

Journal of Alloys and Compounds 417 (2006) 72-84

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The ternary RE–Si–B systems (RE = Dy, Ho, Er and Y) at 1270 K: Solid state phase equilibria and magnetic properties of the solid solution $REB_{2-x}Si_x$ (RE = Dy and Ho)

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> Received 21 July 2005; received in revised form 2 September 2005; accepted 6 September 2005 Available online 13 October 2005

Abstract

The solid state phase equilibria in the ternary RE–Si–B diagrams (RE = Dy, Ho, Er and Y) were determined at 1270 K using experimental techniques such as X-ray diffraction, scanning electron microscopy and electron probe microanalysis. In general, three ternary phases were obtained for each diagram: the line compound RE₃Si₂B₈ with tetragonal symmetry, the boron-inserted Nowotny phase RE₅Si₃B_x of Mn₅Si₃-type and the solid solution REB_{2-x}Si_x of AlB₂-type. Prior to this work, the binary systems RE–Si and RE–B, which form the boundary of each diagram, were also re-investigated. In addition to the structures of RE₅Si₃ (Mn₅Si₃-type, RE = Dy, Ho and Y) and Dy₃Si₄ (Ho₃Si₄-type) which were previously reported or will be presented in a forthcoming paper, the X-ray single crystal structures of RE₅Si₄ (Sm₅Ge₄-type, RE = Dy and Ho), DySi (CrB-type) and HoSi in both polymorphic modifications, i.e. the FeB- (high temperature) and CrB- (low temperature) types, were determined and are described herein. Structural relationships between members of the same series on one side, and between both forms of HoSi on the other side, are also discussed in terms of coordination polyhedra and interatomic distances. Finally, magnetic measurements were performed on the alloys REB_{2-x}Si_x, which in case of RE = Dy exhibit a marked increase of the magneto-crystalline anisotropy, whereas for RE = Ho a change from ferromagnetic to antiferromagnetic behaviour with increasing silicon content is encountered. © 2005 Elsevier B.V. All rights reserved.

Keywords: Rare-earth metal; Silicon; Boron; Phase diagram; X-ray diffraction; Electron microscopy; Crystal structure; Magnetic measurements

1. Introduction

The phase relations in the RE–Si–B systems (RE, rare-earth metal) have not been studied in sufficient detail. Phase diagrams were initially reported for RE = La, Ce, Er and Y at 1070 K [1,2], which did not give evidence concerning the existence of ternary phases, with the exception of very narrow homogeneity ranges around some binary compositions. Recently, we have published the isothermal sections of the ternary systems Gd–Si–B and Nd–Si–B at the higher temperature of 1270 K [3,4]. No ternary phases in the Nd–Si–B system were found with the exception of

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0925-8388/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2005.09.012 the boron-inserted Nowotny phase Nd₅Si₃B_x of Mn₅Si₃-type. With RE = Gd instead, the line compound Gd₅Si₂B₈ of a new structure type [3] was discovered in addition to the Nowotny phase Gd₅Si₃B_{0.64}. This result encouraged us to pursue the investigations on the RE–Si–B systems when RE is a heavy rareearth metal. Our research was focused on the solid phase equilibria in the RE–Si–B system (RE = Dy, Ho, Er and Y) at 1270 K. Prior to this work, the binary systems RE–Si and RE–B, which form the boundary of each diagram, were re-investigated. Generally, all the binary phases reported in literature were confirmed [5,6], as well as the more recently detected binary compounds RE₃Si₄ of the Ho₃Si₄-type [7], formed via a sluggish peritectoidal reaction between RESi and RESi_{2-x} [8,9]. Moreover, the holmium silicide HoSi was encountered in both polymorphic modifications, i.e. the FeB- and CrB-type structures.

This paper deals with the isothermal section of the ternary RE–Si–B phase diagrams (RE = Dy, Ho, Er and Y) at 1270 K. Crystal structures of RE_5Si_3 (Mn₅Si₃-type, RE = Dy, Ho and Y) and Dy₃Si₄ (Ho₃Si₄-type) were reported recently or will appear soon in the literature [9,10]. The X-ray single crystal structures of the binary compounds RE5Si4 (Sm5Ge4- or structurally related Gd₅Si₄-type, RE = Dy and Ho), DySi (FeB-type) and both modifications of HoSi, i.e. the FeB- (high temperature) and CrB-type (low temperature) structures as well as those of the ternary phases $\text{REB}_{2-x}\text{Si}_x$ (RE = Dy and Ho) were solved and are described herein. Structural relationships between members of the same series on one side, and between both forms of HoSi on the other side, are also discussed especially in terms of coordination polyhedra and interatomic distances. Furthermore, the magnetic behaviour for the alloys $REB_{2-x}Si_x$ for RE = Dy and Ho is also reported.

2. Experimental

Polycrystalline samples were prepared from pure elements: rare-earth or yttrium metal as ingots (purity >99.9%), silicon (>99.99%) and boron (>99%) as powders, all supplied by Strem Chemicals. Suitable amounts of powder and freshly filed chips of the rare-earth or Y metal were mixed together and pressed into pellets. Arc-melting of the samples (800 mg each) was performed on a water-cooled copper hearth under a purified argon atmosphere with a Ti/Zr alloy as a getter. To ensure homogeneity, the samples were turned over and re-melted several times. Finally, to reach thermodynamic equilibrium, the ascast samples were sealed in evacuated silica tubes, heat treated at 1270 K for one month and subsequently quenched in cold water. All the single crystals for structure determination were isolated by crushing the solidified samples. They had a metallic appearance and were non-reactive towards air.

Electron probe microanalyses (EPMA) were performed either on a Jeol JSM-6400 scanning electron microscope by energy-dispersive spectroscopy (EDS) of X-rays or on a Camebax SX 50 using wavelength-dispersive spectroscopy (WDS) of X-rays (REB₄, RESi, REB₂C₂ and/or elemental Si as standards).

A small part of each sample was pulverized and analyzed by X-ray diffraction (XRD) using a powder diffractometer (CPS 120 INEL) equipped with a positionsensitive detector ranging from 6° to 120° in 2θ . Refinement of the unit cell parameters was performed with the help of the CSD program package [11].

Single-crystal intensity data of all the binary and ternary phases were collected at ambient temperature using a Nonius KappaCCD X-ray areadetector diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Data collection strategy was performed with the help of the program COLLECT [12] and reflections were corrected using the program DENZO of the KappaCCD software package [13]. A numerical absorption correction was applied in some cases, on the basis of an optimized description of the crystal faces [14]. Structures were solved by direct methods (SIR 97) [15] and least-squares refinements, difference Fourier syntheses were run with SHELXL-97 or JANA 2000 program packages [16,17]. The program Diamond [18] was used for the drawings of the structural units.

