ELSEVIER

Journal of Alloys and Compounds 284 (1999) 42–46

Journal of ALLOYS AND COMPOUNDS

Uniaxial antiferromagnetic ordering in $HoFe_2Ge_2$: a neutron and magnetic study

P. Schobinger-Papamantellos[a,*], J. Rodriguez-Carvajal[b], I.H. Hagmusa[c], N.P. Duong[c], K.H.J. Buschow[c]

[a]*Laboratorium für Kristallographie, ETHZ, CH-8092 Zürich, Switzerland*
[b]*Laboratoire Leon Brillouin, (CEA-CNRS) Saclay, 91191 Gif sur Yvette Cedex, France*
[c]*Van der Waals–Zeeman Institute, University of Amsterdam Valckenierstr. 65, 1018 XE Amsterdam, The Netherlands*

Received 5 October 1998

Abstract

The magnetic structure of the compound $HoFe_2Ge_2$ (*I*4/*mmm* S.G) has been studied by neutron diffraction, magnetic and specific-heat measurements. The paramagnetic neutron data confirmed the $ThCr_2Si_2$ type of structure reported earlier for this compound. The analysis of the data collected in the magnetically ordered regime (T_N=17 K) showed a uniaxial arrangement of the Ho moments along *c* associated with the wave vector **q**=(1/2,1/2,0). The moments of the atoms related by the non-primitive translation (1/2,1/2,1/2) are antiparallel. The refined moment value at 1.5 K is μ_{Ho}=6.6(1) μ_B. In addition to the ordered phase the neutron data comprise diffuse magnetic peaks in the low-angle region demonstrating the coexistence of short-range order effects below 6 K.

Keywords: Rare earth iron germanides; Magnetic properties; Magnetic structure; Neutron diffraction; Specific heat anomaly

1. Introduction

Ternary rare earth (R) compounds of composition RM_2X_2, where M is a 3d element and X a metalloid (Si, Ge, Sn) with the $ThCr_2Si_2$ type of structure (*I*4/*mmm* space group, Th at 2a (000), Cr at 4d (1/2,0,14) and Si at 4e (00*z*)) form a large family of compounds with interesting magnetic properties that have been investigated since a considerable time by several authors [1–6].

According to Ref. [5], the RFe_2Ge_2 compounds formed of the light rare earths (R=Nd, Pr) were found to order antiferromagnetically with a collinear AFII type structure with wave vector (001/2), the moments pointing along the c direction. The Tb compound was reported in Ref. [2] to order with an incommensurate structure of unknown structure type while in a more recent investigation [6] it was reported that $TbFe_2Ge_2$ remains paramagnetic down to 1.8 K. The present study deals with the magnetic ordering of the $HoFe_2Ge_2$ compound. A report on the magnetic properties of RFe_2Ge_2 (Tb, Dy, Ho) compounds comprising also neutron powder data appeared during the course of the present experiments and the corresponding results will be discussed in more detail below.

2. Experimental

The RFe_2Ge_2 compounds with R=Ho and Y were prepared in polycrystalline form by melting the elements (of at least 99.9% purity) in an arc furnace under a reduced argon atmosphere. Because the magnetic properties might become seriously affected when small amounts of Fe occupy the Ge positions we used slightly Fe deficient compositions for the sample preparation (1:1.95:2). The samples were subsequently vacuum annealed at 800°C for 2 weeks. All samples were characterized by X-ray diffraction and shown to be approximately single phase with Bragg peaks consistent with the $ThCr_2Si_2$ structure.

The temperature dependence of the magnetization was determined in a SQUID magnetometer in the temperature range 4.2–300 K. The specific heat was measured in zero field in the temperature range from 1.8 to 200 K. About 200–400 mg of each compound were mounted on a sapphire plate in a thermal frame by using apiezone. This

*Corresponding author. Tel.: +41-632-3773; fax: +41-632-1133.

