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Competing magnetic structures in the DySi FeB-type phase diagram

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ABSTRACT

The temperature magnetic phase diagrams, of the dimorphic DySi compound, have been studied in terms of wave vectors in the range 1.5–45 K, by neutron diffraction. The polycrystalline sample consists of 26% of CrB-type (*Cmcm* no. 63, all atoms at 4c site: (0, *y*, 1/4)) and of 74% of FeB-type (*Pnma* no. 62, all atoms at 4c site: (*x*, 1/4, *z*)). The CrB-ordering is described by the wave vector: $\boldsymbol{q}_1$=(0, 0, 1/2) over the entire magnetically ordered regime with a uniaxial magnetic structure along the shortest axis *c*. The FeB-type magnetic phase diagram reveals three distinct regions of magnetic ordering below T_N and one first order transition at T_2=23.5 K (on heating). The ordering is described by two symmetry independent magnetic vectors $\boldsymbol{q}_2$=(0, 1/2, 1/6) and $\boldsymbol{q}_3$=(0, q_{3y}, q_{3z}) with a temperature variable length. At 1.5 K $q_{3y}\approx 1/2$ and $q_{3z}\approx 1/11$. The two phases coexist in the form of domains. They differ in the moment orientation of the $\boldsymbol{q}_3$ phase that deviates by $\sim 22^\circ$ from the *b*-axis in the (0, 0, 1) plane. The low temperature range (*LT*) 1.5 K—T_2 subdivides into two regions: (i) *LT*-1, between 1.5 K—T_1 where the relative amount of the two phases remains unchanged and in (ii) *LT*-2: T_1–T_2 where the amount of the incommensurate $\boldsymbol{q}_3$ phase increases at the cost of the commensurate $\boldsymbol{q}_2$ amplitude modulated structure which remains unchanged but fully disappears at the first order transition at T_2=23.5 K. The $\boldsymbol{q}_3$ phase undergoes minor changes until 22 K and gets destabilised at T_2 where the q_{3z} component jumps from the *LT* value $q_{3z}\approx 1/11$ to the *HT* value $\approx 1/7$ and the q_{3y} component increases from 0.484(1) to 0.495(1). (iii) The high temperature (*HT*) range T_2–T_N (T_N=40 ± 1 K) is described by a single wave vector $\boldsymbol{q}_3$. The disproportionation of the *HT* magnetic phase $\boldsymbol{q}_3$ below T_2 into two coexisting distinct phases $\boldsymbol{q}_2$, $\boldsymbol{q}_3$ down to 1.5 K is an unusual phenomenon, to our knowledge observed for the first time. Various mechanisms are discussed.

1. Introduction

Since the discovery of the equiatomic *R*Si, RGe, (*R*=rare earth) isomorphic compounds with CrB-type (*Cmcm*) and/or FeB-type (*Pnma*) of structure [1] more than four decades ago, their magnetic properties have been widely investigated. The interest arises from the nonuniform dependence of their magnetic properties ranging from ferromagnetic to antiferromagnetic and the large variety of observed magnetic structures comprising long period commensurate or antiphase domain structures, incommensurately amplitude modulated phases and magnetic phase transitions passing through the series [2,3]. The large variety of observed magnetic behaviours arises from the competition of long-range exchange interactions between 4*f* ions and the magnetocrystalline anisotropy of the underlying trigonal prism rare earth arrangements that results in frustrated magnetic states. Furthermore R-Si compounds are of interest for applications in microelectronics due to the low Schottky barrier.

The low temperature magnetic ordering of the dimorphic [1] antiferromagnetic DySi compound has been studied by us recently [4] by neutron diffraction at 1.5 K. Our study confirms the results of a previous neutron diffraction study [5] on the $DySi_{0.8}Ge_{0.2}$ antiferromagnetic compound (T_N=43 K) where the CrB-type (*Cmcm*, space group) had been stabilised by alloying with germanium. The magnetic ordering corresponds to a uniaxial arrangement associated with a cell doubling of the *c*-axis. The Dy moments point along the shortest axis *c* and change sign from one cell to the other along *c*. The ordered moment value of 8.8(2) μ_B/Dy atom reported by Nguyen et al. at 4.2 K in [5], is in good agreement with the value found by us 8.57(2) μ_B/Dy atom at 1.5 K [4]. Magnetic measurements of the FeB-type DySi compound [6] reveal an ordering temperature of 41 K while more recent data in a study of the magnetotransport properties report for both DySi modifications [7] T_N=38 K and a broad metamagnetic transition in a field of about 65 kOe with hysteresis effects above 20 kOe at 5 K.

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Surprisingly our 1.5 K neutron study led to a rather complex situation for the FeB-type modification (*Pnma* space group). At this temperature, the magnetic ordering is described by two coexisting magnetic phases in form of domains, associated with two nonsymmetry related wave vectors $\boldsymbol{q}_2$=(0, 1/2, 1/6) and $\boldsymbol{q}_3$=(0, q_{3y}, q_{3z}) with $q_{3y} \approx 1/2$ and $q_{3z} \approx 1/11$. In this measurement, the sample was cooled from room temperature down to 1.5 K. The best neutron diffraction data fit was obtained for two amplitude modulated magnetic structures for both vectors. For the long period commensurate phase $\boldsymbol{q}_2$ the Dy magnetic moments point along the shortest axis *b*. This corresponds to a situation similar to that of the CrB-type compound with $\boldsymbol{q}_1$=(0, 0, 1/2), where the preferred orientation of the moments is found as well along the linear chains with the shortest period corresponding in that case to *c*. For the $\boldsymbol{q}_3$ phase, the Dy moment orientation deviates by 22° (3) from the *b*-axis within the plane (0, 0, 1).

