Magnetic order and spin-reorientation in HoGa

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Abstract. We have determined the magnetic structure of the intermetallic compound HoGa by high-resolution neutron powder diffraction. This compound crystallizes in the orthorhombic ($Cmcm$) CrB-type structure and the magnetic structure comprises ferromagnetic order of the Ho sublattice along the c-axis. The Curie temperature is 66(3) K. Upon cooling below 20 K, the Ho magnetic moments cant away from the c-axis towards the ab-plane. At 3 K, the Ho moment is 8.8(2) μ_B and the Ho magnetic moments point in the direction $\theta = 30(2)^\circ$ and $\phi = 49(4)^\circ$ with respect to the crystallographic c-axis. The observation of an ab-plane component at around 50° from the a-axis is in contrast with the suggested magnetic structure of ac order ($\theta = 32^\circ$ and $\phi = 0^\circ$) reported by Delyagin *et al.* [1] on the basis of a ^{119}Sn Mössbauer spectroscopy study of a Sn-doped HoGa sample. However, we find that these two sets of orientations are in fact indistinguishable by Mössbauer spectroscopy.

1. Introduction

The orthorhombic RGa (R = rare earth) compounds crystallize in the CrB-type $Cmcm$ (#63) structure. There is one R site, the $4c$, and one Ga site, also a $4c$. The RGa compounds were first prepared in the early 1960's [2, 3, 4, 5]. They order ferromagnetically with a Curie temperature that ranges from a high of 183 K in GdGa [6, 7, 8] to a low of ∼15 K in TmGa [9]. Neutron diffraction work on TbGa was reported in 1964 by Cable *et al.* [10] who showed that the Tb moments order along the c-axis. In 1971, Barbara *et al.* used neutron diffraction to show that ErGa orders along the b-axis [11]. In 1992, Nesterov *et al.* [12] used ^{119}Sn Mössbauer spectroscopy on Sn-doped samples to show that NdGa, HoGa and ErGa undergo spin-reorientations upon cooling. This Mössbauer work was recently extended by Delyagin *et al.* [1]. Within the last year or two, the RGa compounds have attracted some interest due to their potential for use as magnetocaloric-effect-based low-temperature refrigeration applications [13, 14, 15].

In this paper we present the results of high-resolution neutron powder diffraction carried out on HoGa to examine the spin-reorientation reported to occur at ∼ 20 K. HoGa is a ferromagnet with a Curie temperature of 66(3) K [1, 6, 12, 15]. Its initial easy direction of order is the c-axis and the reorientation was suggested by Delyagin *et al.* [1] to involve a canting towards the a-axis, within the ac-plane. We show that the canting actually tips the Ho moments towards an intermediate planar arrangement, which differs from the structure suggested on the basis of ^{119}Sn Mössbauer spectroscopy. However, we find that the two magnetic structures are, in fact, indistinguishable by ^{119}Sn Mössbauer spectroscopy.

2. Experimental Methods

The HoGa sample was prepared in an argon-arc furnace. Stoichiometric amounts of the pure elements (Ho (99.9%) and Ga (99.999%)) were melted several times under pure (less than 1 ppm impurity) argon to ensure homogeneity. X-ray powder diffraction measurements were made at room temperature using Cu–Kα radiation on a PANalytical X'Pert Pro diffractometer. Neutron diffraction experiments were carried out on the *Echidna* high-resolution powder diffractometer at the OPAL reactor in Sydney, Australia [16]. The neutron wavelength was 1.6220(5) Å. The neutron diffraction data were corrected for absorption effects and all patterns were refined using the Rietveld method and the FullProf/WinPlotr suite [17, 18].

3. Results

Refinement of the x-ray powder diffraction pattern obtained at 295 K confirmed the formation of the CrB-type *Cmcm* orthorhombic phase. Any impurity phases present amounted to less than 1 wt%, undetectable in the powder diffraction pattern. The refined lattice parameters are a = 4.2794(5) Å, b = 10.7869(11) Å, c = 4.0445(5) Å.

3.1. Neutron Diffraction

In figure 1 we show the neutron powder diffraction patterns of HoGa, obtained at 80 K, 45 K, 22 K and 3 K. The Curie temperature of HoGa is 66(3) K, as mentioned earlier, so the 80 K pattern represents the nuclear scattering from the orthorhombic *Cmcm* cell. In Table 1 we show the atomic position parameters for HoGa derived from a refinement to the 80 K nuclear diffraction pattern. The conventional R-factors for this refinement are R_B = 5.65% and R_F = 4.06%.