The magnetic properties were studied with a superconducting quantum interference device (SQUID) magnetometer MPMS-XL (Quantum Design) using small amounts of polycrystalline samples. The temperature dependence of the magnetization was measured for T = 2-300 K in an external field B = 0.1 T. The isothermal magnetization versus applied field was performed in B = 0-5 T at T = 5 K.

3. Results and discussion

3.1. Isothermal section of the ternary phase diagrams

The experimentally found ternary phase diagrams RE–Si–B (RE = Dy, Ho, Er and Y) at 1270 K are presented in Fig. 1. The

solid state phase equilibria for each RE–Si–B system have been established from a total of about 40 samples, which were studied by X-ray diffraction in combination with scanning electron microscopy and electron probe microanalysis (EDS or WDS) investigations.

At the reaction temperature mentioned above, the binary compounds that form the boundary of the diagrams have been confirmed: REB₂ (AlB₂-type), REB₄ (ThB₄-type), REB₆ (CaB₆-type), REB₁₂ (UB₁₂-type) and REB₆₆ (ThB₆₆-type) on the boron side, while RE₅Si₃ (Mn₅Si₃-type), RE₅Si₄ (Sm₅Ge₄type), RESi (FeB- and/or CrB-type), RE₃Si₄ (Ho₃Si₄-type) and RESi_{2-x} (0.33 $\leq x \leq$ 0.5) (AlB₂-type) have been found on the silicon side. The binary compound RESi₂ (orthorhombic, α -GdSi₂-type) has been only observed for RE = Dy and Ho, while the high-temperature tetragonal form of the ThSi₂-type, reported in literature for Dy, Ho and Y, has never been obtained at 1270 K [6]. For the Si–B system, at the present time, the four phases SiB_x (<3 at% Si), SiB_n with 14 < n < 32, SiB_6 and SiB₃ have been found [19]. The crystallographic data for all the binary phases encountered at 1270 K during our studies on the RE-Si-B systems (RE = Dy, Ho, Er and Y) are reported in Table 1.

During our investigations, a lot of single crystals were isolated by crushing the solidified samples, which were tested for structure refinement. Due to the absence of precise structural data in literature so far, single crystal intensity data for the binary compounds RE₅Si₄ and RESi, for RE = Dy and Ho, were collected at ambient temperature. Thus, the crystal structures of Dy₅Si₄, Ho₅Si₄ (Sm₅Ge₄-type), the two polymorphic modifications of HoSi (high temperature FeB and low temperature CrB types) as well as that of DySi (CrB-type) were determined.

Every RE–Si–B phase diagram at 1270 K is generally characterized by the occurrence of three ternary phases: a line compound RE₅Si₂B₈, an interstitial phase RE₅Si₃B_x and a solid solution REB_{2-x}Si_x (Table 1). The line compound RE₅Si₂B₈ of Gd₅Si₂B₈-type structure exhibits an intergrown structure, which is formed by the stacking of ThB₄- and U₃Si₂-type slabs alternating along the c axis of the tetragonal lattice [3,20]. The crystal structures of all the RE₅Si₂B₈ phases (RE=Dy, Ho and Y) were recently reported [21]. On the contrary, no such phase could be synthesized with erbium under our experimental conditions.

The second phase $RE_5Si_3B_x$ results from boron insertion in the binary silicide RE_5Si_3 and belongs to the family of the wellknown Nowotny phases of Mn_5Si_3 -type structure [22,23]. In the ternary phase, boron atoms occupy the centres of octahedral sites generated by one part of the rare-earth metal atoms. From a structural point of view, the highest boron content within the hexagonal structure was found to be equal to x=0.64 for the prototypical compound $Gd_5Si_3B_x$ [3]. The decrease of the unit cell volume after insertion of boron in RE_5Si_3 is indicative of a somewhat stronger bonding between the interstitial boron and the surrounding rare-earth metal atoms. The crystal structures of the binary RE_5Si_3 and ternary $RE_5Si_3B_x$ phases together with their physical properties will be the subject of a forthcoming paper [24].



Fig. 1. Solid state phase equilibria in the ternary RE–Si–B system (RE = Dy, Y, Ho and Er) at 1270 K. Axes are in at%. Two-phase regions are dashed in grey.

The alloy $REB_{2-x}Si_x$ results from boron substitution by silicon in the diboride REB₂. The solid solution REB_{2-x}Si_x extends up to x=0.6 when RE=Ho and Er, while the x value has been found to be less, i.e. x = 0.15 when RE = Dy and Y. It is worth mentioning that the occurrence of the ternary phase RE₅Si₂B₈ is strongly related to the extent of the solid solution $REB_{2-x}Si_x$. Indeed, the ternary compound RE₅Si₂B₈ results from a peritectic reaction between the tetraboride REB₄ and a liquid of composition close to RE₅Si₃. When the solid solution is less extended, the tie-lines REB₄-RE₅Si₂B₈, $RE_5Si_2B_8$ -"RE_5Si_3" and $RE_5Si_2B_8$ -REB_{2-x}Si_x are present as it can be seen on the concentration profile of a bulk sample with atomic composition Dy/Si/B = 30/7/63, where the three phases, $Dy_5Si_2B_8$, $DyB_{2-x}Si_x$ and DyB_4 , are observed (Fig. 2). This is, however, not the case when the solid solution $\text{REB}_{2-x}\text{Si}_x$ is largely extended (RE=Ho and Er), and consequently the tie-line $\text{REB}_4-\text{RE}_5\text{Si}_2\text{B}_8$ disappears. Therefore, owing to the strong competition in the formation of both phases $\text{RE}_5\text{Si}_2\text{B}_8$ and $\text{REB}_{2-x}\text{Si}_x$, especially when x = 0.4, the line compound $\text{RE}_5\text{Si}_2\text{B}_8$ is extremely difficult to obtain. Hence,



Fig. 2. Concentration profile by WDS of a grain of $Dy_5Si_2B_8$ surrounded by grains of DyB_4 and $DyB_{2-x}Si_x$ (composition in at% Dy/Si/B = 30/7/63).

the temperature range for preparing the high-temperature phase $RE_5Si_2B_8$ (RE = Ho and Er) is probably restricted. The backscattered electron image of a sample with atomic composition Ho/Si/B = 27/8/65 as well as the corresponding concentration profile show the occurrence of only two phases, i.e. the binary HoB₄ and the substituted phase HoB_{2-x}Si_x (Fig. 3). In the same manner, on the silicon side, the concentration profile of a bulk

sample with atomic composition Ho/Si/B = 37.5/37.5/25 shows the thermodynamic equilibrium between HoB_{2-x}Si_x and the binary compounds HoSi and HoSi_{2-x} instead of the expected Ho₃Si₄ (Fig. 4). This result is consistent with the fact that this latter phase results from a sluggish peritectoidal reaction between HoSi and HoSi_{2-x} and needs a very long annealing time [7–9]. Since the HoB_{2-x}Si_x phase is largely extended, the ternary phase