0925-8388/99/$ – see front matter
PII: S0925-8388(98)00914-1

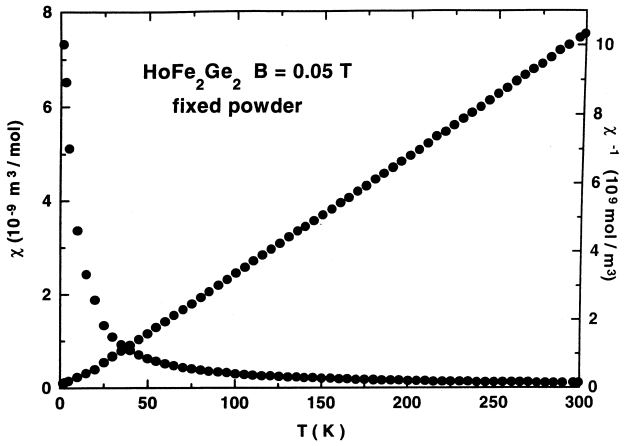


Fig. 1. Temperature dependence of the magnetic susceptibility (left scale) and reciprocal susceptibility (right scale) of $HoFe_2Ge_2$. Measurements were made in a field of 0.05 T.

setup comprises the possibilities for measurements using the standard adiabatic method.

Neutron diffraction experiments were carried out in the temperature range 1.5–20 K at the facilities of the Orphée reactor (LLB-Saclay). The data were collected with the G42 diffractometer (800 cells multidetector) using the wavelength 2.3433 Å. The step increment in 2θ was 0.1°. The data were analysed with the program Fullprof [7].

3. Results of magnetic and specific-heat measurements

Results of the temperature dependence of the magnetic susceptibility and the temperature dependence of the reciprocal susceptibility are shown in Fig. 1. Curie Weiss behaviour is observed over almost the whole temperature range considered. Below about 20-K deviations from Curie Weiss behaviour occur, but there is no clear evidence of a magnetic phase transition. The effective moment derived from the slope of the reciprocal susceptibility equals 11.0 μ_B per formula unit, which is close to the free ion value of 10.60 μ_B per Ho. The field dependence of the magnetic moment is shown for several temperatures in Fig. 2. The curve measured at 4.2 K reflects the magnetically ordered region (see below) and is indicative of antiferromagnetic ordering. From the low-field slope of the curve shown for 4.2 K, one derives an absolute value of 0.333 T fu/μ_B for the intersublattice molecular field constant.

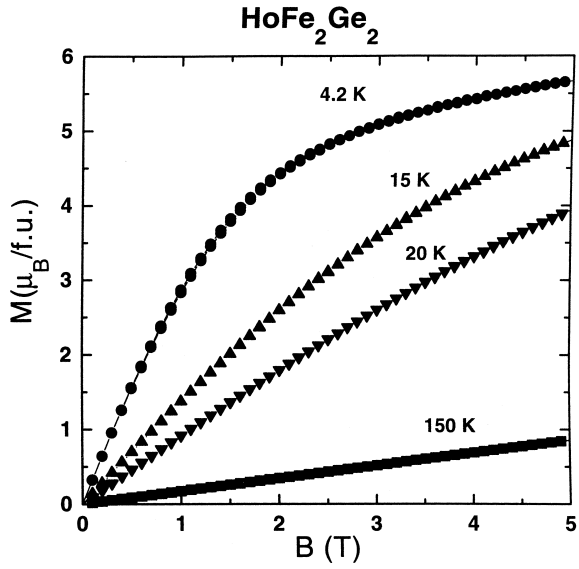
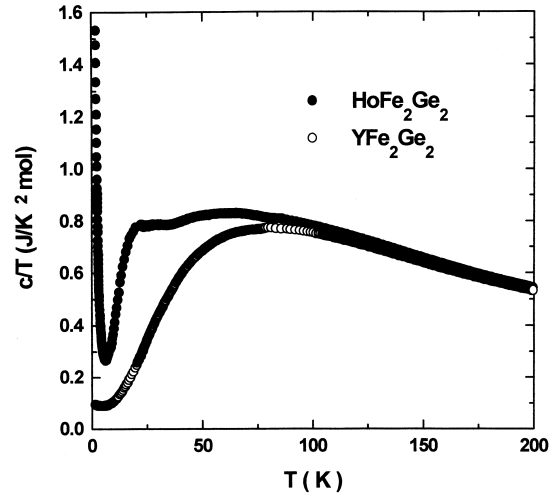


