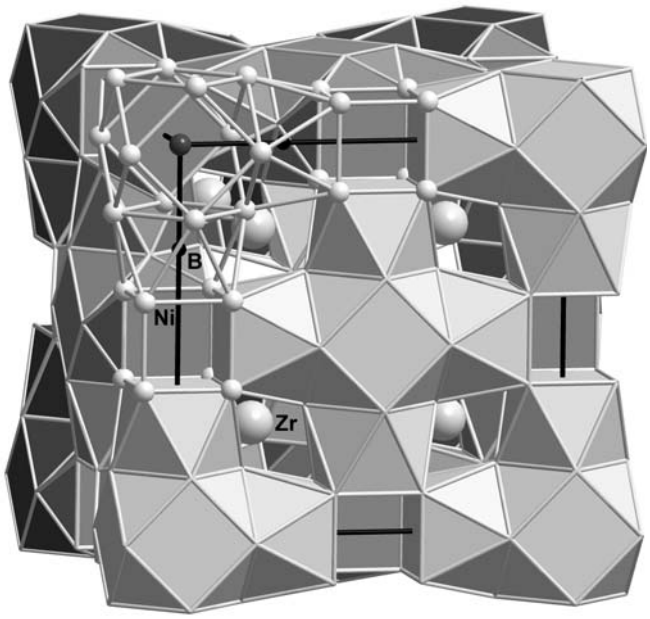
Refinement of the crystal structures of scandium nickel boride, $Sc_2Ni_{21}B_6$ and zirconium nickel boride, $Zr_2Ni_{21}B_6$

Roman Gumeniuk*, Yurii Prots, Walter Schnelle and Andreas Leithe-Jasper

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

Received July 25, 2008, accepted and available on-line October 17, 2008; CSD no. 409959, 409960



Abstract

$B_6Ni_{21}Sc_2$, cubic, $Fm\bar{3}m$ (no. 225), a = 10.5940(3) Å, V = 1189.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.041, T = 293 K.

$B_6Ni_{21}Zr_2$, cubic, $Fm\bar{3}m$ (no. 225), a = 10.6223(4) Å, V = 1198.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.039, T = 293 K.

Source of material

Samples with stoichiometric compositions were synthesized by arc-melting of mixtures of elements: Zr foil (99.99 %, Alfa, Johnson Matthey), Sc pieces (99.95 %, Ames), Ni foil (99.99 %, Alfa Aesar), and crystalline B powder (99.995 %, Chempur). The obtained reguli were sealed in Ta containers and annealed in evacuated silica tubes at 950 °C for 14 days. Needle-like single crystals were separated from well-crystallized ingots by mechanical fragmentation. The magnetization of polycrystalline sample pieces was measured in a SQUID magnetometer (MPMS XL-7, Quantum Design) in external fields between 20 Oe and 70 kOe and temperatures of 1.8 - 400 K.

Experimental details

Refinement of lattice parameters for each compound was performed on 30 reflections by least-squares fitting of powder diffraction data (HUBER G670 Imaging Plate Guinier Camera, CuKα_1 radiation, λ = 1.54056 Å) with LaB_6 as internal standard (a = 4.1569 Å).

Discussion

Ternary borides (structure type $Cr_{23}C_6$ [1]) with the common composition $(Ni,M)_{23}B_6$ (M = transition metal) have been an object of numerous investigations due to their possible application in wear-resistant nickel-base hard alloys. Compounds $Sc_3Ni_{20}B_6$ [2], $Zr_2Ni_{21}B_6$ [3,4] and $Zr_3Ni_{20}B_6$ [5] were shown to crystallize with $Cr_{23}C_6$ type structure on basis of the x-ray powder diffraction data. In further investigations these compounds were found to possess homogeneity ranges at 800 °C: $Sc_{3-4}Ni_{20-19}B_6$ [6] and $Zr_{1.7-5.2}Ni_{21.3-17.8}B_6$ [3,7]. In a recent study on $RE_{2-x}Ni_{21}B_6$ phases (RE = Er, Yb, Lu) [8] it was shown that the 8*c* position is partially occupied by RE atoms and some shortening of the interatomic distances to this position is observed. To clarify these structural peculiarities in $Sc_2Ni_{21}B_6$ and $Zr_2Ni_{21}B_6$ borides we reinvestigated their crystal structures by using single crystal x-ray diffraction data.

