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Crystal structure of the compound $DyGe_3$*

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Abstract

Earlier investigations had indicated the presence of rare earth germanium compounds of a composition RGe_x with x close to 3 of unknown structure. Neutron diffraction data obtained on the corresponding dysprosium compound show that the stoichiometry is $DyGe_3$. This compound crystallizes in a novel type of structure related to the CrB structure type. The structure is orthorhombic and comprises one dysprosium site and three germanium sites. It can be thought to be built up from DyGe by inserting slabs of trigonal prisms consisting of germanium atoms into the CrB type unit cell of DyGe.

1. Introduction

Several previous studies of rare earth (R) and germanium binary systems have shown that the compound richest in germanium has a composition close to RGe_3 [1, 2]. Schmidt *et al.* [1] reported the occurrence of a compound of the composition $YGe_{3.5}$ and indexed their single-crystal X-ray data on the basis of an orthorhombic unit cell, but did not determine the crystal structure. The same type of indexing was also used for various germanium-rich rare-earth compounds by Eremenko *et al.* [2], although the composition of these latter authors was given as $RGe_{2.7}$. In the present study we have chosen the Dy–Ge system to determine the exact composition and the crystal structure of the germanium-rich $RGe_{\sim 3}$ phases.

2. Experimental procedures

Samples of the composition $DyGe_3$ and $DyGe_{3.5}$ were prepared by arc-melting of the appropriate amount of dysprosium and germanium in an atmosphere of purified argon gas. The purity of the starting materials was 99.9% for dysprosium and 99.99% for germanium. After arc-melting the

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samples were vacuum-annealed at 800 °C for 7 weeks. After annealing the samples were powdered and examined by standard X-ray diffraction using Cu Kα radiation at room temperature. The X-ray diagram of the sample $DyGe_{3.5}$ was found to contain the diffraction lines of elemental germanium of substantial intensity. For this reason this sample was discarded for further examination.

Neutron diffraction of $DyGe_3$ was performed on a powdered sample in the paramagnetic state at 30 K with the double axis multicounter system (DMC) at the Reactor Saphir, Wuerenlingen, using the wavelength $\lambda = 1.7059$ Å, and applying the high-intensity mode [3]. The step increment of the diffraction angle 2θ was 0.10°. The data were corrected for absorption and evaluated by the Rietveld line profile analysis method [4, 5]. The scattering lengths used for dysprosium and germanium were taken from ref. 6.

3. Results and discussion

It proved possible to index the powder pattern obtained by X-ray diffraction on the basis of an orthorhombic unit cell with $a = 0.4042$ nm, $b = 2.720$ nm, $c = 0.3919$ nm. This indexing corresponds closely to those reported for $RGe_{\sim 3}$ in refs. 1 and 2. Systematic extinctions suggested space group Cmcm (number 63). A computer program [7] was used to find a trial structure. Subsequent refinement led to a reliability factor equal to 10%. The refined parameters are listed in Table 1.

Figure 1 shows the neutron data obtained at 30 K, which were used for the refinement of the nuclear structure. All diffraction lines observed were indexed with the same orthorhombic C-centred cell as found from the X-ray data. Contrary to the findings for $YGe_{3.5}$ [1] the $DyGe_3$ powder patterns

TABLE 1

Refined parameters from the 30 K (nuclear data) compared with the X-ray data at 293 K of $DyGe_3$

Atom	30 K neutron		293 K X-ray
	x	y	y
Dy	0.0	0.4179(1)	0.4161
Ge(1)	0.0	0.0380(3)	0.0375
Ge(2)	0.5	0.1916(2)	0.1970
Ge(3)	0.5	0.3095(3)	0.3044
a(nm)	0.40278(5)		0.4042(2)
b(nm)	2.0710(3)		2.072(1)
c(nm)	0.38997(5)		0.3919(2)
B_{of} (Å^2)	0.54(3)		
R_n, R_{wp}, R_{exp} (%), χ^2	8.5, 14.3, 9.5, 2.28		10

Space group Cmcm (No. 63) all atoms at 4c (0, y, 1/4)