Table 1 RE–Si–B constituent phases, crystal structure and lattices parameters for RE=Dy, Ho, Er and Y

| Phase | Type structure | Pearson symbol | Space group | RE | Lattice parameters (A) | | |
|---------------------|---------------------------------|----------------|----------------------|-------------------|------------------------|------------|-----------|
| | | | | | a | b | с |
| REB ₂ | AlB ₂ | hP3 | P6/mmm | Dy | 3.2902(3) | | 3.8472(4) |
| | | | | Но | 3.281(1) | | 3.816(1) |
| | | | | Er | 3.265(1) | | 3.770(1) |
| | | | | Y | 3.2875(6) | | 3.836(1) |
| REB ₄ | ThB_4 | tP20 | P4/mbm | Dy | 7.093(1) | | 4.010(1) |
| | | | | Но | 7.116(1) | | 4.024(1) |
| | | | | Er | 7.071(1) | | 3.991(1) |
| | | | | Y | 7.1023(5) | | 4.0179(5) |
| REB ₆ | CaB ₆ | cP7 | Pm3m | Dy | 4.0998(5) | | |
| | | | | Но | 4.116(1) | | |
| | | | | Y | 4.1016(2) | | |
| REB ₁₂ | UB_{12} | cF52 | Fm3m | Dy | 7.493(1) | | |
| | | | | Но | 7.5032(4) | | |
| | | | | Er | 7.4815(3) | | |
| | | | | Y | 7.5013(4) | | |
| REB ₆₆ | ThB ₆₆ | cF1880 | Fm3c | Dy | 23.381(4) | | |
| | | | | Ho | 23.365(4) | | |
| | | | | Er | 23.436(2) | | |
| | | | | Y | 23.390(3) | | |
| RE5Si3 | Mn ₅ Si ₃ | hP16 | P6 ₃ /mcm | Dy ^a | 8.3953(2) | | 6.3138(2) |
| | | | | Ho ^a | 8.3533(2) | | 6.2800(2) |
| | | | | Er | 8.297(1) | | 6.220(1) |
| | | | | Y ^a | 8.4096(4) | | 6.3437(3) |
| RE5Si4 | Sm5Ge4 | oP36 | Pnma | Dy ^a | 7.3673(3) | 14.5245(6) | 7.6616(3) |
| | | | | Ho ^a | 7.3406(2) | 14.4574(4) | 7.6264(2) |
| | | | | Er | 7.306(1) | 14.372(8) | 7.600(1) |
| | | | | Y | 7.499(3) | 14.763(5) | 7.751(3) |
| RESi | CrB | oC8 | Cmcm | Dy ^a | 4.2438(2) | 10.4857(6) | 3.8151(2) |
| | | | | Ho ^a | 4.2313(2) | 10.4474(5) | 3.8054(2) |
| | | | | Er | 4.196(1) | 10.380(2) | 3.786(1) |
| | | | | Y | 4.262(1) | 10.528(2) | 3.832(1) |
| RESi | FeB | oP8 | Pnma | Dy | 7.864(1) | 3.817(1) | 5.667(1) |
| | | | | Ho ^a | 7.8269(3) | 3.8045(2) | 5.6431(2) |
| | | | | Er | 7.870(4) | 3.800(2) | 5.648(3) |
| RE3Si4 | Ho ₃ Si ₄ | oC20 | Cmcm | Dy ^a | 4.2107(2) | 23.892(2) | 3.8144(2) |
| | | | | Ho | 4.181(1) | 23.719(6) | 3.792(1) |
| | | | | Er | 4.160(1) | 23.615(5) | 3.774(1) |
| | | | | Y | 4.200(3) | 23.838(9) | 3.819(2) |
| RESi _{2-x} | AlB ₂ | hP3 | P6/mmm | Dy | 3.8264(3) | | 4.1168(7) |
| | | | | Но | 3.801(1) | | 4.104(1) |
| | | | | Er | 3.7924(5) | | 4.083(1) |
| | | | | Y | 3.840(1) | | 4.142(1) |
| RESi ₂ | α -GdSi ₂ | oI12 | Imma | Dy | 4.029(1) | 3.932(1) | 13.317(2) |
| | | | | Но | 4.029(1) | 3.922(1) | 13.279(6) |
| $RE_5Si_2B_8$ | $Gd_5Si_2B_8$ | tP30 | P4/mbm | Dy ^a | 7.2209(2) | | 8.0545(3) |
| | | | | Ho ^{a,b} | 7.1830(2) | | 7.9900(3) |
| | | | | Y ^a | 7.2234(2) | | 8.0961(3) |

Table 1 (Continued)

| Phase | Type structure | Pearson symbol | Space group | RE | Lattice paramet | ers (Å) | |
|--|---------------------------------|----------------|----------------------|-----------------|-----------------|----------|------------|
| | | | | | a | b | с |
| RE ₅ Si ₃ B _x | Mn ₅ Si ₃ | hP16 | P6 ₃ /mcm | Dy ^a | 8.3675(2) | | 6.2594(2) |
| | | | | Ho ^a | 8.4033(4) | | 6.2392(2) |
| | | | | Er | 8.279(1) | | 6.198(1) |
| | | | | Y ^a | 8.4033(4) | | 6.3351(3) |
| $REB_{2-x}Si_x$ | AlB ₂ | hP3 | P6/mmm | Dy ^a | 3.3171(2) | | 3.8824(4) |
| | | | | Ho ^a | 3.4078(2) | | 3.9849(4) |
| | | | | Er | 3.392(1) | | 3.947(1) |
| | | | | Y | 3.305(1) | | 3.856(1) |
| SiB ₃ ^c | B ₆ P | hR14 | R3m | | 6.319(5) | | 12.713(10) |
| SiB ₆ ^c | SiB ₆ | oP280 | Pnnm | | 14.397(7) | 4.043(3) | 9.911(7) |
| SiB _n | Deriv. β-boron | - | R3m | | 11.0152(3) | | 23.8625(8) |

^a Lattice constants on single crystal counter data.

^b Synthesis by H.F. furnace at 1870 K for 3 h.

^c Lattice constants from Ref. [6].

Ho₅Si₂B₈ could never be synthesized, except under peculiar conditions, i.e. arc-melting followed by a subsequent annealing of the sample at 1870 K for 3 h with the help of a high frequency furnace (sample in an arc-welded sealed tantalum crucible under 0.5 atm of argon gas) and after that slowly cooling it down to room temperature. Unfortunately, for RE = Er, this procedure has not been crowned with success up to now. Consequently, one can conclude that the existence of the ternary phase RE₅Si₂B₈ for the heavier rare-earth metals (RE = Er \rightarrow Lu) is rather unlikely.

