

Comment on “Magnetic structure of  $\text{Gd}_2\text{Ti}_2\text{O}_7$ ”J. R. Stewart,<sup>1,\*</sup> G. Ehlers,<sup>2,†</sup> A. S. Wills,<sup>3,4,‡</sup> S. T. Bramwell,<sup>4,§</sup> and J. S. Gardner<sup>5,6,||</sup><sup>1</sup>ISIS, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, United Kingdom<sup>2</sup>Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6475, USA<sup>3</sup>Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom<sup>4</sup>London Centre for Nanotechnology and Department of Physics and Astronomy, 17-19 Gordon Street,

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M. W. Long and collaborators [Phys. Rev. B **83**, 054422 (2011)] recently proposed magnetic structures for gadolinium titanate that differ from those previously reported by us [J. R. Stewart, G. Ehlers, A. S. Wills, S. T. Bramwell, and J. S. Gardner, J. Phys.: Condens. Matter **16**, L321 (2004)]. In this Comment, we show that the calculated structure factors,  $S(\mathbf{Q})$ , of the newly proposed models are inconsistent with our neutron powder diffraction data. Long and colleagues were led to reconsider the magnetic structure of gadolinium titanate on the basis of a number of theoretical and experimental assumptions. We argue that these assumptions have no basis in fact and conclude that they provide no reason to doubt our published magnetic structures.

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The authors of Ref. 1 have proposed magnetic structures for the two ordered phases of  $\text{Gd}_2\text{Ti}_2\text{O}_7$ <sup>1</sup> that differ from those previously shown by us to be consistent with high precision powder neutron diffraction data. We have carefully tested the models of Ref. 1 and show here that they do not produce the observed magnetic structure factors reported earlier.<sup>2-4</sup> Hence the models proposed in Ref. 1 do not represent the magnetic structures of  $\text{Gd}_2\text{Ti}_2\text{O}_7$ .

Magnetic neutron diffraction measures the structure factor  $S(\mathbf{Q})$  directly, so while there may be several possible models that are consistent with neutron scattering data, any model that is inconsistent with it (like those of Ref. 1) can be definitively ruled out. Multi- $\mathbf{k}$  variants of a magnetic structure correspond to ones where the moment orientations are constructed from a summation of symmetry-related structures that are generated from an initial single- $\mathbf{k}$  structure by application of the coset generating elements,  $A$  of the star of the propagation vector. The powder average of the neutron diffraction scattering structure factors for the different reciprocal lattice vectors ( $hkl$ ) is necessarily identical for each value of  $\mathbf{k}$  involved in this summation as they are themselves related by the operations of  $A$ . Following this, we have previously shown that  $S(\mathbf{Q})$  for  $\text{Gd}_2\text{Ti}_2\text{O}_7$  is consistent with either a  $1\mathbf{k}$  or  $4\mathbf{k}$  structure.<sup>3</sup> Both the  $1\mathbf{k}$  and  $4\mathbf{k}$  model require two inequivalent Gd sites. The inequivalency of one of the sites that arises for the single  $\mathbf{k}$  vector is retained in the  $4\mathbf{k}$  structure, because the extension of the structure to include components from the four propagation vectors involves the coset generating elements,  $A$ , rather than the symmetry elements within  $G_k$ , as discussed later. It is, however, adapted to follow the symmetry of the  $4\mathbf{k}$  vectors and so leads to inequivalent tetrahedra. Three quarters of the positions of the  $\text{Gd}^{3+}$  sublattice have moments derived from Bragg diffraction that are relatively large, indicating that these spins are involved in long-range order. Their thermally averaged moments approach the maximum expected for  $\text{Gd}^{3+}$  in the low temperature limit. In contrast, one in four  $\text{Gd}^{3+}$  moments do not contribute to the Bragg intensity of the high

temperature phase above 770 mK and are therefore disordered on the length and time scales probed with neutrons. They do, however, acquire a relatively small ordered moment in the low temperature phase.