Fig. 2. Field dependence of the magnetic moment of $HoFe_2Ge_2$ at several temperatures.



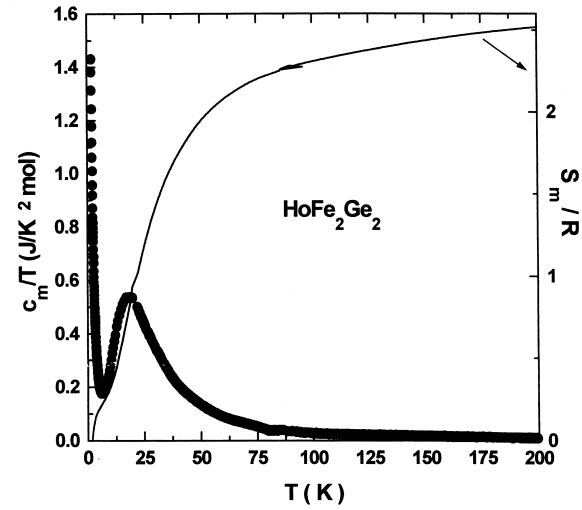


Fig. 3. (a) Temperature dependence of the specific heat (c/T) of the compounds $HoFe_2Ge_2$ and YFe_2Ge_2. (b) Temperature dependence of the magnetic contribution to the specific heat (c_m/T) of $HoFe_2Ge_2$ (left scale). The solid curve represents the temperature dependence of the magnetic entropy (right scale).

The specific heat of the compounds $HoFe_2Ge_2$ and YFe_2Ge_2 has been measured as a function of temperature. Plots of c/T versus T of both compounds can be compared

with each other in Fig. 3a. The strong upturn of the specific heat below about 2 K is attributed to the nuclear contribution of the Ho atoms. Because Y is non-magnetic, the data of YFe_2Ge_2 can be taken to be representative of the phonon contributions because the Fe atoms do not carry a magnetic moment, meaning that there in no magnetic contribution of the Fe sublattice to the specific heat. Before subtracting the YFe_2Ge_2 data from the $HoFe_2Ge_2$ data, the former have been corrected for the mass difference between Ho and Y. The resulting magnetic contribution of the Ho sublattice is shown in Fig. 3b. These data have been used, in turn, to obtain the temperature dependence of S_m/R, where S_m is the magnetic entropy. The temperature dependence of S_m/R is also shown in Fig. 3b. As can be seen in Fig. 3b, there is a pronounced low-temperature anomaly leading to a sharp peak in the temperature dependence of the specific heat at about 17 K. Very likely all these anomalies are associated with magnetic phase transition in which the Ho moment become magnetically ordered.

