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Refinement of the crystal structures of trinickel boron, Ni_3B, and tripalladium boron, Pd_3B

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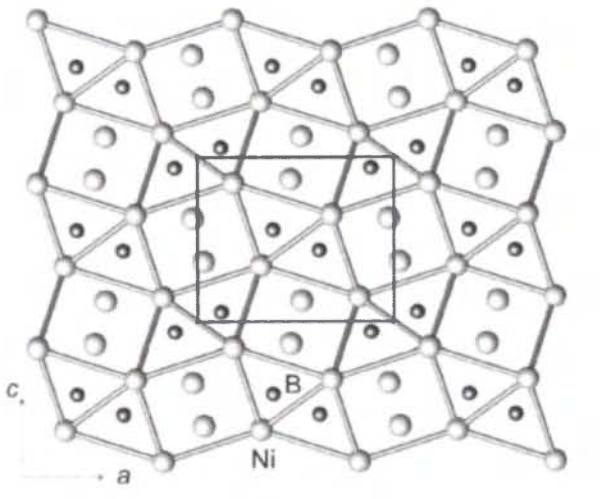

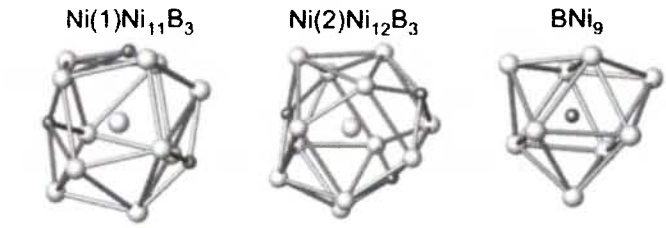

Abstract

BNi_3, orthorhombic, *Pnma* (no. 62), a = 5.2219(2) Å, b = 6.6171(2) Å, c = 4.3918(1) Å, V = 151.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.022, $wR_{ref}(F^2)$ = 0.036, T = 293 K.

BPd_3, orthorhombic, *Pnma* (no. 62), a = 5.4644(2) Å, b = 7.5632(3) Å, c = 4.8506(1) Å, V = 200.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.049, T = 293 K.

Source of material

Samples were obtained by arc-melting of mixtures of elemental components: Ni foil (99.99 %, Alfa Aesar), Pd foil (99.95 %, Chempur) and crystalline B powder (99.995 %, Chempur). The samples were sealed in tantalum tubes and annealed in evacuated silica tubes at 920 °C for 7 days. Needle-like single crystals were mechanically extracted from crushed samples. All manipulations were carried out in a argon-filled glove box ($p(O_2/H_2O)$ < 1 ppm).

Experimental details

Lattice parameters of both compounds were refined from 58 reflections by least-squares fitting of powder diffraction data (Huber G670 imaging plate Guinier-camera, Cu$K_{\alpha 1}$ radiation, λ = 1.54056 Å) with LaB_6 as internal standard (a = 4.15692 Å).

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In order to get sufficiently large data sets scattering intensities for Ni_3B and Pd_3B were measured up to high $\sin\theta/\lambda$ values, 1.414 and 1.293, respectively. This ensured an equal amount of independent intensities for all three crystals. During the crystal structure refinement special attention was payed to correlations between displacement and occupational parameters. After initial refinement of atomic coordinates, an extinction coefficient, displacement parameters and weighting scheme the occupational parameters for Ni1 (Pd1) were refined while occupancies of the other atoms were kept fixed. No deviation from full occupancy was observed. The same procedure was applied for the other atoms with similar results. After these steps displacement parameters for all atoms were refined anisotropically while fixing the occupation to 100 %. This resulted in a significant reduction of the reliability factors. In the further course of the refinement the occupational parameters for Ni (Pd) and B atoms were again treated separately for each species and finally the occupational parameters were refined freely for all atoms.

Discussion

The crystal structures of the isotypic compounds Ni_3B and Pd_3B have been subject of several investigations [1-4]. Nevertheless, in all previous studies the occupancies of the metal and boron positions were not refined. With respect to a discussion and evaluation of chemical composition, a detailed refinement of high resolution single-crystal XRD data was desirable. For this purpose we studied two Ni_3B and one Pd_3B single crystals of high quality which were isolated from the bulk samples with the nominal composition of 3:1.