At first glance these models may appear surprising. This is because not all of the symmetry information of the parent crystal structure carries through to the magnetic ordering. The pyrochlore lattice consists of four interpenetrating face centered cubic Bravais lattices, and the four Gd sites of the tetrahedral basis differ only in the orientation of the local trigonal axis of point symmetry. The authors of Ref. 1 argue from a local perspective, invoking Mössbauer results, that each of the four sites should have an identical thermally averaged moment. However, this argument can be ruled out once the  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  propagation vector is accepted. The magnetic structure is defined with respect to the symmetry operations of the space group  $G_0$  that leave the  $\mathbf{k}$  vector invariant. These form the so-called little group  $G_k$ . For  $\mathbf{k} = \frac{1}{2}\frac{1}{2}\frac{1}{2}$ ,  $G_k$  contains only 12 rotational-translational symmetry operations with only one threefold axis being retained of the four present in the crystal space group  $G_0$ . This loss of symmetry means that there are insufficient symmetry operations in  $G_k$  to generate the four equivalent positions of the  $\text{Gd}^{3+}$  crystallographic site and this site is correspondingly split into two disjoint groups, called orbits. Taking the four Gd positions as forming a tetrahedron with the  $\mathbf{k}$  vector going along one of the threefold axes, the first orbit contains the three equivalent positions of the triangular face perpendicular to  $\mathbf{k}$ ; the second orbit contains the single position that the  $\mathbf{k}$  vector passes through. As there are no symmetry operations within  $G_k$  that relate the magnetic moments of all four moments of the  $\text{Gd}^{3+}$  tetrahedron, there is therefore a 3:1 splitting of the sites in the magnetic structure that occurs irrespective of the details of the irreducible representations that are involved in the ordering. Equal moments are possible by accidental coincidence, but this possibility can be ruled out from the observed Bragg peak intensities, as shown in Fig. 1 (top panel). Another important