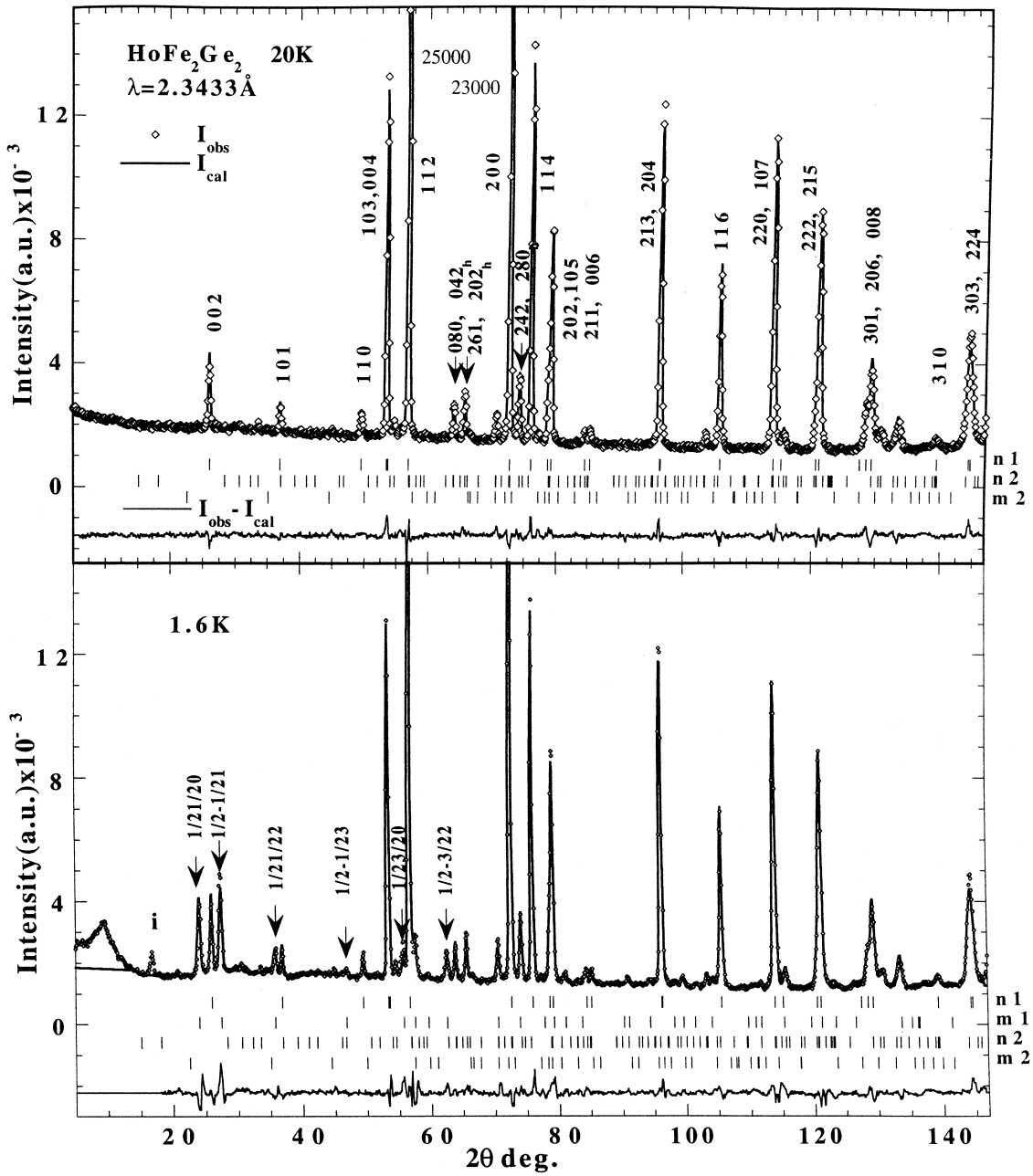


Fig. 4. Observed, calculated and difference neutron diagrams of $HoFe_2Ge_2$ measured in the paramagnetic state at 20 K (top part), and measured in the magnetically ordered state at 1.5 K (bottom part).

