Magnetic ordering in Gd₅Ir₂Bi and Gd₅Ir₂Sb

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¹⁵⁵Gd Mössbauer spectroscopy and neutron powder diffraction have been used to study magnetic ordering in Gd₅Ir₂Bi and Gd₅Ir₂Sb. Despite the hyperfine fields (Bhf) at the two Gd sites differing by more than a factor of two for both compounds, the moments derived from neutron diffraction are essentially equal in Gd₅Ir₂Bi. This implies an unusual departure from the commonly assumed scaling between Bhf and µGd. Neutron powder diffraction shows that Gd₅Ir₂Bi is a c-axis ferromagnet at 3.6 K. We find no evidence for a FM→AF transition. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4944770]

I. INTRODUCTION

The RE₃Ir₂X (RE = Y, Gd–Ho, X = Sn, Sb, Pb, Bi) family of compounds crystallises in a body-centre tetragonal structure (I4/mcm, #140, Mo₂SiB₂-type) that is an ordered variant of the Cr₃B₃-type structure.¹ The Gd-based members of this new family of intermetallic compounds has been shown to exhibit a strong magnetocaloric effect with relatively high magnetic ordering temperatures, leading to interest in possible applications.³ An investigation of the magnetic properties showed fairly conventional ferromagnetic (FM) behaviour with positive Curie-Weiss temperatures and effective moments slightly larger than expected for the free ion. However, in two cases (Gd₅Ir₂Bi and Gd₅Ir₂Sb) evidence for a secondary magnetic event below Tc, was found, and Schäfer et al.¹ suggested that this could be the result of antiferromagnetic (AF) ordering. Both materials saturate readily in modest applied fields and the saturation moments measured at 5 K in a field of 8 T were 7.3(1) µB/Gd and 7.2(1) µB/Gd for Gd₅Ir₂Bi and Gd₅Ir₂Sb respectively,¹ so any AF order would appear to be easily suppressed.

Here we use ¹⁵⁵Gd Mössbauer spectroscopy and neutron powder diffraction to study the magnetic ordering of the Gd ions in these two materials. ¹⁵⁵Gd Mössbauer spectroscopy is limited to temperatures below about 50 K by the very rapid loss of signal (the recoil-free fraction or “f– factor” is very strongly temperature dependent because of the relatively high energy, 86.55 keV, of the transition) so we could not access either the ferromagnetic transitions (Tc²Ir =124 K and Tc²Sb =119 K¹) or the secondary events (Tc²Ir =118 K and Tc²Sb =91 K¹) and spectra were only taken at 5 K. Attempts to lower Tc at constant structure by replacing some of the Gd with Y were not successful as the phase proved unstable.

Contrary to common belief, it is indeed possible to carry out neutron powder diffraction experiments using samples prepared with natural Gd, despite the extremely large absorption cross-section (49700 b). Here we use a large-area flat-plate sample mount² that allows us to place about 400 mg of Gd₅Ir₂Bi in the beam (about a 1/e thickness) and obtain usable diffraction patterns. We have used this method to study a variety of Gd³⁻⁶ and Eu⁷⁻¹⁰-based magnetic materials. The loss of magnetic scattering as we approached Tc from below precluded any meaningful search for a change in magnetic structure near Tc², so we restrict our analysis to the diffraction patterns measured at 200 K (well above Tc²Ir =124 K) and at 3.6 K in the fully ordered state.
II. EXPERIMENTAL METHODS

Gd₅Ir₂Bi and Gd₅Ir₂Sb were prepared from stoichiometric mixtures of the high purity elements (better than 99.9%). The antimony compound was prepared by induction melting in a welded tantalum tube, while the bismuth compound was made in an argon-filled arc-furnace. Full details of the structural and basic magnetic characterisation have been published elsewhere¹ and will not be repeated here. The crystallographic data used for the refinement of the neutron diffraction patterns were taken from a synchrotron x-ray diffraction study and were not refined further here.

The 50 mCi ¹⁵⁵Sm source and sample (about 700 mg) were mounted vertically in a helium flow cryostat and the Mössbauer drive was operated in sinusoidal mode. The system was calibrated using a laser interferometer with velocities cross-checked against both ⁵⁷Co/Rh-Fe at room temperature and ¹⁵⁵Sm/Pd/GdFe₂ at 5 K.

The ¹⁵⁵Gd Mössbauer spectra were fitted using a non-linear least-squares minimization routine with line positions and intensities derived from an exact solution to the full Hamiltonian.¹¹ A transmission integral correction was applied in order to deal with the significant line overlap present in the spectra.