3.2. Crystal structures

3.2.1. Dy₅Si₄ and Ho₅Si₄

The binary compounds RE_5Si_4 (RE=Dy, Ho, Er and Y) have been previously reported in literature [6], to exhibit the



Fig. 3. Backscattered electron image of a sample with composition in at% Ho/Si/B = 27/8/65 showing the two phases HoB₄ (black) and HoB_{2-x}Si_x (grey) (a). The corresponding concentration profile by WDS is given in (b).

orthorhombic Sm₅Ge₄-type structure [25], but no precise atomic coordinates can be found so far, with the exception of the very recent paper by Mozharivskyj et al. on Er₅Si₄ [26]. The authors reveal a reversible first-order phase transition in this binary phase with a high-temperature phase adopting the orthorhombic Gd₅Si₄-type structure (closely related with the Sm₅Ge₄-type) [27] and a low-temperature phase with a monoclinic Gd₅Si₂Ge₂type structure [28]. The heat capacity and the magnetic susceptibility indicate a phase transition to occur between 205 and 235 K while heating the sample. Both the Gd₅Si₄₋ and Sm₅Ge₄-types are known to differ slightly in the atomic coordinates of metalloid atoms, but the shift is sufficient to modify in particular the coordination scheme of some Si(Ge) atoms [25,27]. Indeed, each Si atom in the structure of Gd₅Si₄ forms one covalent bond with another Si atom (Si-Si distances of 2.45-2.47 Å), in contrast to Sm₅Ge₄, where only half of the Ge atoms are covalently bonded to another Ge atom (Ge–Ge distance of 2.658 Å).

The crystal structure determination of Dy_5Si_4 and Ho_5Si_4 confirms their isotypy with the Gd_5Si_4 -type structure (Tables 2–4). Indeed, all Si atoms form Si–Si pairs with Si–Si distances of 2.52–2.53 Å. These distances are somewhat larger than those measured for Gd_5Si_4 , but remain acceptable for Si–Si single bonds (2.35 Å) [29]. The crystal structures of Dy_5Si_4 and Ho_5Si_4 can simply be considered as being built up from two 3D slabs alternating along the [0 1 0] direction (Fig. 5), the first one of U_3Si_2 -type while the second one is formed by rare-earth



Fig. 4. Concentration profile by WDS of a grain of $HoB_{2-x}Si_x$ surrounded by grains of HoSi and $HoSi_{2-x}$ (composition in at% Ho/Si/B = 37.5/37.5/25).

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Table 2 Crystal data, intensity collection and refinement for Dy₅Si₄ and Ho₅Si₄

| Empirical formula | Dy ₅ Si ₄ | Ho ₅ Si ₄ |
|--|---------------------------------|---------------------------------|
| Molecular weight | 924.85(1) | 937.00(1) |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | Pnma | Pnma |
| Unit cell dimensions | | |
| <i>a</i> (Å) | 7.3673(3) | 7.3406(2) |
| <i>b</i> (Å) | 14.5245(6) | 14.4574(4) |
| <i>c</i> (Å) | 7.6616(3) | 7.6264(2) |
| $V(Å^3)$ | 819.8(1) | 809.4(1) |
| Crystal size (mm ³) | $0.032 \times 0.010 \times$ | $0.070 \times 0.042 \times$ |
| • | 0.010 | 0.011 |
| Calculated density $(g \text{ cm}^{-3}); Z$ | 7.493; 4 | 7.690; 4 |
| Linear absorption coefficient (mm^{-1}) | 45.492 | 48.799 |
| θ range (°) | $3.8 \le \theta \le 27.5$ | $3.8 \le \theta \le 35$ |
| h | $-9 \le h \le 9$ | $-11 \le h \le 11$ |
| k | $-18 \leq k \leq 18$ | $-23 \le k \le 23$ |
| l | $-9 \le l \le 9$ | $-12 \le l \le 7$ |
| Refinement method | SHELXL; F^2 | SHELXL; F^2 |
| Reflections collected | 9589 | 12628 |
| Independent reflections; $R_{\rm int}$ | 971; 0.080 | 1822; 0.077 |
| Reflections in refinement $(I > 2\sigma(I))$ | 772 | 1374 |
| Number of variables | 47 | 47 |
| $R(I > 2\sigma(I)); wR_2$ | 0.025; 0.039 | 0.031; 0.041 |
| R (all data); wR_2 | 0.043; 0.042 | 0.056; 0.041 |
| Extinction coefficient | 0.00005(3) | 0.00008(2) |
| Goodness-of-fit on F^2 | 1.04 | 1.00 |
| $\Delta \rho$ (min, max) (e/Å ³) | -1.70/+1.96 | -2.60 / +2.97 |

trigonal prisms, separated by empty tetrahedral and "square" pyramidal sites. Within the trigonal prisms sharing a common face, the Si3 atoms form Si3–Si3 pairs, in addition to the Si1–Si2 pairs of the U₃Si₂ slab, with Si–Si distances of 2.52 Å.

Finally, the common structural character of all the binary silicides RE_5Si_4 suggests the assumption that a first-order phase transition might exist in these phases too, as observed for Er_5Si_4 [26].

3.2.2. DySi and HoSi

Single crystals of DySi (FeB-type) and HoSi in both modifications (CrB- and FeB-types) were studied (Table 5). Experi-

Table 3 Atomic positional and isotropic displacement parameters for Dy₅Si₄ and Ho₅Si₄

mentally, it is worth noting that both structure types have been found for the binary silicide HoSi in the same arc-melted buttons. That part of the button in contact with the water-cooled copper plate was quenched rapidly. It contained single crystals of the FeB-type while the slowly cooled part of the button showed single crystals of the CrB-type. It was then concluded that the FeB-type structure is indeed a high temperature modification and conversely that the CrB-type structure is a low temperature form, as previously mentioned in the literature. A general overview of the monosilicides RESi was proposed by Hohnke and Parthé [30]. They concluded that this polymorphism occurs in several RESi binaries (RE = Dy, Ho and Er), but no structural data on single crystals were proposed for both modifications of a same rare-earth monosilicide. We put forward that several of these monosilicides belonging to one or the other type were studied from X-ray powder diffraction data [31,32] and that only the single crystal structures of ErSi and YSi (CrB-type) were reported in the literature so far [33,34]. The atomic coordinates, displacement parameters and selected interatomic distances for DySi and HoSi are given in Tables 6 and 7.