4. Results of neutron diffraction

4.1. Crystal structure of $HoFe_2Ge_2$

The neutron diffraction pattern collected in the (HT) paramagnetic state at 20 K is shown in Fig. 4 (top part). The refined parameters given in Table 1 confirm the type of structure [1,2] with $ThCr_2Si_2$ structure (*I*4/*mmm*, Th at 2a (000) Cr at 4(d) (1/2,0,14) and Si at 4(e) (00*z*). The powder pattern contains some additional reflections (denoted by arrows in the upper part of Fig. 4) that were identified to pertain to a small amount (7%) of the coexisting orthorhombic phase $HoFe_6Ge_6$ (a=0.809504 nm, b=1.766839 nm, c=0.510042 nm, *Cmcm* space group [8]). The latter phase orders with collinear Fe moments along x below T_N=480 K, μ_{Fe}=2.0 μ_B) [9]. The corresponding nuclear and magnetic contributions have been included in the refinement, which is denoted by n_2, m_2 in the margin of Fig. 4. The strongest nuclear lines are labeled by (h) in the figure. The *R*-factor values are satisfactory and indicate no other significant deviation from the basic structure and no admixture of the Fe and Ge sites.

4.2. Magnetic ordering of $HoFe_2Ge_2$

Magnetic ordering becomes visible below 15 K. It is characterized by the appearance of some weak additional reflections at positions different from those of the I-centered lattice and by a wavy broad background in the low 2θ region (10°) indicating the coexistence of short-range order effects (see Fig. 5). Furthermore, the data comprise at 2θ=17°, an additional magnetic peak (i) which also disappears above 6 K where the short-range contributions are negligible.

The indexing of the resolved magnetic reflections, indicated by arrows in the lower part of Fig. 4, has been possible using the wave vector **q**=(1/2,1/2,0) which corresponds to a four-fold cell enlargement ($2a\times2a\times c$).

Table 1
Refined parameters of $HoFe_2Ge_2$ (*I*4/*mmm*) at 20 K (paramagnetic state) and 1.5 K (magnetically ordered state)

Parameter	1.5 K	20 K
z_{Ge} 4(e) (00z)	0.3788(2)	0.3788(1)
μ_{Ho} [μ_B]	6.6(1)	–
$B_i\times10^2$ nm^2: Ho	0.49(6)	0.65(5)
Fe,Ge	1.48(5)	1.26(3)
a (nm)	0.39497(1)	0.39497(1)
c (nm)	1.03665(3)	1.03676(2)
R_n (%), R_m (%)	2.3, 17.8	1.8, –
R_{wp} (%), R_{exp} (%)	11.6, 4.9	8.8, 5.6

μ is the moment value. B_i (nm^2) is the atomic temperature factor. R_n (%), R_m (%) are the reliability factors for the integrated nuclear and magnetic intensities, respectively.

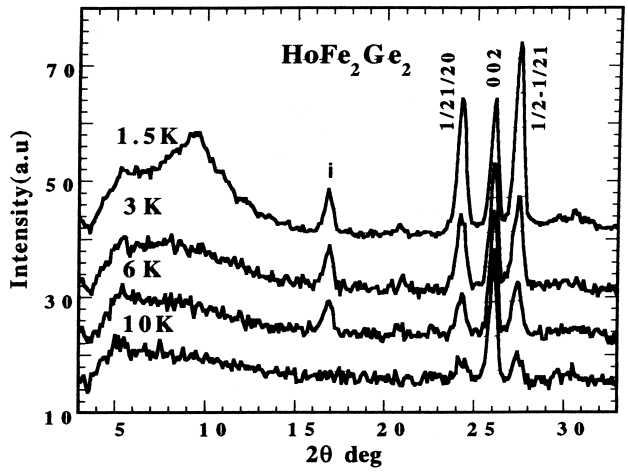


Fig. 5. Neutron diffraction patterns collected between 1.5 and 10 K indicating the coexistence of long-range and short-range order in $HoFe_2Ge_2$ below 6 K.