Table 1. Crystallographic data for HoGa in the orthorhombic *Cmcm* cell, refined from the neutron diffraction patterns. The 4c site occupied by both the Ho and Ga atoms is defined by the atomic positions $(0\ y\ \frac{1}{4})$.

T(K)	a(Å)	b(Å)	c(Å)	Atom	y
80	4.2779(5)	10.7595(10)	4.0353(4)	Ho	0.3592(3)
				Ga	0.0750(5)
45	4.2762(5)	10.7571(11)	4.0344(5)	Ho	0.3595(4)
				Ga	0.0752(6)
22	4.2760(5)	10.7589(11)	4.0337(5)	Ho	0.3596(3)
				Ga	0.0752(6)
3	4.2758(5)	10.7582(11)	4.0337(5)	Ho	0.3594(3)
				Ga	0.0751(6)

The diffraction patterns obtained at 45 K, 22 K and 3 K show considerable magnetic contributions from the Ho sublattice. There are no additional peaks that would signal antiferromagnetic order and all magnetic contributions simply add to the existing Bragg nuclear peaks i.e. the propagation vector k = 0. The dominant magnetic contributions occur at the (020), (110) and (021) positions, with scattering angles $2\theta \sim 17.3°$, $23.6°$ and $29.1°$, respectively.

In order to consider all possible magnetic structures allowed for HoGa, we carried out Representational Analysis for the Ho site using the *BASIREPS* program, part of the

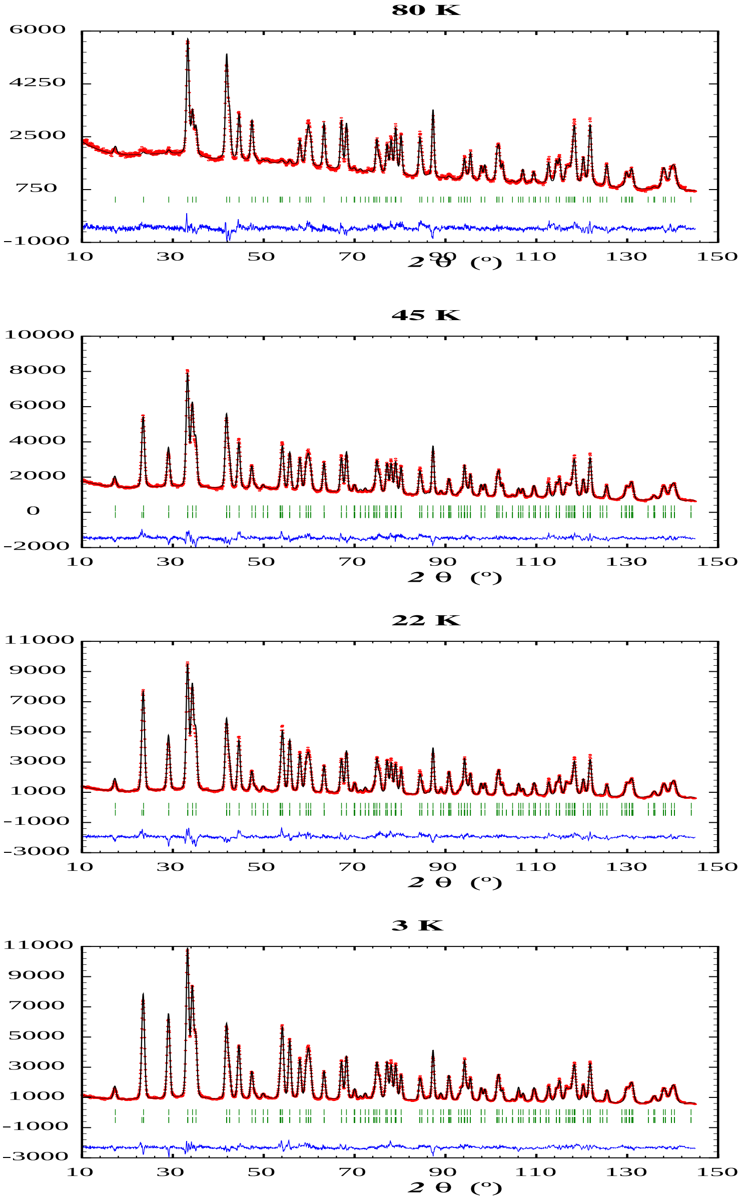

Figure 1. Neutron powder diffraction patterns of HoGa obtained at 80 K, 45 K, 22 K and 3 K, with a neutron wavelength of 1.6220(5) Å. The two sets of Bragg markers represent the nuclear and magnetic contributions to the patterns.