For all refinement cycles full occupation at all atomic sites (within standard deviations of < 2 %) was observed without any significant variation of the displacement parameters. Moreover refined crystallographic parameters for the two Ni_3B single crystals are identical within one e.s.d. Derived compositions of $Ni_{75.0(9)}B_{25.1(4)}$ and $Pd_{75(1)}B_{25.1(6)}$ are in very good agreement with results from WDXS ($Ni_{72(3)}B_{27.6(8)}$ and $Pd_{75(2)}B_{24(2)}$) and chemical analysis ($Ni_{75.1(6)}B_{24(1)}$ and $Pd_{74.0(1)}B_{26.0(1)}$).

Ni_3B and Pd_3B crystallize with the cementite (Fe_3C) type structure, which is closely related to the U_3Si_2 and $Cu_{11}Al_2$ structure types, as discussed in detail in [5] and [6]. Ni (Pd) atoms form puckered $3^2.4.3.4$ nets, which are stacked along the c axis (figure, top). One more peculiarity of the Fe_3C structure type is the presence of empty octahedra, formed by d elements. In Ni_3B and Pd_3B structures Ni and Pd, respectively, are situated in the centers of 15- and 14-vertices polyhedra (figure, bottom), while B atoms are located in 3 capped trigonal prisms formed by Ni (Pd). The shortest interatomic distances Ni1—B at 2.0337(7) A, Ni1—Ni1 at 2.4538(1) Å, Pd1—B at 2.158(2) Å and Pd1—Pd1 at 2.7163(2) Å are in good agreement with the sum of atomic radii of the elements (r(Ni) = 1.25 Å, r(Pd) = 1.38 Å and r(B) = 0.83 Å [7]; shortening is less than 3 %.

1. Trinickel boron, Ni_3B

Table 1. Data collection and handling.

Crystal:	metallic needle, size 0.017 × 0.024 × 0.054 mm
Wavelength:	Ag K_α radiation (0.5608 Å)
μ:	47.08 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS SPIDER, φ/ω
$2\theta_{max}$:	104.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9768, 1622
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1404
$N(param)_{refined}$:	26
Programs:	SHELXL-97 [8], WinCSD [9], ATOMS [10]

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}
Ni(1)	8*d*	1.00(1)	0.17986(1)	0.06150(1)	0.15443(2)	0.00598(2)	0.00438(4)	0.00514(2)	0.00008(2)	–0.00045(2)	–0.00035(2)
Ni(2)	4*c*	1.00(1)	0.02798(2)	¼	0.63106(2)	0.00545(3)	0.00510(5)	0.00611(3)	0	0.00091(2)	0
B	4*c*	1.01(2)	0.3822(2)	¼	0.4380(2)	0.0061(3)	0.0078(4)	0.0085(3)	0	–0.0007(2)	0

2. Tripalladium boron, Pd_3B

Table 3. Data collection and handling.

Crystal:	metallic platelet, size 0.007 × 0.022 × 0.043 mm
Wavelength:	Ag K_α radiation (0.5608 Å)
μ:	137.77 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS SPIDER, φ/ω
$2\theta_{max}$:	93°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7184, 1754
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1381
$N(param)_{refined}$:	26
Programs:	SHELXL-97 [8], WinCSD [9], ATOMS [10]

Table 4. 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}
Pd(1)	8*d*	1.00(2)	0.18010(2)	0.07043(2)	0.17244(3)	0.00570(3)	0.00622(4)	0.00681(5)	–0.00003(3)	–0.00034(3)	–0.00017(3)
Pd(2)	4*c*	1.00(2)	0.03773(3)	¼	0.65475(3)	0.00519(4)	0.00652(5)	0.00657(6)	0	0.00017(4)	0
B(1)	4*c*	1.01(2)	0.3890(5)	¼	0.4370(5)	0.0082(7)	0.0145(9)	0.0100(9)	0	–0.0011(7)	0

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