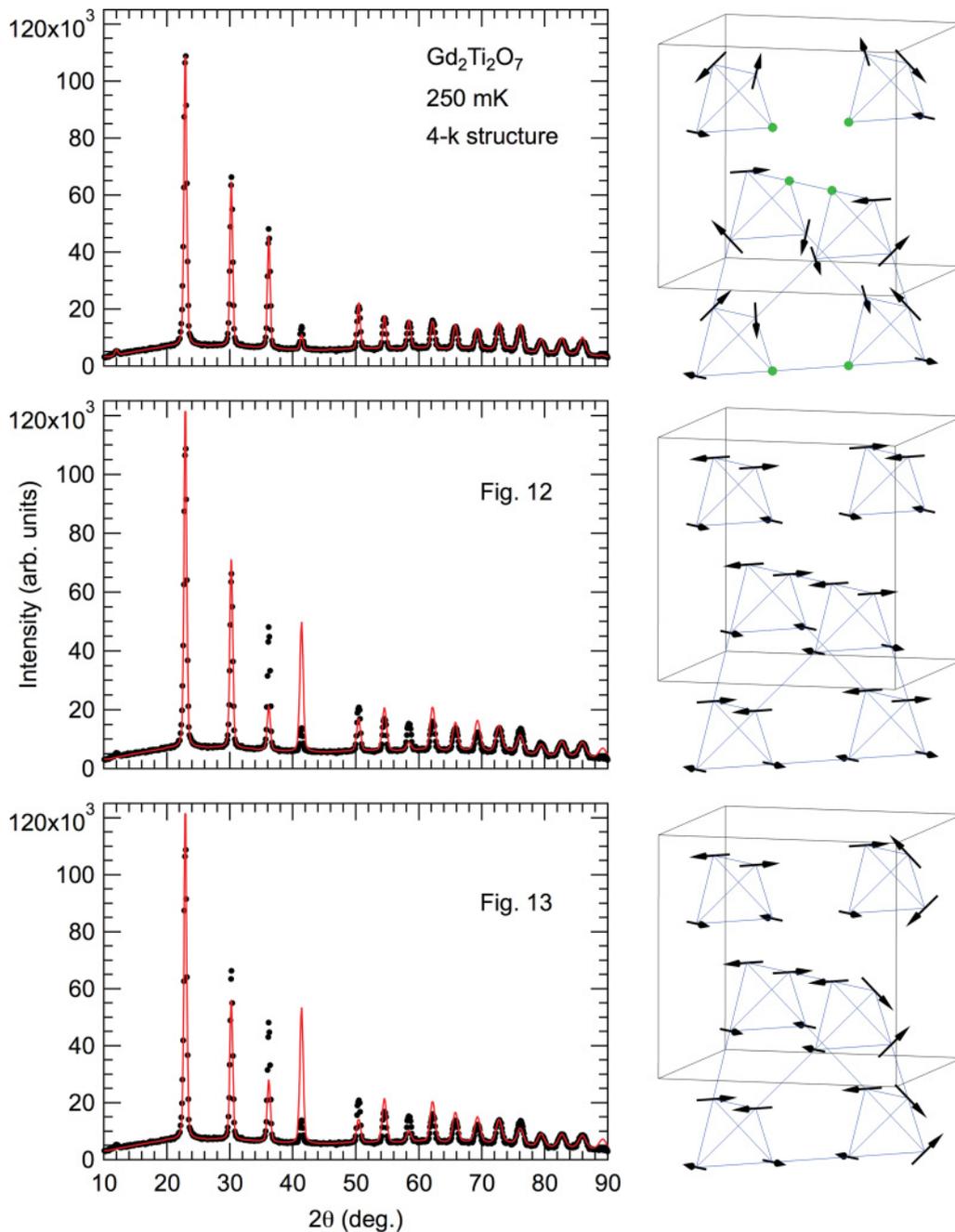


FIG. 1. (Color online) Neutron diffraction data in the low temperature phase of  $Gd_2Ti_2O_7$  at 250 mK. (Top panel) Data with our  $4k$  model fit published earlier.<sup>3</sup> (Middle panel) The same data with the profile expected from the intermediate phase discussed in Ref. 1 (Fig. 12) with the moments forced to be  $7 \mu_B$ .<sup>1</sup> (Lower panel) The data and the calculated neutron profile assuming  $7\mu_B$  on the  $Gd^{3+}$  site for the noncollinear, low temperature phase proposed in Ref. 1 (Fig. 13).<sup>1</sup> In each panel, the proposed magnetic structure is drawn in relation to the chemical unit cell. In the top panel, the smaller ordered spin is represented by a green ball. Error bars are statistical in nature in the figure and represent  $\pm 1\sigma$ .

feature of the neutron diffraction data is a considerable amount of diffuse magnetic scattering persisting to low temperature. This is consistent with the incompletely ordered sublattice of Gd moments proposed in our work, but it is inconsistent with the models proposed in Ref. 1.

The authors of Ref. 1 base their scepticism of our published magnetic structure on two arguments, but in our opinion, neither argument is convincing. First, they assume that the  $Gd^{3+}$  ion is in a pure  $S = 7/2, L = 0$  state, and hence is

an ideal Heisenberg spin. However, even in the free ion this premise is false, as intermediate coupling of angular momenta admix extra terms into the  $Gd^{3+}$  ground state. In the pyrochlore structure, the rare-earth (RE) site has trigonal point symmetry and a highly asymmetric local environment of oxide ligands. This induces a local crystal field anisotropy in  $Gd^{3+}$  that is of a magnitude comparable to the magnetic couplings in the system. Thus, using ESR, Sosin and coworkers<sup>5</sup> found a single-ion energy gap of 0.25 K. They also report the presence

of two low lying gaps in  $\text{Gd}_2\text{Ti}_2\text{O}_7$  consistent with two unique  $\text{Gd}^{3+}$  sites,<sup>6</sup> similar to that seen in Mössbauer<sup>7</sup> and neutron scattering.<sup>2-4</sup> Second, the authors of Ref. 1 suggest that there is an inconsistency between neutron and Mössbauer results, but this is not necessarily the case. Mössbauer spectroscopy measures the local fields perturbing the nuclear transitions and might see a full length spin while neutrons see the thermally and translationally averaged structure. Both neutrons and Mössbauer conclude the spins are perpendicular to the local  $\langle 111 \rangle$  axis and are consistent with two Gd sites in the intermediate phase above 770 mK.

In summary, the suggested magnetic structures proposed in Ref. 1 are inconsistent with neutron diffraction data and can surely be ruled out.

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