The $\boldsymbol{q}_2$=(0, 1/2, 1/6) *phase was alternatively described as an antiphase domain structure* with two amplitudes $m_0/2$ and m_0. Along the *c*-axis the magnetic moments are stacked in the sequence: ($+m_0/2$, $-m_0/2$, $-m_0$, $-m_0/2$, $+m_0/2$, $+m_0$, etc.). The axis of preferred orientation *b* acts as an antitranslation (t'_b). The existence of competing magnetic structures $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$ in the FeB-type was brought into connection with geometric frustration associated with the underlying structure of rare earth trigonal prisms with antiferromagnetic interactions. Such arrangements may lead to a plethora of thermodynamically equivalent solutions as the symmetry is getting lost and the number of free parameters increases. It is expected that a change of an external parameter will favour thermodynamically one of the two structures.

The present study focuses on the evolution of magnetic ordering with temperature by extending the experimental information over the entire magnetically ordered regime. It seems of interest to check, whether the commensurate $\boldsymbol{q}_1$ (CrB-type) and $\boldsymbol{q}_2$ (FeB-type) structures transform to incommensurate phases at higher temperatures, as for the isomorphic FeB-type compound TbSi [8] and whether the $\boldsymbol{q}_2$ phase transforms to an incommensurate *HT* phase different from that found for $\boldsymbol{q}_3$. Finally, the thermal behaviour of the wave vectors $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$ and other magnetic structure parameters are of interest. The results will be summarised in a temperature magnetic phase diagram for both structure types CrB and FeB in terms of wave vectors.

2. Experimental and results

2.1. Neutron diffraction experiments

Neutron data were collected on the dimorphic DySi sample (II) containing 74% of the FeB-type and 26% of the CrB-type, as reported in [2]. One data set was collected at the ILL in Grenoble with the high-flux D20 diffractometer in the high resolution option and (λ=1.8679 Å) with a temperature window of 1 K for 34 temperatures (on heating) in the range 10–45 K. D20 has a position-sensitive multidetector composed of 1600 micro-strips spaced by 0.1° spanning 160° in 2θ. The second data set was collected with the high resolution D1A diffractometer (λ=1.9085 Å, 2θ: 0–160°, step increment 0.10°) for 12 temperatures on heating and 4 temperatures on cooling in the range 1.5–45 K see Table 1. In view of the high absorption cross-section, a sample holder of 0.5 cm outer diameter was used and the DySi sample was diluted by polycrystalline Al metal that was included in the refinements. The data analysis has been made with the *Fullprof Suite* of programs [9]. The plots of the magnetic structure were made with the program *Fullprof Studio* [10] incorporated in [9]. The D20 data were used in "sequential" refinements [9] to derive the magnetic phase diagrams and the thermal variation of various physical quantities. The D1A data were used for the refinements and the results compared with those of the D20 instrument.

Table 1
The behaviour of the first magnetic FeB triple satellite from the thermal history of the DySi sample (D1A data).

Cooling from 10 K down to 1.5 K			Cooling from 20 K down to 10 K			Cooling from 45 K down to 1.5 K and collect data on heating		
T (K)	I_2/I_1	Conclusions	*T* (K)	I_2/I_1	Conclusions	*T* (K)	I_2/I_1	Conclusions
10	$c<1$	The $\boldsymbol{q}_3$ phase gets stabilised as a metastable phase by fast cooling down to 10 K and no substantial changes are visible going down to 1.5 K within the *LT*-1 range	10	$c<1$	Cooling from a temperature $T<T_2$ to $T<T_1$ favours the $\boldsymbol{q}_3$ phase as a metastable phase	4	$c>1$	Cooling from $T>T_N$ to $T<T_1$ favours the $\boldsymbol{q}_2$ *LT*-1 phase that disappears gradually in favour of the $\boldsymbol{q}_3$ phase in the *LT*-2 range $T_1<T<T_2$
8	$c<1$					6	$c>1$	
6	$c<1$					8	$c>1$	
4	$c<1$					10	$c>1$	
1.5	$c<1$					13	$c>1$	
			Heating to 45 K and cooling to 1.5 K			16	$v<1$	
				$c>1$	Contrary cooling from $T>T_N$ to $T<T_1$ favours the $\boldsymbol{q}_2$ *LT* phase	19	$v<1$	
						22	$v<1$	At T_2 the $\boldsymbol{q}_3$ phase undergoes a further transition to a new *HT* $\boldsymbol{q}_3$ phase up to T_N
						25	*HT* $\boldsymbol{q}_3$	
						28	*HT* $\boldsymbol{q}_3$	
						45	Param.	

The ratio I_2/I_1 relates to the relative amount of the $\boldsymbol{q}_2/\boldsymbol{q}_3$ phases. I_1 is the peak intensity of the (1 0 0) $\pm q_3$ satellite and I_2 is the peak intensity of the unresolved {(1, 1/2, 1/6), {1 1 0}$-\boldsymbol{q}_3$} satellites. For the I_2/I_1 ratio the labels c and v correspond to c=constant and v=variable value.