

Magnetic structure of $\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$

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$\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$ is a new member of the intermetallic compounds $\text{RE}_5T_x\text{Sb}_{3-x}$ and $\text{RE}_5T_x\text{Bi}_{3-x}$ (RE is a rare-earth, T is a late $3d$ metal) that adopt the orthorhombic Yb_5Sb_3 -structure type [1]–[3]. While compositionally the $\text{RE}_5\text{Tb}_x\text{Sb}_{3-x}$ and $\text{RE}_5\text{Tb}_x\text{Bi}_{3-x}$ phases can be viewed as T -substituted variants of the corresponding binaries RE_5Sb_3 and RE_5Bi_3 , the introduction of Ni either introduces or stabilizes the high-temperature polymorphs of the corresponding binaries [1]–[3].

Predominantly, magnetic behavior of the LT hexagonal polymorphs of RE_5Sb_3 and RE_5Bi_3 have been studied [4]–[9]. The magnetic order for the T -substituted orthorhombic variants was investigated only through magnetic susceptibility measurements and only for selected members [1]–[3].

From the $\text{RE}_5T_x\text{Bi}_{3-x}$ series, only magnetic data for $\text{Gd}_5\text{Ni}_{0.71}\text{Bi}_{2.29}$ have been reported so far.³ Contrary to $\text{Gd}_5\text{Ni}_{0.71}\text{Bi}_{2.29}$, $\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$ shows two transitions (Figure 1). The goal of study was to uncover the origin of the observed magnetic behavior in $\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$ through the neutron powder diffraction.

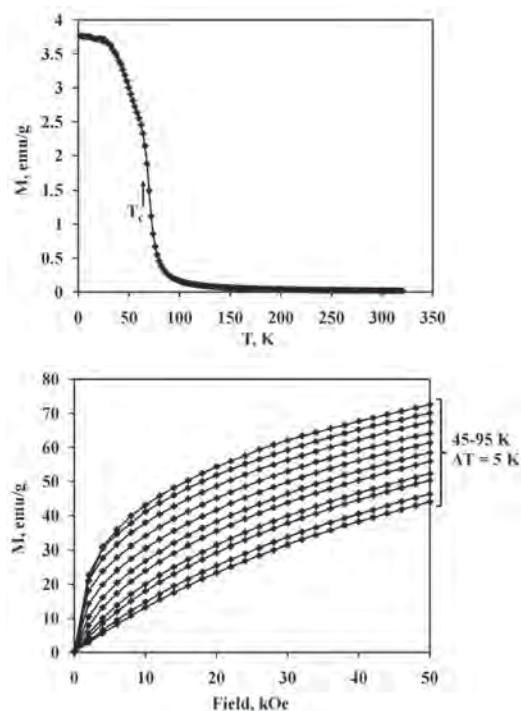


Fig 1. Magnetization as a function of temperature (top) and of field (bottom) for $\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$.

The starting materials were Dy (99.9 wt. %, CERAC Inc.), Bi (99.9999 wt. %, CERAC Inc.) and Ni (99.9+ wt. %, Alfa Aesar). A sample with the $\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$ composition was arc-melted and annealed at 1350°C for 3 hours in Argon atmosphere.

Single crystal data for a crystal extracted from the annealed alloy were collected on a STOE IPDS II diffractometer with the $\text{MoK}\alpha$ radiation in the whole reciprocal sphere. Numerical absorption correction was based on the crystal shape obtained from optical face indexing and optimized against equivalent reflections using the STOE X-Shape software [10]. The structure was solved and refined using the SHELXS and SHELXL programs [11], respectively (Table 1, 2). Ni was found to mix with Bi on the $4c$ sites resulting in the $\text{Dy}_5\text{Ni}_{0.69(1)}\text{Bi}_{2.31(1)}$ composition.

Table 1. Crystal data and structure refinement for $\text{Dy}_5\text{Ni}_{0.69(1)}\text{Bi}_{2.31(1)}$

Composition	$\text{Dy}_5\text{Ni}_{0.66(1)}\text{Bi}_{2.34(1)}$
Space group	$Pnma$
Lattice parameters (Å)	$a = 12.075(2)$ $b = 9.165(2)$ $c = 8.072(1)$
Volume (Å ³)	893.3(2)
Z	4
Density (calculated) (g/cm ³)	10.145
2θ range for data collection	6.08 – 58.50°
Index ranges	$-16 \leq h \leq 16$, $-12 \leq k \leq 12$, $-9 \leq l \leq 11$
Reflections collected	9480
Independent reflections	1275 [$R_{\text{int}} = 0.2844$]
Completeness to max 2θ (%)	98.8
Data/restraints/parameters	1275 / 0 / 45
Goodness-of-fit on F^2	0.782
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0621$, $wR_2 = 0.0644$
R indices (all data)	$R_1 = 0.1697$, $wR_2 = 0.0876$
Extinction coefficient	0.000066(16)
Largest diff. peak/hole, (e/Å ³)	–584/591