This wave vector leads to the antitranslations (1/200) and (01/20) and the translations (000) and (1/21/20). Therefore, the tetragonal enlarged magnetic cell is C centered and can be reduced to a two-fold enlarged tetragonal cell ($a\sqrt{2}\times a\sqrt{2}\times c$) which has a C_p magnetic lattice **q**=

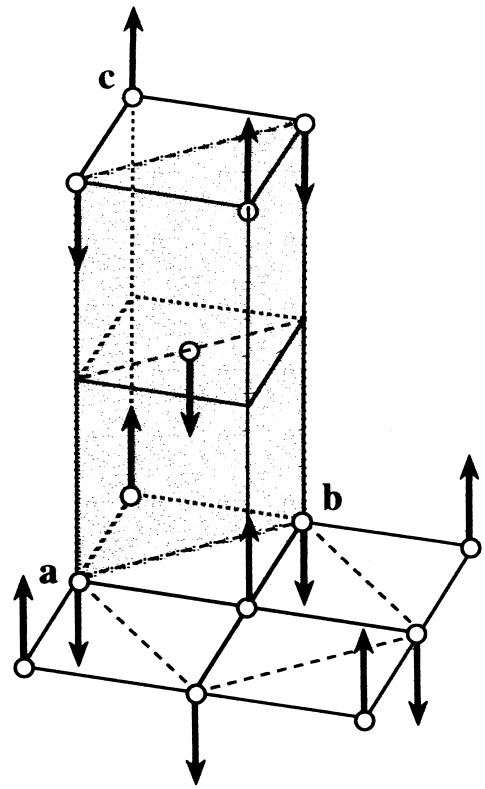


Fig. 6. Schematic representation of the uniaxial antiferromagnetic ordering of $HoFe_2Ge_2$.

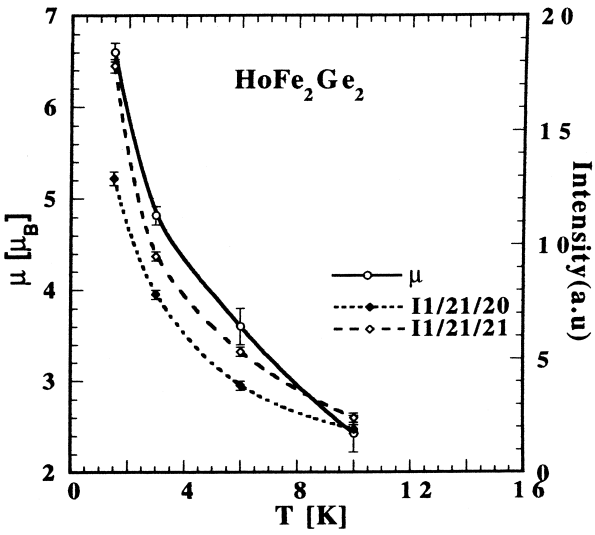


Fig. 7. Thermal variation of the integrated intensities of the strongest magnetic satellites and of the Ho magnetic moment in $HoFe_2Ge_2$.

(010). The magnetic structure shown in Fig. 6 is similar to that observed for $TbNi_2Si_2$ [10] and $CeRh_2Si_2$ [11].

The refinement has shown that the moments of the Ho atoms are oriented along the *c*-axis. The moments of the Ho atoms at (000) and (1/2,1/2,1/2) are antiparallel ($\cos 2\pi(\mathbf{q}.\mathbf{r}_j)=\cos\pi$, for $\mathbf{q}=(1/2,1/2,0)$). This arrangement corresponds to a stacking of ferromagnetic Ho planes (*xx*0) coupled antiferromagnetically to those in the perpendicular direction [*x*,-*x*,0]. The refined moment value at 1.5 K $\mu_{Ho}=6.6(1)$ [μ_B] is considerably reduced from the free ion Ho^{3+} value gJ [μ_B]=10 [μ_B] which is most probably due to crystal field effects, but also to the presence of short-range order effects. From measurements made at a few other temperatures, it can be inferred that the temperature dependences of the magnetic intensities and the ordered moment values display a rather peculiar behaviour. Saturation is not achieved even at 1.5 K, although the ordering temperature obtained from the specific heat data is close to 17 K. From the data points shown in Fig. 7, one may conclude that the ordering temperature lies well above 10 K and that the ordering mechanism does not proceed according to a Brillouin function.

