Refinement of the crystal structure of diholmium trinickel hexaboride, $Ho_2Ni_3B_6$

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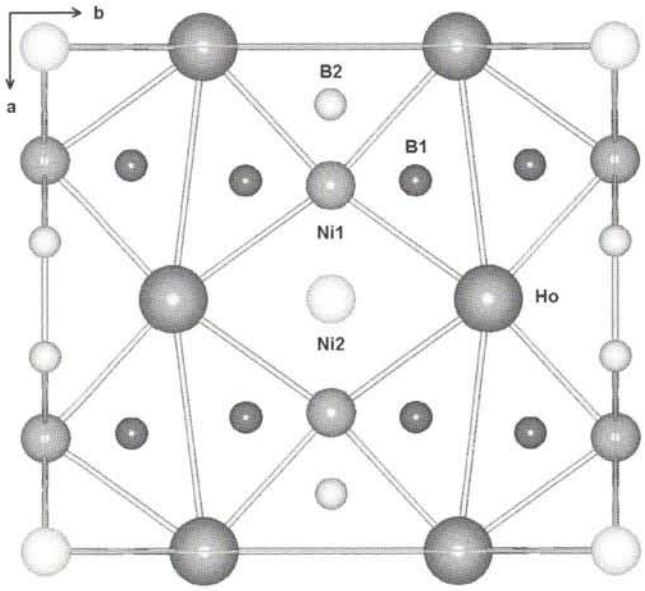

Abstract

$B_6Ho_2Ni_3$, orthorhombic, *Cmmm* (No. 65), $a = 7.6865(9)$ Å, $b = 8.6679(9)$ Å, $c = 3.4742(4)$ Å, $V = 231.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.021$, $wR_{ref}(F^2) = 0.048$, $T = 300$ K.

Source of material

A coarse-grained sample with nominal composition $Ho_2Ni_3B_6$ was prepared from holmium pieces, nickel powder and boron powder. A stoichiometric mixture of the high-purity elements was pressed to pellets, which have been arc melted under argon atmosphere on a water-cooled copper heart. Melting of the buttons has been repeated three times in order to improve the sample homogeneity. A special annealing treatment (duration 75 h, temperature up to 1733 K) was performed within a resistance furnace under argon atmosphere. The composition of the annealed sample was determined with electron probe microanalysis applying the WDX mode. A single grain was extracted from the polycrystalline aggregate for single-crystal diffractometry.

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Experimental details

Accurate lattice parameters of $Ho_2Ni_3B_6$ were measured at temperatures between 300 K and 100 K using a STOE STADI4 four-circle diffractometer equipped with a CRYOSTREAM cooling system (Oxford Cryosystems).

Discussion

The title compound, which is isotypic with $Lu_2Ni_3B_6$ [1], was first characterized with X-ray powder diffraction [2], but no structure refinement has been performed. The crystal structure of $Ho_2Ni_3B_6$ (*Cmmm* - pjhga) is closely related to that of $ThMoB_4$ (*Cmmm* - pjihg), with 1/3 of Ni atoms replaced by B-B dumb-bells [3]. The structure consists of two equidistant planar layers which are alternately stacked along the *c* axis. Within the Ho-Ni1 network, each Ni1 atom is coordinated by 2 Ho atoms at 2.865 Å and 2 Ho atoms at 2.958 Å, leading to a distorted square-planar arrangement. Both symmetry-independent B atoms are located inside trigonal prisms formed by 4 Ho atoms and 2 Ni1 atoms. Within the Ni2-B1-B2 network, each B2 atom is coordinated by 2 B1 atoms at 1.74 Å and 1 B2 atom at 1.75 Å, whereas the Ni2 atom is surrounded by 4 B1 atoms at 2.22 Å. The two layers are connected by the Ni2 atom with a square-planar coordination by Ni1 atoms. The Ni1—Ni2 distances of 2.452 Å are slightly shorter than those found in metallic nickel (2.50 Å), indicating a strong metal-metal bonding. The analysis of the U_{ij} shows a preferred displacement in the *a-b* plane for the metal atoms, but in the *c* direction for the boron atoms. The refinement of site occupancies results in the composition $Ho_{1.90(1)}Ni_3B_6$. Atomic coordinates correspond to the standardized form according to STRUCTURE TIDY [4], shifting the origin by [0 0 1/2]. The coefficients of linear thermal expansion at temperatures between 300 K and 100 K are $\alpha_a = 8.5 \times 10^{-6}$ K^{-1}, $\alpha_b = 6.7 \times 10^{-6}$ K^{-1}, and $\alpha_c = 1.4 \times 10^{-5}$ K^{-1}.

Table 1. Data collection and handling.

Crystal:	metallic lustre, block, size 0.02 × 0.04 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	455.78 cm^{-1}
Diffractometer, scan mode:	STOE STADI4, ω/θ
$2\theta_{max}$:	62.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	815, 246
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 222
$N(param)_{refined}$:	24
Programs:	STRUCTURE TIDY [4], SHELX-97 [5], SCHAKAL92 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ho	4*j*	0.951(5)	0	0.27673(5)	1/2	0.0069(2)	0.0055(3)	0.0033(2)	0	0	0
Ni(1)	4*h*		0.2251(2)	0	1/2	0.0076(6)	0.0064(5)	0.0039(6)	0	0	0
Ni(2)	2*a*		0	0	0	0.0073(8)	0.0085(8)	0.0046(8)	0	0	0
B(1)	8*p*		0.2345(9)	0.1497(9)	0	0.006(3)	0.008(3)	0.014(3)	0.001(3)	0	0
B(2)	4*g*		0.386(1)	0	0	0.008(4)	0.010(4)	0.015(5)	0	0	0

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