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Magnetic phase diagrams of the CrB- and FeB-type HoSi compounds

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ABSTRACT

The temperature magnetic phase diagrams of the dimorphic HoSi compound were studied by neutron diffraction. The sample comprises 35.5% CrB- (*Cmcm*) and 64.5% FeB-type (*Pnma*) of structure. Both phases order antiferromagnetically below $T_N=25$ K and undergo first-order magnetic transitions at $T_{ic}=16.5$ K. Their T-phase diagrams comprise a low temperature (*LT*) 2.7 K$-T_{ic}$ and a high temperature (*HT*) range $T_{ic}-T_N$ with distinct wave vectors.

The *LT* magnetic ordering of the CrB-type HoSi with the wave vector $\boldsymbol{q}_1=(1/2, 0, 1/2)$ corresponds to a uniaxial magnetic structure, with the Ho moments along the shortest axis *c*. At 2.7 K the ordered moment value is 8.6(2) μ_B/Ho atom. The *HT* ordering, described by the wave vector $\boldsymbol{q}_2=(q_{2x}, 0, q_{2z})$ with a T-variable length, corresponds to an amplitude modulated structure.

The magnetic ordering of the FeB-type HoSi requires two symmetry independent vectors $\boldsymbol{q}_3=(0, q_{3y}, q_{3z})$ for the *LT*- and $\boldsymbol{q}_4=(q_{4x}, q_{4y}, 0)$ for the *HT* range. Both vectors correspond to sine wave modulated structures with the Ho magnetic moments confined along the shortest axis *b*. The $\boldsymbol{q}_3$ vector has an almost invariable length vs. *T* close to $\approx(0, 9/17, 1/11)$. At 2.7 K the amplitude of the wave is 10.9(1) μ_B/Ho atom. At T_{ic} $\boldsymbol{q}_3$ jumps to the wave vector $\boldsymbol{q}_4=(q_{4x}, q_{4y}, 0)$ with a T-variable length. At 17 K $\boldsymbol{q}_4=(0.092(1), 0.538(3), 0)$. Around T_{ic} there is a narrow coexistence range of the $\boldsymbol{q}_3$ and $\boldsymbol{q}_4$ competing phases. Various models are discussed and compared with the isomorphic *R*Si (*R*=rare earth) compounds counterparts of HoSi, a comparison that has led us to briefly review the magnetic structures available in the literature for this interesting class of compounds.

1. Introduction

HoSi, like the other *R*Si (*R*=heavy rare-earth) compounds, occurs with two orthorhombic structures [1]: the CrB-type (*Cmcm* Nr. 63, all atoms at 4*c* site: (0, *y*, 1/4)) and the FeB-type (*Pnma* Nr. 62, all atoms at 4*c* site: (*x*, 1/4, *z*)). The compound TmSi is an exception and adopts exclusively the CrB-type. The two structures are related and can be viewed as transposed stacking variables of a common unit; the elongated trigonal rare earth prisms are centred by Si zigzag chains that are stacked so that they share their rectangular sides to infinite prism rows. 3D representations of the two structures will be given in later sections.

Apparently, the rare earth arrangement at the corners of the trigonal prism rows implies competing antiferromagnetic interactions that give rise to geometric frustration effects. For both structure types, these effects lead to the formation of a large variety of long-period commensurate (C) or incommensurate (IC) magnetic structures that can transform into each with changing temperature [2]. More recent results on the *R*Si magnetism not given in the review of reference [2] are discussed below and are summarised in the appendix to facilitate reading.

The CrB-type HoSi compound according to a previous study [3] orders antiferro-magnetically below $T_N=25$ K with a collinear magnetic moment arrangement, with the wave vector $\boldsymbol{q}_1=(1/2, 0, 1/2)$. At 4.2 K the Ho moments ($\mu_{Ho}=7.0$ μ_B) were oriented 12° off the *c*-direction in the plane (*a*, *c*), in agreement with the crystal field calculations [4]. However no further information exists concerning the thermal evolution of this phase. The HoSi sample examined later on by us, in relation to the CrB-type (*T*, *x*) phase diagram [5] of the pseudo-binary system $HoGe_{1-x}Si_x$ (solid solution), was dimorphic (35% CrB- and 64.5% FeB-type) and the high temperature (*HT*) neutron data could not be refined. The reason was the large number of overlapping satellites at higher temperatures as both magnetic structures become incommensurate with the crystal lattice.