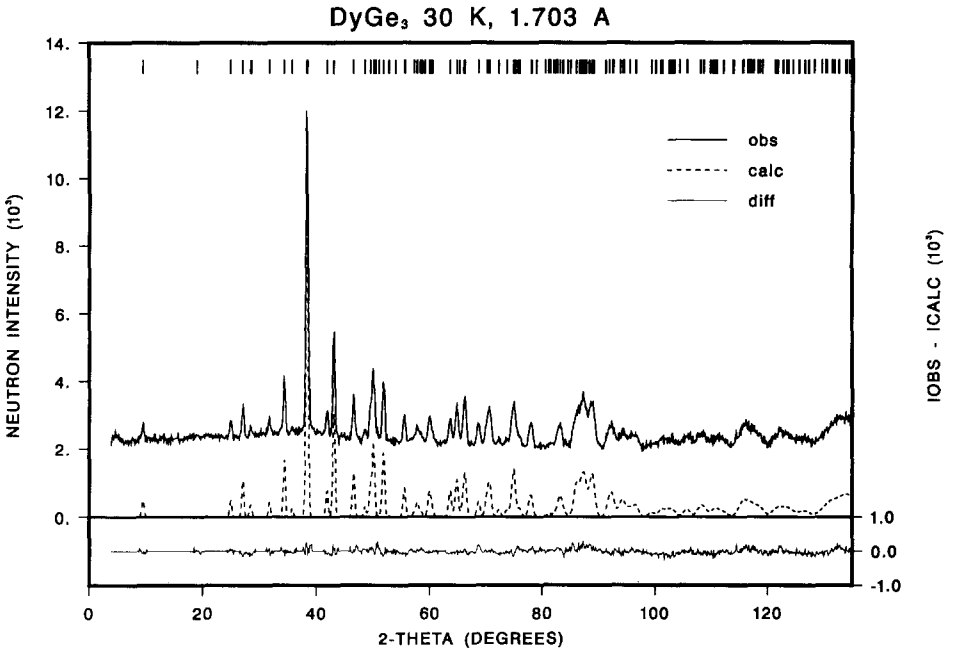

Fig. 1. Observed (solid line) and calculated (broken line) neutron diffraction pattern of the compound $DyGe_3$ at 30 K.

TABLE 2

Interatomic distances in the $DyGe_3$ compound from the 30 K neutron data

Atom coordination		Distance (Å)	Atom coordination		Distance (Å)
Dy	–4Ge(1)	2.948(2)		–2Dy	3.200(5)
(10)	–2Ge(2)	2.990(5)			
	–2Ge(3)	3.016(5)	Ge(2)	–1Ge(3)	2.442(8)
	–2Ge(1)	3.200(5)	(7)	–4Ge(3)	2.803(1)
				–2Dy	2.990(5)
Dy	–2Dy	3.900(1)			
(6)	–2Dy	3.920(4)	Ge(3)	–1Ge(2)	2.442(8)
	–2Dy	4.028(1)	(7)	–4Ge(2)	2.803(1)
				–2Dy	3.016(5)
Ge(1)	–2Ge(1)	2.505(5)			
(8)	–4Dy	2.948(2)			

do not contain within experimental error any additional lines indicating the existence of a superstructure demanding quadrupling of the *c*-axis and eventually an increase also of the *b*-axis. Most probably the corresponding satellites are not detectable from the background. The refined parameters are included in Table 1 where they can be compared with the parameters obtained from the refinement of the X-ray data.

The interatomic distances occurring in the structure of $DyGe_3$ are listed in Table 2. A schematic representation of its unit cell is displayed in Fig. 2. It may be inferred from Fig. 2 that the crystal structure of $DyGe_3$ can be thought to be built up from layers of double trigonal prisms of rare earth atoms centred by germanium atoms, the axis of these prisms being oriented along the a direction. The layers of the trigonal prisms mentioned are parallel to the (a, c) plane. They are sandwiched between layers of trigonal prisms consisting exclusively of germanium atoms. These latter prisms have their axis along the b direction.