FullProf/WinPlotr suite [17, 18]. The decomposition of the magnetic representation comprises six one-dimensional representations, each appearing once:

$$\Gamma^{4c}_{Mag} = 1\Gamma_2 + 1\Gamma_3 + 1\Gamma_4 + 1\Gamma_5 + 1\Gamma_7 + 1\Gamma_8 \qquad (1)$$

and the basis vectors of these irreducible representations are given in table 2.

We can rule out the antiferromagnetic modes Γ_2, Γ_4 and Γ_8 on the strength of the magnetometry and susceptibility work which clearly indicates ferromagnetic order. Thus, we are left with ferromagnetic order along one of the orthorhombic crystal axes. The observation of

Table 2. Representational Analysis for the Ho(4c) site in HoGa with a propagation vector k = 0. The respective atomic positions are $(x,\ y,\ z)$, $(-x,\ -y,\ -z)$, $(\frac{1}{2}+x,\ \frac{1}{2}+y,\ z)$, and $(\frac{1}{2}-x,\ \frac{1}{2}-y,\ -z)$.

Representation	Ordering Mode	Moment directions
Γ_2	G_Y	$+-+-$
Γ_3	F_Z	$++++$
Γ_4	G_X	$+-+-$
Γ_5	F_Y	$++++$
Γ_7	F_X	$++++$
Γ_8	G_Z	$+-+-$

substantial magnetic contributions to the (020) and (200) peaks, combined with the absence of any magnetic intensity at the (002) peak, clearly indicates ferromagnetic order along the *c*-axis, corresponding to the Γ_3 mode. At 45 K we find a refined Ho magnetic moment of 6.2(2) μ_B, which increases to 8.2(2) μ_B by 22 K. The conventional R-factors for the 45 K refinement are R_B = 6.44%, R_F = 4.32% and R_{mag} = 7.27%. The R-factors for the 22 K refinement are R_B = 7.30%, R_F = 5.29% and R_{mag} = 6.93%.

Upon further cooling below 22 K we observe an increase in the magnetic intensity at the (021) peak at $2\theta = 29.1°$, relative to the magnetic intensity at the (110) peak at $2\theta = 23.6°$. Similar changes occur at other peaks, indicating that the magnetic order tips away from the crystal *c*-axis. This spin-reorientation has been observed in ac-susceptibility measurements [15]. At 3 K, the Ho magnetic moments are canted away from the *c*-axis by 30(2)°. The moments amount to 8.8(2) μ_B at 3 K, i.e. the 'free-ion' value (9 μ_B). The R-factors for the 3 K refinement are R_B = 5.27%, R_F = 4.04% and R_{mag} = 4.38%. Our refinement of the 3 K pattern also shows that the canting Ho moments tip towards an intermediate planar arrangement between the crystal *a*- and *b*-axes. We find polar angles of $\theta = 30(2)°$ and $\phi = 49(4)°$. This reorientation is driven by competition between the different crystal-field orders acting on the Ho^{3+} ions, with the higher-order (4^{th} and 6^{th}) terms becoming significant as the temperature is lowered. The observation of *c*-axis order just below T_c is consistent with the signs and relative magnitudes of the diagonal and off-diagonal second-order crystal-field terms derived from single-crystal susceptibility measurements by Shohata *et al.* [7, 8].