It is to be noted that the CrB-type $HoGe_{1-x}Si_x$ (*T*, *x*) magnetic phase diagram [5] for $x>0.2$ comprises (i) a low temperature (*LT*) lock-in phase $\boldsymbol{q}=(1/2, 0, 1/2)$ and (ii) an incommensurate *HT* phase with $\boldsymbol{q}=(q_x, 0, q_z)$ and a first order transition between them at T_{ic}. Contrary, the magnetic structures of CrB-type compounds with $x<0.2$: HoGe and $HoGe_{0.8}Si_{0.2}$ remain incommensurate $\boldsymbol{q}=(q_x, 0, q_z)$ down to 1.2 K. Above T_{ic} the wave vector has a temperature variable

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length of mainly the q_x component and the Ho magnetic moments order with a pure sinusoidal modulation 5–7° off the shortest axis *c*. T_{ic} and T_N were found to increase linearly with increase in Si concentration (x). Apparently, the *LT* commensurate phase becomes destabilised with decrease in silicon content (x).

Preliminary results [6] on the FeB-type HoSi compound at 8 K suggest a sine wave modulated magnetic structure associated with the incommensurate wave vector $\boldsymbol{q}=(q_x, q_y, q_z)$, which has an almost temperature invariable length in the *LT* range close to $\approx(0, 1/2, 1/11)$. Similar wave vectors were found in isomorphic rare earth *R*Si compounds as mentioned in detail below.

Our T-dependent neutron diffraction study [7,8] on TbSi (T_N=57 K) has shown that the previously reported *LT* commensurate [9] wave vector $\boldsymbol{q}=(0, 1/2, 0)$ remains unchanged between 2 K and T_c and jumps by a first order transition above T_c=36 K to a general reciprocal lattice position $\boldsymbol{q}=(q_x, q_y, q_z)$ with a strongly variable length in a narrow intermediate region 36–40 K and slowing down above 40 K. At 42 K up to T_N the wave vector has again a commensurate $\boldsymbol{q}=(0, 1/2, 1/8)$ value. The CeSi compound has a commensurate wave vector (0, 1/2, 1/16) [10,11] over the entire magnetically ordered regime as found by neutron powder diffraction and μ_{SR} measurements. Our more recent preliminary single crystal neutron data confirmed this wave vector (unpublished results).

Recently the FeB-type DySi compound was found by us to display quite an exotic behaviour [12–14]. At 1.5 K the magnetic ordering requires two wave vectors: a commensurate (0, 1/2, 1/6) and an incommensurate $\boldsymbol{q}=(0, q_y, q_z)$ close to $\approx(0, 1/2, 1/11)$ location with a slightly temperature variable length [12,13]. With increase in temperature the amount of the incommensurate phase increases at the cost of the commensurate phase, which fully disappears above T_{ic}=23.5 K. The wave vector $\boldsymbol{q}=(0, q_y, q_z)$ jumps simultaneously to another location close to $\approx(0, 1/2, 1/7)$ that remains almost unchanged up to $T_N=39\pm1$ K. This quite unusual phenomenon of a single-$\boldsymbol{q}$ *HT* magnetic phase and of a multiple symmetry independent $\boldsymbol{q}$-vectors *LT* phase could be brought into connection with a first order magnetoelastic transition at T_{ic} with a minor monoclinic distortion recently detected by high resolution X-ray diffraction [14]. Apparently the *HT Pnma* orthorhombic DySi structure transforms at T_{ic} to the monoclinic $P2_1/n$ *LT* phase. The two phases have a broad coexistence range below T_{ic}=23.5 K down to 2.7 K where the *HT* phase exists as a metastable phase. Most likely the presence of two slightly different magnetic structures below T_{ic} is related to the structural sample inhomogeneity.