The CrB- and the FeB-type structures are characterized by face-sharing metal trigonal prisms of AlB₂-type, which are packed in such a way that infinite prismatic rows centered by infinite zigzag chains of metalloid atoms are observed [35,36]. Both the CrB- and the FeB-types differ only in the way these rows are arranged with respect to each other (Fig. 6). The stacking variation and structural relationship between the FeB- and the CrB-types have been previously discussed in detail [30,37].

In the CrB-type structure, the rows of trigonal prisms develop parallel to the ac plane along the [001] direction, while along the *b* axis, two successive rows are translated each other from 1/2a, and separated by empty metal tetrahedra and "square" pyramids. In the more distorted FeB-type structure, the rows of trigonal prisms propagate infinitely along the [010] direction, but in two different orientations. Between two adjacent rows, empty metal tetrahedra and "square" pyramids are always present.

Comparison of both modifications indicates that there is no essential difference in the coordination number (CN) of the holmium and silicon atoms. Indeed, the Si atom is surrounded by seven Ho and two Si atoms corresponding to a tri-capped trigonal

| ritorine positional and isotropic displacement parameters for Dy3014 and H03014 | | | | | | |
|---|------|--------------|------------|------------|------------|--|
| Compound | Atom | Wyckoff site | x | у | Z | $U_{\rm eq}{}^{\rm a}$ (Å ²) |
| Dy ₅ Si ₄ | Dy1 | 4 <i>c</i> | 0.35015(8) | 1/4 | 0.01197(7) | 0.0077(2) |
| | Dy2 | 8d | 0.02453(5) | 0.09682(3) | 0.18126(5) | 0.0088(2) |
| | Dy3 | 8 <i>d</i> | 0.31928(5) | 0.87713(3) | 0.17915(5) | 0.0075(2) |
| | Si1 | 4 <i>c</i> | 0.2324(5) | 1/4 | 0.3732(4) | 0.0093(7) |
| | Si2 | 4c | 0.9768(5) | 1/4 | 0.8965(5) | 0.0094(7) |
| | Si3 | 8 <i>d</i> | 0.1495(3) | 0.9605(2) | 0.4713(3) | 0.0101(5) |
| Ho ₅ Si ₄ | Ho1 | 4c | 0.35003(5) | 1/4 | 0.01172(4) | 0.0072(1) |
| | Ho2 | 8 <i>d</i> | 0.02418(3) | 0.09652(2) | 0.18038(3) | 0.0087(1) |
| | Ho3 | 8 <i>d</i> | 0.31915(3) | 0.87722(2) | 0.17911(3) | 0.0074(1) |
| | Si1 | 4c | 0.2315(3) | 1/4 | 0.3719(3) | 0.0078(4) |
| | Si2 | 4 <i>c</i> | 0.9775(3) | 1/4 | 0.8956(3) | 0.0088(4) |
| | Si3 | 8d | 0.1499(2) | 0.9603(1) | 0.4713(2) | 0.0090(3) |
| | | | | | | |

^a $U_{eq} = \exp[-2\pi^2 (h^2 a^{*2} U_{11} + \dots + 2klb^* c^* U_{23})].$

| Table 4 Selected inter | ratomic distances (Å) | for Dy ₅ Si ₄ and Ho ₅ Si ₄ | |
|---------------------------|-----------------------|---|--|
| At #1 | At #2 | DysSi4 | |

| At. #1 | At. #2 | Dy ₅ Si ₄ | Ho ₅ Si ₄ | At. #1 | At. #2 | Dy ₅ Si ₄ | Ho ₅ Si ₄ |
|--------|--------|---------------------------------|---------------------------------|--------|--------|---------------------------------|---------------------------------|
| Si1 | 1Si2 | 2.521(5) | 2.531(3) | RE1 | 2RE2 | 3.482(1) | 3.476(1) |
| | 1RE1 | 2.901(3) | 2.881(2) | | 2RE2 | 3.520(1) | 3.507(1) |
| | 1RE1 | 2.950(3) | 2.937(2) | RE2 | 1Si3 | 3.009(2) | 2.991(2) |
| | 2RE3 | 3.008(3) | 3.002(2) | | 1Si3 | 3.070(2) | 3.060(2) |
| | 2RE2 | 3.075(2) | 3.062(2) | | 1Si3 | 3.115(2) | 3.107(2) |
| | 2RE2 | 3.123(2) | 3.114(3) | | 1Si1 | 3.075(2) | 3.062(2) |
| Si2 | 1Si1 | 2.521(5) | 2.531(3) | | 1Si1 | 3.123(2) | 3.114(2) |
| | 1RE1 | 2.889(4) | 2.874(2) | | 1Si2 | 3.136(2) | 3.124(2) |
| | 2RE3 | 2.905(3) | 2.887(2) | | 1RE1 | 3.482(1) | 3.475(1) |
| | 2RE3 | 2.916(3) | 2.907(2) | | 1RE1 | 3.520(1) | 3.507(1) |
| | 2RE2 | 3.136(2) | 3.124(2) | | 1RE3 | 3.690(1) | 3.670(1) |
| | 1RE1 | 3.266(3) | 3.244(2) | | 1RE3 | 3.766(1) | 3.743(1) |
| Si3 | 1Si3 | 2.522(5) | 2.520(3) | | 2RE2 | 3.831(1) | 3.821(2) |
| | 1RE3 | 2.836(2) | 2.820(2) | | 1RE3 | 3.860(1) | 3.839(1) |
| | 1RE3 | 2.855(2) | 2.843(2) | RE3 | 1Si3 | 2.836(2) | 2.820(2) |
| | 1RE3 | 2.952(3) | 2.942(2) | | 1Si3 | 2.855(3) | 2.843(2) |
| | 1RE2 | 3.009(2) | 2.991(2) | | 1Si2 | 2.905(3) | 2.887(2) |
| | 1RE2 | 3.070(2) | 3.060(2) | | 1Si2 | 2.916(3) | 2.907(2) |
| | 1RE1 | 3.074(2) | 3.056(2) | | 1Si3 | 2.952(3) | 2.942(2) |
| | 1RE2 | 3.115(2) | 3.107(2) | | 1Si1 | 3.008(3) | 3.002(2) |
| RE1 | 1Si1 | 2.901(3) | 2.881(2) | | 1RE1 | 3.387(1) | 3.371(1) |
| | 1Si2 | 2.889(4) | 2.874(2) | | 1RE1 | 3.389(1) | 3.376(1) |
| | 1Si1 | 2.950(3) | 2.937(2) | | 1RE2 | 3.690(1) | 3.670(1) |
| | 2Si3 | 3.074(2) | 3.056(2) | | 1RE3 | 3.693(1) | 3.679(1) |
| | 1Si2 | 3.266(3) | 3.244(2) | | 1RE2 | 3.766(1) | 3.743(1) |
| | 2RE3 | 3.389(1) | 3.371(1) | | 1RE2 | 3.860(1) | 3.839(1) |
| | 2RE3 | 3.387(1) | 3.376(1) | | 1RE3 | 3.840(1) | 3.826(2) |



Fig. 5. Representation of the structure RE_5Si_4 (RE = Dy and Ho) of Sm_5Ge_4 - (or Gd_5Si_4 -) type. The two successive 3D slabs (right) are given in projection on the *ac* plane. The body-centered cubes and empty pyramids and tetrahedra formed by the RE atoms are emphasized.