5. Concluding remarks.

The neutron diffraction study of the compound $HoFe_2Ge_2$ was undertaken by us in order to check whether this compound could possibly interfere with the interpretation of the neutron diffraction data obtained by us on the compound $HoFe_6Ge_6$ [12]. In the course of the present experimental investigation a paper has appeared [12] on the magnetic properties of several RFe_2Ge_2 (Tb, Dy, Ho) compounds also comprising neutron powder data. This paper reports the absence of long-range magnetic order down to 1.5 K for the R=Ho compound and the neutron data show only diffuse magnetic contributions. The existence of a modulated structure is then suggested by analogy to the compounds with R=Tb and Dy which display at very low temperatures a sine wave modulated magnetic order with moments parallel to the *c*-axis, which is associated with a two-component wave vector of the type $\mathbf{q}=(q_x,0,q_z)$.

Our results confirm the existence of short-range magnetic order effects in $HoFe_2Ge_2$ with the same thermal behaviour as given in Ref. [12]. However, interestingly, they show the existence of an ordered majority phase with the same moment orientation but with interactions different from those found in the Tb and Dy compounds. Note that the wave vector (1/2,1/2,0) is compatible with a negative nearest neighbour interaction within the (001) plane and ferromagnetic interactions within (*xx*0) planes, the moments being coupled antiferromagnetically to those in the corresponding perpendicular direction [*x*,−*x*,0].

The existence of two magnetic structures in the $HoFe_2Ge_2$ compound is most likely related to subtle structural differences, i.e. a different degree of atomic order of the non magnetic atoms or to a different concentration of defects. Such phenomena have been widely observed in binary RX_{2-x} (X=Ge,Si,Sn..) and ternary rare earth compounds of the RMX or RM_xX_2 type [4].

References

[1] W. Rieger, E. Parthé, Mh. Chem. 100 (1969) 444.
[2] H. Pinto, M. Melamud, M. Kuznietz, Phys. Rev. B 31 (1985) 508.
[3] A. Szytula, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, vol. 6. Elsevier, Amsterdam, 1991, pp. 85.
[4] D. Gignoux, D. Schmitt, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, vol. 10. Elsevier, Amsterdam, 1997, p. 239.
[5] A. Szytula, W. Bazela, J. Leciejewicz, Solid State Commun. 48 (1983) 1053.
[6] W. Bazela, J. Leciejewicz, H. Ptasiewicz-Bak, A. Szytula, J. Magn. Magn. Mater. 72 (1988) 85.
[7] J. Rodriguez-Carvajal, The manual of FullProf can be obtained from a Web browser at ftp://bali.saclay.cea.fr/pub/divers/fullp/doc, Physica B 192 (1993) 55.
[8] R.R. Olentich, L.G. Akselrud, Y.P. Yarmoliuk, Dopov. Akad. Nauk. Ukr. RSR Ser. A 2 (1981) 84.
[9] O. Zaharko, P. Schobinger-Papamantellos, J. Rodriguez-Carvajal, K.H.J. Buschow, (in press).
[10] V.N. Nguyen, F. Tcheou, J. Rossat-Mignod, R. Ballestracci, Solid State Commun. 45(2) (1983) 209.
[11] S. Quezel, J. Rossat-Mignod, B. Chevalier, P. Lejay, J. Etourneau, Solid State Commun. 49(7) (1984) 685.
[12] A. Szytula, S. Baran, J. Leciejewics, B. Penc, N. Stüsser, A. Yon fan Ding, J. Zygmunt, J. Zukrowski, J. Phys. Condens. Matter 9 (1997) 6781.