The present study, on one hand, completes the CrB-type $HoGe_{1-x}Si_x$ (T, x) magnetic phase diagram [5] and, on the other hand, provides information on the FeB-type magnetic structure and its thermal behaviour not studied before. It extends the preliminary information on the HoSi FeB-type magnetic ordering reported by us in [6] at 8 K to the entire magnetically ordered regime of the same sample on the basis of neutron diffraction powder data. The results are summarised in a phase diagram and are compared to those of the *R*Si (*R*=rare earth) isomorphic compounds.

2. Experimental and procedures

2.1. Sample preparation

The HoSi sample was prepared by arc melting of the appropriate amount of the elements in an atmosphere of purified argon gas. The purity of the starting materials was 99.9% for holmium and 99.99% for silicon. After arc melting the sample has been vacuum-annealed in a quartz tube for 1 month at 800 °C. Standard X-ray diffraction using CuKα radiation showed that the annealed sample is dimorphic.

2.2. Neutron diffraction

Neutron data were collected on a HoSi powder sample with the DMC multicounter system at the reactor Saphir, Würenlingen (λ=1.703 and 1.709 Å, 2θ: 3–83° and step increment of 0.10°) for a full set of temperatures in the magnetically ordered state in order to derive the T-magnetic phase diagrams. The data analysis is done by the *FullProf Suite* of programs [15]. The structure plots are made by the program FullProf Studio [16] incorporated in [15].

2.3. Paramagnetic state

The refinements of the 26 K HoSi data in the paramagnetic state confirm the sample composition given in [6] with 64.5% FeB-type and 35.5% CrB-type. Results are given in the next sections in Tables 1–4 and Figs. 1 and 2. The obtained low *R*-factors are satisfactory. The refined structural parameters are in fair agreement with more recently obtained room temperature structural parameters based on a precise single crystal X-ray study [17]. The individual calculated profiles of magnetic origin (dotted curves) of the CrB- and FeB-structure types are given in red and blue colours, respectively, below the standard Iobs and

Table 1
Refined structural and magnetic parameters in the paramagnetic and the magnetically ordered state from neutron data of the CrB-type HoSi compound. Space group *Cmcm* (Nr 63), all atoms at sites 4*c*: ±(0, *y*, 1/4). In the range T_{ic}–T_N the wave vector is incommensurate $\boldsymbol{q}=(q_x, 0, q_z)$ with the crystal lattice.

HoSi	CrB-type (*Cmcm*) (35.5%)				
Parameter	26 K	2.7 K	10.9 K	17 K	20 K
a (Å)	4.2159(9)	4.229(1)	4.228(1)	4.227(1)	4.227(1)
b (Å)	10.400(2)	10.426(3)	10.427(3)	10.439(3)	10.429(4)
c (Å)	3.787(1)	3.795(1)	3.793(1)	3.793(1)	3.792(1)
y_{Ho}	0.142(1)	0.138(1)	0.139(1)	0.139(1)	0.142(1)
y_{Si}	0.425(2)	0.431(3)	0.428(2)	0.423(2)	0.424(2)
$\boldsymbol{q}=(q_x, 0, q_z)$	–	$\boldsymbol{q}_1=(1/2, 0, 1/2)$	$\boldsymbol{q}_1=(1/2, 0, 1/2)$	$\boldsymbol{q}_2=(q_x, 0, q_z)$	$\boldsymbol{q}_2=(q_x, 0, q_z)$
q_x, q_z		1/2, 1/2	1/2, 1/2	0.4709(3), 0.5	0.4471(6), 0.5103(6)
$\mu_{oz}(\mu_B)$, φ_c^o	–	8.6(2), 0	8.3(2), 0	9.5(2), 0	8.3(2), −15(2)
R_B%, R_m%	5.2, –	3.4, 3.5	3.7, 3.3	3.0, 3.6	3.2, 5.9
R_{wp}%, R_{exp}%, χ^2	18, 16.3,1.3	10, 4.0, 5.7	10.6, 3.0, 3	10.2, 3.3, 3.5	13.8, 7.0, 3.9

μ_{oz} is the refined wave amplitude (Fourier coefficient) parallel to the *c*-axis or ordered moment value of holmium in the commensurate range for $T\le T_{ic}$=16.5 K. R_B, R_{wp}, R_m% and R_{exp} are the Bragg factor, the reliability factor for the magnetic intensities, the weighted profile intensities, and the expected value related to the statistical accuracy of the data, respectively.