Table 5

Crystal data, intensity collection and refinement for DySi and HoSi

| Empirical formula | DySi | HoSi | HoSi |
|--|-----------------------------------|-----------------------------------|--------------------------------|
| Molecular weight | 190.59(1) | 193.02(1) | 193.02(1) |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | Cmcm | Cmcm | Pnma |
| Structural type | CrB | CrB | FeB |
| Unit cell dimensions | | | |
| <i>a</i> (Å) | 4.2438(2) | 4.2313(2) | 7.8269(3) |
| <i>b</i> (Å) | 10.4857(6) | 10.4474(5) | 3.8045(2) |
| c (Å) | 3.8151(2) | 3.8054(2) | 5.6431(2) |
| $V(Å^3)$ | 169.77(2) | 168.22(2) | 168.04(2) |
| Crystal size (mm ³) | $0.030 \times 0.026 \times 0.011$ | $0.054 \times 0.024 \times 0.018$ | $0.04 \times 0.03 \times 0.02$ |
| Calculated density $(g cm^{-3}); Z$ | 7.456; 4 | 7.620; 4 | 7.630; 4 |
| Linear absorption coefficient (mm^{-1}) | 44.084 | 47.156 | 47.156 |
| Absorption method | Analytical | Analytical | Analytical |
| (T_{\min}, T_{\max}) | 0.3903; 0.6348 | 0.1567; 0.3884 | 0.2895; 0.4876 |
| θ range (°) | $3.9 \le \theta \le 42$ | $3.9 \le \theta \le 40$ | $4.4 \le \theta \le 40$ |
| h | $-7 \le h \le 5$ | $-7 \le h \le 5$ | $-12 \le h \le 14$ |
| k | $-18 \le k \le 19$ | $-16 \le k \le 18$ | $-6 \le k \le 6$ |
| l | $-7 \leq l \leq 7$ | $-6 \le l \le 5$ | $-9 \le l \le 10$ |
| Refinement method | SHELXL; F^2 | SHELXL; F^2 | SHELXL; F^2 |
| Reflections collected | 2077 | 1847 | 4096 |
| Independent reflections; R _{int} | 358; 0.035 | 315; 0.025 | 575; 0.030 |
| Reflections in refinement $(I > 2\sigma(I))$ | 340 | 304 | 511 |
| Number of variables | 10 | 10 | 14 |
| $R(I > 2\sigma(I)); wR_2$ | 0.016; 0.034 | 0.013; 0.030 | 0.014; 0.021 |
| R (all data); wR_2 | 0.019; 0.034 | 0.014; 0.030 | 0.020; 0.021 |
| Extinction coefficient | 0.0027(5) | 0.0072(7) | 0.0075(3) |
| Goodness-of-fit on F^2 | 1.03 | 1.04 | 1.06 |
| $\Delta \rho$ (min, max) (e/Å ³) | -1.56/+1.76 | -2.94/+1.85 | -1.38/+1.84 |

prismatic polyhedron, while the Ho atom, although CN = 15 for both forms (8Ho + 7Si), presents a somewhat different coordination polyhedron stemming from the shift of one Si atom (Fig. 7). Nevertheless, all the Si atoms form zigzag chains with similar single bond Si–Si distances of 2.48–2.49 Å in both structural variants. The corresponding bonding angles within the zigzag chains for HoSi are quite identical, i.e. 99.6° for the CrB and 100.2° for the FeB-type (Table 7).

From a theoretical point of view, it was mentioned that the FeB-type compounds have a higher valence electron concentration (VEC) than the CrB-type ones [34]. The electron population of the 4f- and 5d-transition shells of the rare-earth metals should have an influence on the occurrence of either one or another of these structural modifications. To confirm this hypothesis, theoretical calculations for both modifications of HoSi are currently in progress [38].

3.2.3. $DyB_{2-x}Si_x$ and $HoB_{2-x}Si_x$

The structure determination of the substituted phases $DyB_{2-x}Si_x$ and $HoB_{2-x}Si_x$, for the silicon-rich limit, were also solved on single crystals (Tables 8 and 9). The highest silicon content has been found to be 5 at% for the Dy- and 20 at% for the Ho-containing alloys. This value is also in good accord with the experimental analyses on bulk samples by WDS (Figs. 2–4). In the previous results by Chaban et al., the silicon content on bulk samples prepared at 1070 K were found to be less than 5 at% for the Er- and 2 at% for the Y-ternary alloys [1,2]. Our structural results on ternary phases $DyB_{1.85}Si_{0.15}$ and $HoB_{1.40}Si_{0.60}$ confirm isotypism with the AlB₂-type structure [39]. No defects on the metalloid substructure were observed and the silicon atoms substitute the boron ones in a randomly disordered manner. One can see in Fig. 8 that the unit cell parameters increase with the Si content, in agreement with the respective covalent radius of Si

| Table 6 |
|--|
| Atomic positional and isotropic displacement parameters for DySi and HoS |

| Compound | Atom | Wyckoff site | x | у | Z | $U_{\rm eq}{}^{\rm a}$ (Å ²) |
|-----------------|------|--------------|-----------|-----------|-----------|--|
| DySi (CrB-type) | Dy | 4 <i>c</i> | 0 | 0.1409(1) | 1/4 | 0.0057(1) |
| | Si | 4c | 0 | 0.4234(1) | 1/4 | 0.0067(2) |
| HoSi (CrB-type) | Но | 4c | 0 | 0.1409(1) | 1/4 | 0.0053(1) |
| | Si | 4c | 0 | 0.4230(1) | 1/4 | 0.0061(2) |
| HoSi (FeB-type) | Но | 4 <i>c</i> | 0.3209(1) | 1/4 | 0.3851(1) | 0.0052(1) |
| | Si | 4 <i>c</i> | 0.4616(1) | 1/4 | 0.8695(2) | 0.0061(2) |