3.2. ^{119}*Sn Mössbauer spectroscopy*

Delyagin *et al.* [1] used ^{119}Sn doping in the RGa compounds to study the magnetic order of the R sublattice by ^{119}Sn Mössbauer spectroscopy. The Sn dopant is non-magnetic so any hyperfine field at this dopant site is transferred from the neighbouring magnetic order of the R sublattice. Information about the ordering directions can be deduced by determining the orientation of the hyperfine field (assumed collinear with the R magnetic order) within the principal axis frame of the Electric Field Gradient (EFG) at the ^{119}Sn site. Delyagin *et al.* showed that the EFG axes are aligned along the orthorhombic axes, as expected from the $m2m$ point symmetry of the Ga 4c sites, the location of the ^{119}Sn dopant. The particular identification of the EFG axes is $(xyz)=(bca)$. Within this EFG frame, the temperature dependence of the quadrupole splitting showed that above about 20 K the hyperfine field makes an angle of 90° with the z(EFG) axis, along the y(EFG) axis. In other words, Ho magnetic ordering is along the *c*-axis, as we found by neutron diffraction. Below 20 K, this angle decreases to about 58° at 4 K, with the hyperfine field lying in the yz(EFG) plane, i.e. Ho magnetic order in the crystal *ac*-plane. In figure 2 we show the orientational relationship between the Mössbauer and neutron diffraction measurements, in terms of the crystal (abc) and EFG (xyz) axes.

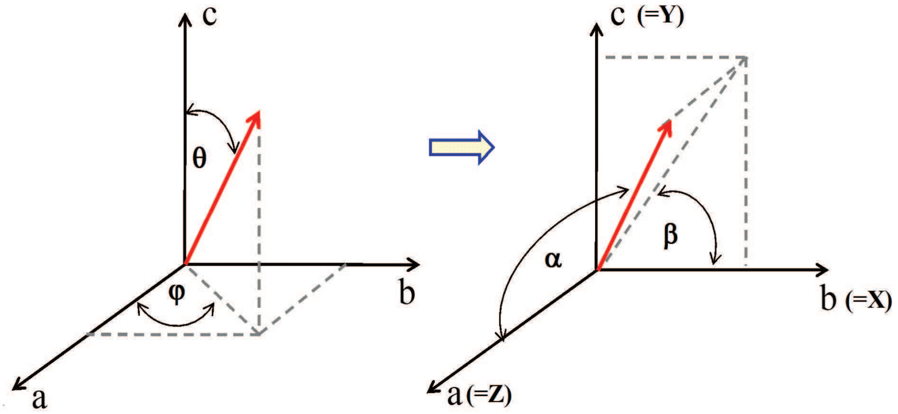

Figure 2. Orientation of the Ho magnetic moment (and hence hyperfine field at ^{119}Sn sites) relative to the crystal (abc) and EFG(xyz) axes, used in the interpretation of the neutron powder diffraction and Mössbauer data.

The quadrupole shift in a magnetically split Mössbauer spectrum, as defined by Delyagin *et al.*, is

$$QSH \;=\; \frac{eQV_{zz}}{8} \times [3cos^2\alpha - 1 + \eta(sin^2\alpha)cos(2\beta)] \tag{2}$$

using standard notation. Here, α and β are the polar angles of the hyperfine magnetic field in the principal axis frame of the EFG at the ^{119}Sn nuclei. The asymmetry of the EFG tensor is described by the η parameter. Using the accepted conventions for describing the components of the EFG tensor, Delyagin *et al.* deduced $eQV_{zz} = 1.10(8)$ mm/s and $\eta = 0.65(9)$. Thus, taking $\theta = 58°$ and $\phi = 90°$, one obtains the experimentally observed value of QSH i.e. $-0.087(4)$ mm/s.

As shown earlier, the principal z-axis of the EFG frame lies along the crystal's orthorhombic a-axis. Our neutron diffraction results are determined relative to the crystal c-axis. It is straightforward to show that our angles $\theta = 30(2)°$ and $\phi = 49(4)°$ correspond to $\alpha = 71(3)°$ and $\beta = 66(3)°$ in the EFG frame employed in the Mössbauer work and using equation (2), our magnetic structure yields a QSH value of $-0.15(4)$ mm/s, fully consistent with the Mössbauer result.

4. Conclusions

We have used high-resolution neutron powder diffraction to show that the magnetic order of the Ho sublattice in HoGa is ferromagnetic along the orthorhombic c-axis below its Curie temperature of 66(3) K. Below ∼20 K, the Ho moments cant away from the c-axis towards the ab-plane and at 3 K the Ho magnetic order is defined by the polar angles of $\theta = 30(2)°$ and $\phi = 49(4)°$, relative to the orthorhombic abc axes.

Acknowledgments

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