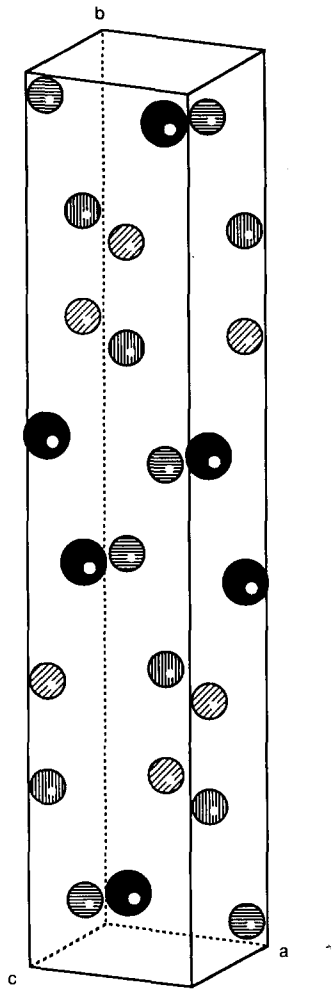

Fig. 2. Schematic representation of the unit cell of $DyGe_3$. The dysprosium atoms are represented by the larger black circles. The smaller circles represent the germanium atoms, the three types of different shading indicating the three different crystallographic germanium positions.

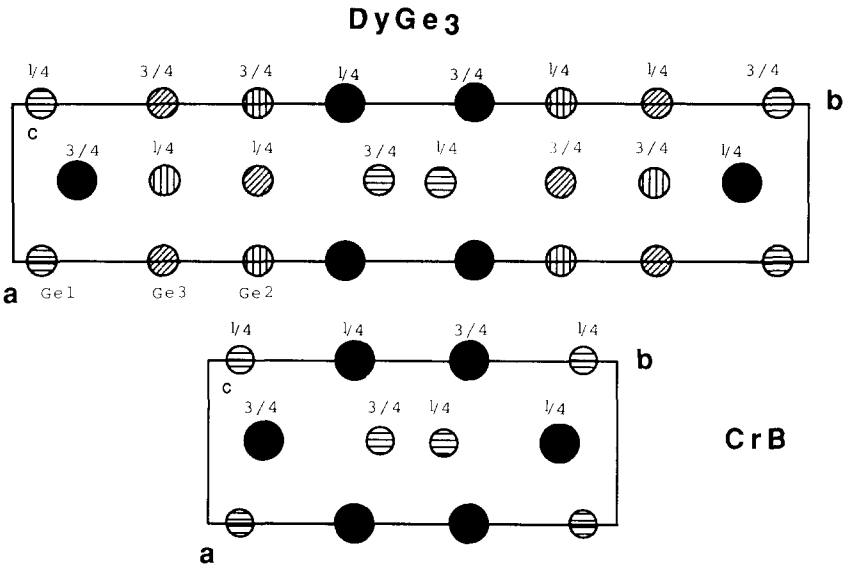

Fig. 3. Unit cell projection on the (001) plane of the $DyGe_3$ type (left) and the CrB type (right).

The trigonal prisms of rare-earth atoms centred by germanium atoms can be regarded as building blocks favoured by other structures adopted by rare earth germanium compounds. Most obvious examples are the CrB structure found for most RGe compounds [8, 9] and the a-$ThSi_2$ structure encountered in RGe_2 compounds for light rare earth elements [10]. The structural relation of $DyGe_3$ with CrB type compounds can conveniently be illustrated by means of the corresponding unit cell projections on the (001) planes. This is shown in Fig. 3 where the top part projection pertains to the presently described structure of $DyGe_3$. The bottom part projection refers to the CrB type structure found, for instance for DyGe. It is fairly easily seen that the former structure can be derived from the latter by inserting the layers of trigonal prisms referred to above that are exclusively formed by germanium atoms.

Preliminary investigations have shown that the $DyGe_3$ structure is adopted also by several other rare earth elements, although its occurrence does not extend across the whole rare earth series. A more detailed investigation as to the occurrence of this structure type and the concomitant magnetic properties is in progress.

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