^a $U_{eq} = \exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})].$

Table 7 Selected interatomic distances (Å) and angles (°) for DySi and HoSi

| At. #1 | At. #2 | DySi (CrB-type) | HoSi (CrB-type) | At. #1 | At. #2 | HoSi (FeB-type) |
|----------|--------|-----------------|-----------------|--------|--------|-----------------|
| Si | 2Si | 2.494(1) | 2.492(2) | Si | 2Si | 2.480(1) |
| | 4RE | 2.932(1) | 2.923(1) | | 2Ho | 2.918(1) |
| | 1RE | 2.963(1) | 3.947(1) | | 2Ho | 2.929(1) |
| | 2RE | 3.115(1) | 3.107(1) | | 1Ho | 2.947(1) |
| RE | 4Si | 2.932(1) | 2.923(1) | | 1Ho | 3.111(1) |
| | 1Si | 2.963(1) | 2.947(1) | | 1Ho | 3.135(1) |
| | 2Si | 3.115(1) | 3.107(1) | Но | 2Si | 2.918(1) |
| | 2RE | 3.517(1) | 3.505(1) | | 2Si | 2.929(1) |
| | 4RE | 3.658(1) | 3.647(1) | | 1Si | 2.947(1) |
| | 2RE | 3.815(1) | 3.805(1) | | 1Si | 3.111(1) |
| | | | | | 1Si | 3.135(1) |
| | | | | | 4Ho | 3.580(1) |
| | | | | | 2Ho | 3.628(1) |
| | | | | | 2Ho | 3.805(1) |
| Si–Si–Si | | 99.80(3) | 99.59(3) | | | 100.2(1) |

(1.17 Å) and B (0.87 Å) [29]. The average metalloid–metalloid distances of 1.92 Å (Dy) and 1.97 Å (Ho) are well comprised between those of HoB₂ (1.89 Å) and HoSi_{2-x}, $x \sim 0.4$, (2.24 Å), both adopting the AlB₂-type structure. In the metalloid substructure, each atom adopts a sp²-type coordination mode with respect to the bonding angles of 120°.

3.3. Magnetic properties

The magnetic susceptibilities for the phases $\text{REB}_{2-x}\text{Si}_x$ (RE = Dy and Ho) have been measured in a moderate external field B = 0.1 T in the temperature range T = 2-300 K. All samples were polluted with traces of secondary phases, so in single field measurements the influence of impurities cannot be excluded (Honda–Owen plot) [40]. Thus, the derived values for the effective moments vary slightly from the ideal tri-positive ion moment $\mu_{\text{eff}} = 10.6 \,\mu_{\text{B}}$ for either compound, but are still within the errors. Since the results of the paramagnetic regime were considered of minor interest in our study, we just present the data of μ_{eff} and θ_{p} in Table 10, as calculated.

3.3.1. The solid solution $DyB_{2-x}Si_x$

In Fig. 9, the magnetization M(T) curves for the three compounds with x values equal to 0, 0.09 and 0.15 are presented in increasing and decreasing temperatures. Silicon substitution for boron has indeed a remarkable influence on the magnetic behaviour in the ordered state. The ordering temperatures $T_{\rm C}$ decrease slightly with increasing x (Table 10). However, we observe a pronounced influence on the magneto-crystalline anisotropy. The M(T) plots for the zero field cooled samples (zfc) resemble the typical shape of narrow domain wall ferromagnets. The origin of the presence of narrow walls is a high magneto-crystalline anisotropy energy resulting from crystal field interactions of rare-earth moments containing an orbital contribution, comparable in magnitude with the magnetic coupling energy [42]. The magnetization values increase by thermal activation of wall movement, pass through maxima or plateaus and decrease near the ordering temperatures (Figs. 9b and c). Measurements of M(T) in decreasing temperatures (field cooled, fc) hence result in a much higher net magnetization at the lowest temperature (2 K).



Fig. 6. Representation of the structure RESi (Dy and Ho) of CrB-type (a) and HoSi of FeB-type (b). The rows of infinite silicon zigzag chains are emphasized.

Table 8 Crystal data, intensity collection and refinement for $DyB_{2-x}Si_x$ and $HoB_{2-x}Si_x$

| , | | |
|---|-----------------------------------|-----------------------------------|
| Empirical formula | $DyB_{2-x}Si_x$ (x = 0.15) | $HoB_{2-x}Si_x$ (x = 0.60) |
| Molecular weight | 186.89(1) | 196.92(1) |
| Crystal system | Hexagonal | Hexagonal |
| Space group | P6/mmm | P6/mmm |
| Unit cell dimensions | | |
| <i>a</i> (Å) | 3.3171(2) | 3.4078(2) |
| c (Å) | 3.8824(4) | 3.9849(4) |
| $V(Å^3)$ | 36.995(5) | 40.077(5) |
| Crystal size (mm ³) | $0.045 \times 0.032 \times 0.007$ | $0.025 \times 0.020 \times 0.012$ |
| Calculated density $(g cm^{-3}); Z$ | 9.525; 1 | 8.893; 1 |
| Linear absorption coefficient (mm ⁻¹) | 50.610 | 49.463 |
| Absorption method | Analytical | _ |
| (T_{\min}, T_{\max}) | 0.0011; 0.0203 | _ |
| θ range (°) | $5.2 \le \theta \le 36.6$ | $6.9 \le \theta \le 39.6$ |
| h | $-3 \le h \le 5$ | $-6 \le h \le 3$ |
| k | $-5 \le k \le 5$ | $-6 \le k \le 6$ |
| 1 | $-6 \leq l \leq 6$ | $-7 \leq l \leq 7$ |
| Refinement method | SHELXL; F^2 | SHELXL; F^2 |
| Reflections collected | 630 | 648 |
| Independent reflections; R _{int} | 58; 0.052 | 73; 0.032 |
| Reflections in refinement $(I > 2\sigma(I))$ | 58 | 73 |
| Number of variables | 7 | 7 |
| $R(I > 2\sigma(I)); wR_2$ | 0.016; 0.036 | 0.007; 0.016 |
| R (all data); wR_2 | 0.016; 0.036 | 0.007; 0.016 |
| Extinction coefficient | 0.16(3) | 0.28(2) |
| Goodness-of-fit on F^2 | 1.02 | 1.09 |
| $\Delta \rho (\min, \max) (e/Å^3)$ | -1.92/+1.06 | -0.92/+0.86 |
| | | |

The enhancement of the magneto-crystalline anisotropy is also evidenced in the isothermal magnetization M(B) curves at 5 K from insets of Fig. 9. The hysteresis loop becomes more open with increasing x. Hence, the remnant magnetization, M_r , and the coercive (critical) field increase with x, whereas the values of the saturation moment decrease (Table 10). The energy product $(B \cdot H)$ and consequently the magnetic hardness improves with silicon content.



Fig. 7. Coordination polyhedra for the Si (black) and RE (white) atoms in the CrB- (a) and FeB-type (b) structures.