Neutron powder diffraction experiments were carried out on the C2 800-wire powder diffractometer (DUALSPEC) at the NRU reactor, Chalk River Laboratories, Ontario, Canada, using a neutron wavelength (λ) of 1.3286(2) Å. The 400 mg powdered sample was mounted on a large-area single-crystal silicon plate to reduce the impact of the severe absorption by the natural Gd in the sample.² Diffraction patterns were obtained at 200 K and 3.6 K and fitted using GSAS/EXPGUI.¹³

III. RESULTS AND DISCUSSION

The Gd atoms in Gd₅Ir₂Bi and Gd₅Ir₂Sb occupy two sites with quite different multiplicities and point symmetries (see Table I) so that the two contributions to the observed ¹⁵⁵Gd Mössbauer spectrum are readily distinguishable. The 4/m point symmetry of the 4c site requires the asymmetry parameter (η) to be zero and places the principal axes of the efg tensor (Vzz) along the crystallographic c-axis. The much lower point symmetry of the 16l site imposes no constraints. As the angle (θ) between the hyperfine field (Bhf) and Vzz can be determined from a fit to the ¹⁵⁵Gd Mössbauer spectrum, the knowledge that Vzz is parallel to the c-axis can be used to establish the magnetic ordering direction. Unfortunately as we show below, the Gd in the 4c site experiences an anomalously small hyperfine magnetic field and so cannot provide an unambiguous result.

The spectra of both pnictides (shown in Figure 1) exhibit several well-defined features, but fitting them proved surprisingly difficult, largely because our expectations for Bhf were wrong, and we could not “see” the solution by inspection of the spectra. Two subspectra with an area ratio of 4:1 were expected based on the occupation of the 16l and 4c sites. In addition, magnetisation data suggested that a full 7 \( \mu_B \) moment would be present on all of the Gd atoms,¹ so models with approximately equal hyperfine fields for the two sites were tried, with no success. The final fits were obtained using a multi-dimensional grid search. A broad range of “reasonable” values were identified for Bhf, eQVzz and θ for both sites (only \( \theta = 0^\circ, 90^\circ \) were considered for the 4c site,

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Site symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>4c</td>
<td>4/m</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Gd</td>
<td>16l</td>
<td>m</td>
<td>0.1584</td>
<td>1/2+x</td>
<td>0.1343</td>
</tr>
<tr>
<td>Ir</td>
<td>8h</td>
<td>mm2</td>
<td>0.6378</td>
<td>1/2+x</td>
<td>0</td>
</tr>
<tr>
<td>Bi</td>
<td>4a</td>
<td>422</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
</tr>
</tbody>
</table>

Tetragonal I4/mcm (140)

\( a = 7.806(1) \text{ Å} \)
\( c = 13.732(1) \text{ Å} \)
FIG. 1. $^{155}$Gd Mössbauer spectra of (top) Gd$_5$Ir$_2$Bi and (bottom) Gd$_5$Ir$_2$Sb measured at 5.0 K. The solid magenta lines in each case show the best fit with the hyperfine field parallel to the $c$-axis. For Gd$_5$Ir$_2$Bi we also show the individual contributions from the 4$c$ (blue) and 16$l$ (gray) sites. The fits were calculated using a full solution to the nuclear Hamiltonian with a transmission integral correction to account for the effects of a significant line overlap.

Given the point symmetry and the FM ordering) and both $\eta$, and a polar angle ($\phi$) for the 16$l$ site. Over $4 \times 10^7$ initial guesses were generated and refined. The results were tabulated and searched for the lowest $\chi^2$ values. There was a clear jump in $\chi^2$ (about 25%) between the “best” and the next nearest potential solution, with misfit structure evident in the residuals. The same “best fit” was found to arise from several different starting points and therefore appears to represent a global minimum in $\chi^2$. The final fit was obtained using a transmission integral to correct for the impacts of line overlap.

The two components of the best fit are shown with the data in Figure 1 and the values used are given in Table II. The two Gd environments are quite different: Gd atoms in the 4$c$ site experience a very small hyperfine field but a rather large quadrupole interaction, while those in the 16$l$ site see the reverse. Values derived for Gd$_5$Ir$_2$Bi and Gd$_5$Ir$_2$Sb are broadly consistent. The dominance of the quadrupole interaction at the 4$c$ site, where one might have been able to determine the ordering direction (as $V_{zz}$ is parallel to the $c$-axis by symmetry), makes a strong conclusion impossible. In both compounds the fit quality as defined by $\chi^2$ is only weakly dependent on the assumed field direction: 1.58 vs. 1.51 for Gd$_5$Ir$_2$Bi and 1.53 vs. 1.41 for Gd$_5$Ir$_2$Sb for $\theta = 0^\circ$ and 90$^\circ$ respectively. While both appear to favour planar ordering ($\theta = 90^\circ$) the differences are not statistically significant.

