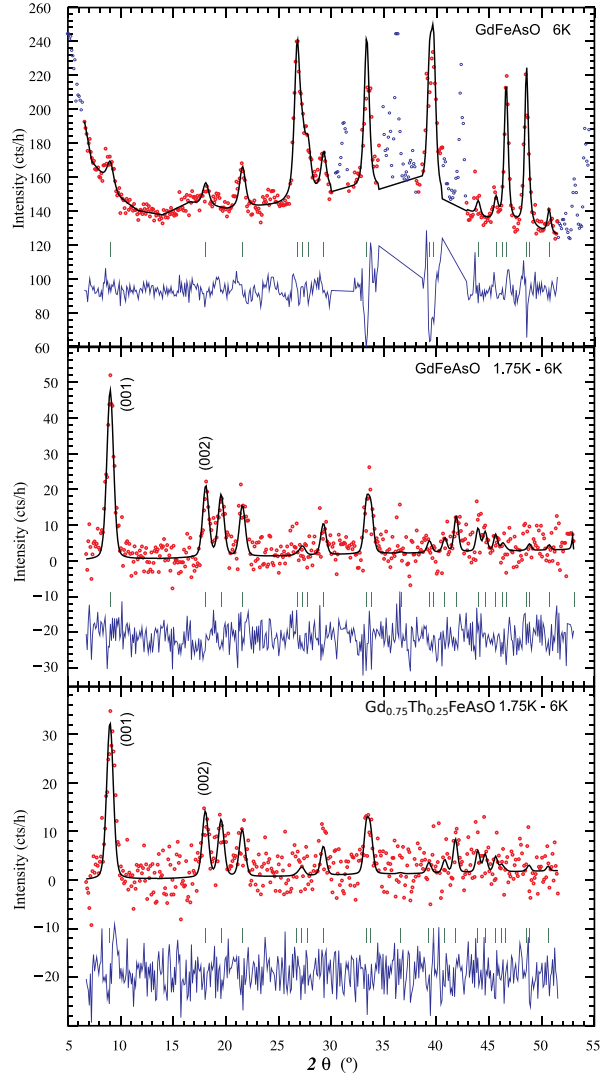


FIG. 1. LeBail refinement of the 6 K neutron diffraction pattern of GdFeAsO (top panel), and Rietveld refinements of the difference patterns for GdFeAsO (middle panel) and  $\text{Gd}_{0.75}\text{Th}_{0.25}\text{FeAsO}$  (bottom panel). Blue dots show the excluded regions, the solid line is the result 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.

All magnetic peaks can be indexed with the commensurate propagation vector  $k = [0, 0, 0]$ . We carried out Representational Analysis for the Gd site using BasIreps<sup>15,16</sup> in order to consider all possible allowed magnetic structures. Ferromagnetic arrangements were discarded as of previous susceptibility measurements clearly show antiferromagnetic behaviour.<sup>7,8</sup> The remaining 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 Figure 1, which rules out  $c$ -axis ordering. As we cannot resolve the orthorhombic distortion in our patterns we are limited to describing the magnetic moments as ordering in the basal plane.

We also performed <sup>155</sup>Gd Mössbauer spectroscopy on the GdFeAsO and Gd<sub>0.75</sub>Th<sub>0.25</sub>FeAsO samples, and found that fitting the pattern with  $\eta = 1$  gave  $\chi^2 = 2.25$ , whereas fitting with  $\eta = 0$  gave  $\chi^2 = 1.70$ . The complex peak structure observed in the <sup>155</sup>Gd Mössbauer spectra is also correctly reproduced with  $\eta = 0$  but not with  $\eta = 1$ . The angle between the principal  $efg$  axis and the magnetic moments was found to be  $\theta = 90^\circ$ , which is consistent with the results from neutron powder diffraction under the reasonable assumption that the  $efg$   $z$ -axis aligns with the crystallographic  $c$ -axis in the low temperature orthorhombic phase.

This study has shown that the Gd moments in both GdFeAsO and Gd<sub>0.75</sub>Th<sub>0.25</sub>FeAsO order in the basal plane. A complete description of this work has been published in the Journal of Applied Physics.<sup>17</sup>

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