3.3.2. The solid solution $HoB_{2-x}Si_x$

HoB₂ is a simple ferromagnet at $T_{\rm C} = 15-20$ K [42]. The zfc sample magnetization versus temperature passes a maximum whereas the fc magnetization remains constant below $T_{\rm C}$ as shown in Fig. 10a. The domain wall thickness is obviously large, which leads to a narrow hysteresis loop and a small remnant magnetization as it can be seen in the inset of Fig. 10a and Table 10.

Table 9

Atomic positional, displacement parameters and selected interatomic distances (Å) for $DyB_{2-x}Si_x$ and $HoB_{2-x}Si_x$

| | | $DyB_{2-x}Si_x (x=0.15)$ | $HoB_{2-x}Si_x$ (x=0.60) |
|-------|------------------------|--------------------------|--------------------------|
| RE | x | 0 | 0 |
| 1a | у | 0 | 0 |
| | z | 0 | 0 |
| | $U_{\rm eq}{}^{\rm a}$ | 0.0072(3) | 0.0051(1) |
| B, Si | x | 1/3 | 1/3 |
| 2b | у | 2/3 | 2/3 |
| | z | 1/2 | 1/2 |
| | $U_{eq}{}^{a}$ | 0.010(2) | 0.009(1) |
| | τ^{b} | 0.92(3) | 0.70(2) |
| RE | 12B, Si | 2.7269(2) | 2.8002(2) |
| | 6RE | 3.3171(2) | 3.4078(2) |
| | 2RE | 3.8824(4) | 3.9849(4) |
| B, Si | 3B, Si | 1.9151(2) | 1.9675(1) |
| | 6RE | 2.7269(2) | 2.8002(2) |

^a $U_{eq} = \exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})].$

^b Boron content in the mixed position (B, Si).

| Table 10 | |
|-----------------------------------|--|
| Magnetic data for the compounds R | EB_2 and $REB_{2-x}Si_x$ (RE = Dy, Ho) |

| Compound | $\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}}\right)$ | $\theta_{\rm p}~({\rm K})$ | <i>T</i> _C (K) | $T_{\rm N}$ (K) | $\mu_{\mathrm{S}}\left(\mu_{\mathrm{B}}\right)$ | $M_{\rm r}~({\rm Am^2/kg})$ | $B_{\rm crit.}$ (T) | Ref. |
|--|---|----------------------------|---------------------------|-----------------|---|-----------------------------|---------------------|---------|
| DyB ₂ | 10.7 | 33 | 55 | _ | 5.4 | _ | _ | [41,42] |
| | 11.3 ^a | 14 | 55 | - | 7.9 | 10.4 | 0.05 | b |
| DyB _{1.91} Si _{0.09} | 10.1 ^a | 40 | 52 | _ | 6.7 | 20.0 | 0.10 | b |
| DyB _{1.85} Si _{0.15} | 10.5 ^a | 34 | 49 | - | 6.1 | 22.1 | 0.20 | b |
| HoB ₂ | 10.2 | 25 | 15 | _ | 7.5 | _ | _ | [41,42] |
| | 11.2 ^a | 30 | 20 | - | 8.5 | 8.9 | 0.05 | b |
| HoB _{1.4} Si _{0.6} | 10.6 ^a | -6.4 | _ | 12 | 6.0 | 0 | - | b |

^a Data not corrected for impurities.

^b This work.



Fig. 8. Variations of the unit cell constants as a function of *x* in the substitution solid solution $HoB_{2-x}Si_x$.

Silicon substitution in the diboride has a dramatic consequence for the magnetic behaviour (Fig. 10b). As both zfc and fc M(T) plots pass a maximum, we suggest that HoB_{1.4}Si_{0.6} is an antiferromagnet at a Néel temperature $T_{\rm N} = 12$ K. This finding corroborates with a negative value of $\theta_{\rm p}$. Looking at the isothermal magnetization M(B) curve at T=5 K (inset of Fig. 10b), a linear field dependence up to about B=1.5 T is observed, which is then followed by a metamagnetic-like transition and finally M(B) tends to saturate in high fields. The value of the saturation moment is reduced when compared with the one of the pure binary compound (Table 10). Furthermore, the magnetization is fully reversible in decreasing field which proves that HoB_{1.4}Si_{0.6} is indeed a metamagnet. A similar alteration



Fig. 9. Magnetization versus temperature in applied field B = 0.1 T for DyB₂ (a), DyB_{1.91}Si_{0.09} (b) and DyB_{1.85}Si_{0.15} (c) (open circles, zfc and filled symbols, fc). *Inset:* Isothermal magnetization versus external field (open circles, field up and filled symbols, field down).



Fig. 10. Magnetization versus temperature in applied field B = 0.1 T for HoB₂ (a) and HoB_{1.4}Si_{0.6} (b) (open circles, zfc and filled symbols, fc). *Inset*: Isothermal magnetization versus external field (open circles, field up and filled symbols, field down).

of magnetic ordering was previously reported for $Ho_3C_{4-x}B_x$ (*x* < 0.8), but boron insertion in this case changes the pure binary antiferromagnetic carbide into a ferromagnetic compound [43].

4. Conclusion

The solid state phase equilibria in the ternary RE-Si-B diagrams (RE = Dy, Ho, Er and Y), determined at 1270 K, show the occurrence of three ternary phases: a line compound RE₅Si₂B₈, not found at present with RE = Er, a boron-inserted Nowotny phase $RE_5Si_3B_x$ and a substitution phase $REB_{2-x}Si_x$. The binary phases that form the boundary of each diagram have also been reinvestigated. The crystal structures of RE₅Si₄ (Sm₅Ge₄-type), DySi (CrB-type) and HoSi in the two polymorphic modifications (FeB- and CrB-types), as well as the alloys within the silicon-rich limits of the solid solution $REB_{2-x}Si_x$ with the AlB_2 -type (RE = Dy and Ho) have been determined. Besides, it has been demonstrated that the occurrence of the compound RE₅Si₂B₈ is strongly depending on the extent of the solid solution $\text{REB}_{2-x}\text{Si}_x$. Finally, magnetic measurements on the substitution phases $REB_{2-x}Si_x$ lead to a marked increase of the magneto-crystalline anisotropy with RE = Dy with increasing silicon content, whereas a change from ferromagnetic to antiferromagnetic behaviour is observed in the solid solution $HoB_{2-x}Si_x$.

Acknowledgments

The authors acknowledge support from the Austrian (ÖAD)—French (MAE) Amadeus exchange program under projects 9/2005 (Austria) and 08940YH (France). They also thank J. Bauer for fruitful discussions, T. Roisnel (CDIFX, Université de Rennes 1) for X-ray intensity data collection, as well as J. Le Lannic (CMEBA, Université de Rennes 1), and M. Bohn (IFREMER, Brest) for their assistance in SEM and EPMA studies.

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