Given the expectation that $B_{hf}^{Gd}$ is proportional to $\mu_{Gd}$ (the temperature dependences of the two parameters generally track together, see for example Gd$_2$Fe$_2$Si$_2$C$_3$), the very different hyperfine fields at the two Gd sites might suggest that the moments on the Gd in these two sites are also different, a view that would be inconsistent with the bulk magnetisation data. While it is conceivable that the moment on the 4$c$ is field-induced, (i.e. it is zero or very small in the absence of an
TABLE II. Parameters for the best fits to the $^{155}\text{Gd}$ Mössbauer spectra of Gd$_5$Ir$_2$Bi and Gd$_5$Ir$_2$Sb at 5 K. Values without errors were not refined in the final fit. Fields marked "—" were not used either because they were zero by symmetry (e.g. $\eta$ for the 4c site) or had no meaning (e.g. $\phi$ for the 16f site as we found $\eta = 0$).

<table>
<thead>
<tr>
<th>Site</th>
<th>$aQV_{zz}$ (mm/s)</th>
<th>$B_{hf}$ (T)</th>
<th>$\theta$ (degrees)</th>
<th>$\eta$ (degrees)</th>
<th>$\phi$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$_5$Ir$_2$Bi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd 4c</td>
<td>$-8.16(7)$</td>
<td>$9.7(9)$</td>
<td>$0$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Gd 16f</td>
<td>$+2.73(6)$</td>
<td>$25.6(4)$</td>
<td>$82(3)$</td>
<td>$0$</td>
<td>—</td>
</tr>
<tr>
<td>Gd$_5$Ir$_2$Sb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd 4c</td>
<td>$-7.46(4)$</td>
<td>$6(1)$</td>
<td>$0$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Gd 16f</td>
<td>$+1.7(2)$</td>
<td>$23(1)$</td>
<td>$50(2)$</td>
<td>$0$</td>
<td>—</td>
</tr>
</tbody>
</table>

applied field) the high ordering temperature (124 K$^1$) and soft ferromagnetic response make this unlikely, while the neutron diffraction data (see below) allow us to rule out this possibility. We note that the $B_{hf}^{Gd}$,$\mu_{Gd}$ scaling is far from perfect and hyperfine fields of $\sim 40$ T (GdGa$_{14}^{15}$) to $\sim 20$ T (2d site in Gd$_3$Ag$_4$Sn$_4$) have been reported for systems in which the Gd carries a full $7\mu_B$ moment. Therefore, we turn to neutron diffraction to confirm the ordering direction and check whether the two Gd sites have similar or very different moments, before returning to this issue.

Figure 2 shows a comparison of powder diffraction patterns for Gd$_5$Ir$_2$Bi taken at 3.6 K and 200 K, with a difference pattern to emphasise the changes associated with the magnetic ordering. A small number of magnetic contributions are evident, most notably near $2\theta = 23^\circ$ and $28^\circ$, in structurally allowed positions. No new peaks (i.e. at non-nuclear-allowed positions) are evident, consistent with ferromagnetic ordering. The large changes in lattice parameters between 3.6 K and 200 K makes the difference pattern an unreliable guide by $2\theta = 40^\circ$.

FIG. 2. Neutron powder diffraction patterns for Gd$_5$Ir$_2$Bi taken at 3.6 K for 76 hours (top) and 200 K taken for 25 hours (middle) using a neutron wavelength of 1.33 Å. The scaled difference between the 200 K and 3.6 K patterns is shown at the bottom of the figure. Thermal expansion between 3.6 K and 200 K leads to significant shifts in the line positions that cause spurious effects in the difference pattern for $2\theta \geq 40^\circ$. The spike at $2\theta \sim 31^\circ$ is an artefact from the sample mount. The positions of three key reflections are indicated (see text for more details).
FIG. 3. Fitted neutron powder diffraction patterns for Gd$_5$Ir$_2$Bi taken at 3.6 K. The Bragg markers indicate the reflections from the magnetic (top) and nuclear (bottom) contributions (see text for details). The residual pattern is shown at the bottom of the figure.

A search through the 16 possible magnetic space groups led us to $I4/mcm'$ as it was the only one that yielded the observed scattering pattern. This group permits $c$-axis FM order at the $4c$ site, and a combination of $c$-axis FM plus planar AF order at the $16f$ site.