Table 2. Atomic and isotropic temperature (U) parameters for $\text{Dy}_5\text{Ni}_{0.69(1)}\text{Bi}_{2.31(1)}$

Atom	Site	Occupancy	x/a	y/b	z/c	U (Å ²)
Dy1	$4c$	1	0.2862(2)	1/4	0.6666(4)	0.021(1)
Dy2	$4c$	1	0.2035(2)	1/4	0.1334(4)	0.023(1)
Dy3	$4c$	1	0.4978(3)	1/4	0.9645(4)	0.016(1)
Dy4	$8d$	1	0.4346(2)	0.0473(2)	0.3180(3)	0.026(1)
Bi1	$8d$	1	0.3267(1)	0.9892(1)	0.9284(2)	0.015(1)
Bi2/Ni	$4c$	0.31(1)/0.69(1)	0.5220(3)	1/4	0.5918(6)	0.017(1)

Because of the extremely large cross section of Dy, the sample mounting procedure developed by scientists at Chalk River [12] was employed for the $\text{Dy}_5\text{Ni}_{0.69}\text{Bi}_{2.31}$ phase. The sample was ground, mixed with diluted G vanish and deposited as a thin layer between the two single crystal silicon wafers.

Two sets of experiments were performed. During the first time

slot in July 2008, the data were collected at room temperature and base temperature at the C2 diffractometer. Those were test runs to establish the optimal collection routine. The later runs in October 2008 were performed to elucidate the magnetic structure. Experimental diffractograms in the 3.8-74.8 K region, at 99.8 K and 299.7 K were collected on the C2 diffractometer in the 3.303-83.397° 2θ range with 0.1002425° step. Integrated intensities for the magnetic peaks at 2θ of 20.51°, 22.74° and 28.57° were generated by the XFIT software (Figure 2) [13].

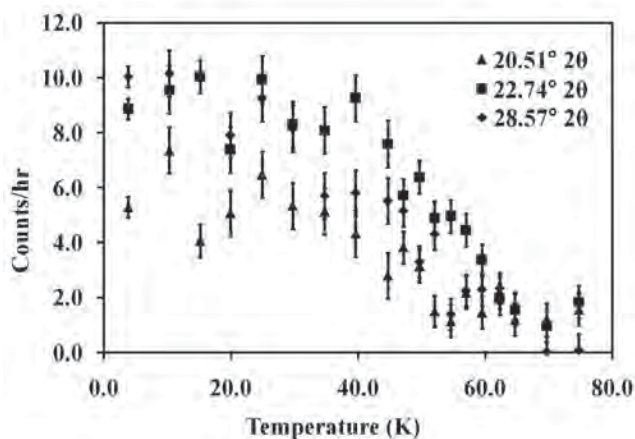


Fig 2. Integrated intensities for the magnetic peaks at 20.51°, 22.74° and 28.57° 2θ .

Unfortunately, during the three-month period (July-October, 2008) the sample degraded significantly (Figure 3), and the quality of the data did not allow obtaining a reliable refinement of the magnetic structure.

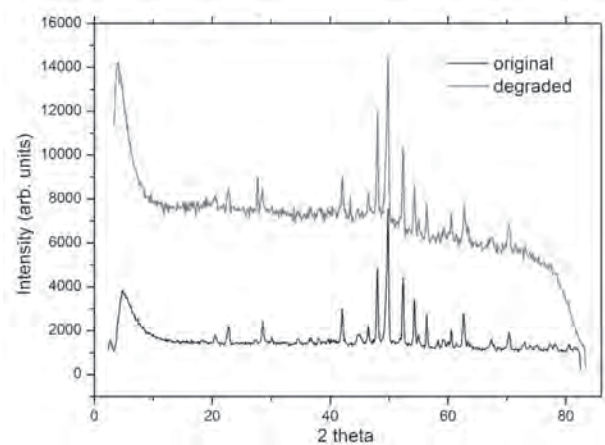


Fig 3. Comparison of two runs at the base temperature: the red data are from July, 2008 and the blue data from October, 2009.

Magnetic structure of the $\text{Dy}_5\text{Ni}_{0.66}\text{Bi}_{2.34}$ compound was attempted to refine using the FULLPROF software package [14] but reliable solution could not be obtained due to the small contribution of the magnetic scattering to the total scattering of the phase. Temperature dependant fit of the magnetic peaks at 2θ of 20.51°, 22.74° and 28.57° shows distinct intensity fluctuations around 35 K, 50 K and after 60 K (Figure 2).

These features substantiate magnetization data but they do not shade light on the nature of the transition. Non-homogeneity of the transition can be caused by the presence of a canted ferromagnetism but this hypothesis must be supported by the magnetic refinement data.

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