Our best fit to the 3.6 K diffraction pattern for Gd$_5$Ir$_2$Bi is shown in Figure 3. There are four regions that were excluded from the fit as they contained contributions from the sample mount. Most do not overlap significant sample peaks, however the one at $2\theta = 31^\circ$ does. The $7.6(4) \mu_B$ Gd moments on the $16f$ site are ordered FM parallel to the $c$-axis:

$$\mu_x = \mu_y = 0.8(4) \mu_B; \quad \mu_z = 7.5(4) \mu_B.$$ 

This settles the issue of the ordering direction that could not be established by $^{155}$Gd Mössbauer spectroscopy. The small AF planar component allowed by symmetry is probably not significant. Allowing a moment on the $4c$ site greatly improves the fit, and is indeed required to match the magnetisation data.$^1$ The fitted moment is unrealistically large at $8.9(8) \mu_B$/Gd. The low multiplicity of the site ($4$ vs. $16$) and the fact that the scattering primarily contributes to low intensity peaks greatly reduce the reliability of the moment determination, however it is clear that the moment on this site is not small. By generating a series of patterns with increasing Gd-$4c$ moments we determined that the rather weak (110), (112) and (200) peaks in the diffraction pattern (see Figure 2) were key indicators of the Gd-$4c$ moment magnitude. With no moment on the Gd-$4c$ site, the (110) and (200) peaks are stronger than the (112) peak. Increasing the size of the Gd-$4c$ moment rapidly suppresses these two peaks while enhancing the (112) peak. Balancing these trends leads to the fitted moment. The weakness of all three peaks in the diffraction pattern despite the very long counting time used (76 hours) leads to an overestimate of the actual moment, and is reflected in the large uncertainty on the fitted value.

The factor of ~3 between $B_{hf}^{Gd}$ at the two Gd sites in Gd$_5$Ir$_2$Bi contrasts strongly with the neutron diffraction result that clearly shows that the Gd moments on the two sites are essentially equal. This contrast presents a striking counter-example to the common observation that $B_{hf}^{Gd} \sim 25$ T is associated with $\mu_{Gd} \sim 7 \mu_B$. As Gd$_5$Ir$_2$Sb is FM, one cannot easily appeal to the effects of negative transferred fields from antiparallel neighbouring moments, nor are crystal field effects a likely source of a reduced hyperfine field as the half-filled 4$f$ configuration for Gd$^{3+}$ is very stable and bulk magnetisation measurements favour FM order with a full $7 \mu_B$ moment on all of the Gd atoms. We can rule out a field-induced Gd-$4c$ moment as the neutron diffraction work
was carried out in zero applied field. Finally, observing a non-zero $B_{hf}^{Gd}$ only requires that the Gd moments be close to static on the Mössbauer time-scale (~10 ns) while the observation of resolution-limited magnetic Bragg peaks imposes a much stronger requirement: the moments to be organised – correlations must be present and persist over distances of at least 10 nm. The opposite situation is encountered in the geometrically frustrated Gd$_2$Ti$_2$O$_7$ where a small (~$2\mu_B$) moment is seen on 1/4 of the Gd sites by neutron diffraction, but a full $B_{hf}^{Gd}$ is observed below 0.8 K by Mössbauer spectroscopy. In this case some of the Gd moments are isolated by frustration and do not order fully, but at low enough temperatures they are static. The static moments yield a full hyperfine field, but disorder in their orientations leads to a greatly reduced Bragg diffraction signal.

We are left therefore with a $B_{hf}^{Gd}$:μ$Gd$ scaling failure. While we are not aware of any other examples of such extreme scaling failures in Gd (possibly because of limited data, as $^{155}$Gd Mössbauer spectroscopy and neutron powder diffraction are not commonly combined to study Gd compounds) divalent Eu compounds (Eu$^{2+}$ and Gd$^{3+}$ share the same electronic configuration – a half-filled 4$f$ shell) exhibit a very wide range of scale factors (somewhat over a factor of two) so it is possible that Gd$_3$Ir$_2$Bi and Gd$_3$Ir$_2$Sb are just the first examples of a larger set of systems. The issue certainly will bear further study.

IV. CONCLUSIONS

The Gd-16$f$ and Gd-4$c$ moments in Gd$_3$Ir$_2$Bi order ferromagnetically and are parallel to the c-axis. Despite the very different hyperfine fields seen at the two sites using $^{155}$Gd Mössbauer spectroscopy, neutron powder diffraction confirms that the moments at both sites are essentially the same size. The fitted values ($μ_1^{hf}$ = 7.6 (4) $μ_B$, and $μ_2^{hf}$ = 8.9 (8) $μ_B$ are somewhat larger than both the $7μ_B$ expected for Gd and the $μ_{hf}^{Gd}$ = 7.3 (1)$μ_B$ derived from magnetisation data. This likely reflects the weak magnetic contributions to the total scattering in this system. As the magnetic structure at 3.6 K is clearly FM, we find no evidence to support a change from FM to AF ordering on cooling through $T_s^{hf}$ =118 K in Gd$_3$Ir$_2$Bi, and by extension, at $T_s^{hf}$ =91 K in Gd$_3$Ir$_2$Sb.

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