This study confirms the $Cr_{23}C_6$ type for both compounds. Nearly the same displacement parameters of all atoms as well as a simultaneous refinement of displacement and occupational parameters corroborate $Sc_2Ni_{21}B_6$ and $Zr_2Ni_{21}B_6$ to be stoichiometric defect-free compounds. The shortest interatomic distances d(Sc—Ni2) = 2.4890(6) Å, d(Ni3—Ni3) = 2.4071(9) Å, d(B—Ni3) = 2.083(3) Å and d(Zr—Ni2) = 2.5042(7) Å, d(Ni3—Ni3) = 2.401(1) Å, d(B—Ni3) = 2.078(4) Å are close to the sum of Pauling's single bond radii (r(Sc) = 1.439 Å, r(Zr) = 1.454 Å, r(Ni) = 1.154 Å and r(B) = 0.81 Å [9]); the deviation is less than 4 %. In the structure of $Zr_2Ni_{21}B_6$ there are columns consisting of tetragonal antiprisms [BNi_8] and empty cubes [$\square Ni_8$] parallel to the 4-fold axes, which are separated by cubooctahedra [Ni1Ni_{12}]. Zr and Sc atoms have the largest coordination number CN = 16, coordination numbers of Ni2 and Ni3 are 13 and 14, respectively. The magnetic susceptibility of $Sc_2Ni_{21}B_6$ (single crystals) and $Zr_2Ni_{21}B_6$ (polycrystalline material) was determined. The corrected susceptibilities extrapolated to T = 0 are positive and weakly temperature-dependent ($Sc_2Ni_{21}B_6$: χ = $+1.7.10^{-3}$ emu/mol; $Zr_2Ni_{21}B_6$: $\chi = +1.9.10^{-3}$ emu/mol) and indicate that the compounds are Pauli-paramagnetic metals with rather similar electronic density of states at the Fermi level.

* Correspondence author (e-mail: gumeniuk@cpfs.mpg.de)

1. Scandium nickel boride, $Sc_2Ni_{21}B_6$

Table 1. Data collection and handling.

Crystal:	metallic block, size 0.065 × 0.050 × 0.030 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	333.49 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, oscillation
$2\theta_{max}$:	67.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3146, 154
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 153
$N(param)_{refined}$:	14
Programs:	SHELXL-97 [10], CSD [11], ATOMS [12]

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sc	8*c*	¼	¼	¼	0.0065(3)	0.0065(3)	0.0065(3)	0	0	0
Ni(1)	4*a*	0	0	0	0.0066(3)	0.0066(3)	0.0066(3)	0	0	0
Ni(2)	32*f*	0.38564(3)	0.38564(3)	0.38564(3)	0.0056(2)	0.0056(2)	0.0056(2)	0.0004(1)	0.0004(1)	0.0004(1)
Ni(3)	48*h*	0	0.16967(3)	0.16967(3)	0.0061(2)	0.0057(2)	0.0057(2)	0	0	0.0003(2)
B	24*e*	0.2691(5)	0	0	0.007(2)	0.007(1)	0.007(1)	0	0	0

2. Zirconium nickel boride, $Zr_2Ni_{21}B_6$

Table 3. Data collection and handling.

Crystal:	metallic block, size 0.025 × 0.060 × 0.070 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	336.91 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, oscillation
$2\theta_{max}$:	67.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2652, 153
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 152
$N(param)_{refined}$:	14
Programs:	SHELXL-97 [10], CSD [11], ATOMS [12]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	8*c*	¼	¼	¼	0.0059(2)	0.0059(2)	0.0059(2)	0	0	0
Ni(1)	4*a*	0	0	0	0.0041(4)	0.0041(4)	0.0041(4)	0	0	0
Ni(2)	32*f*	0.38611(4)	0.38611(4)	0.38611(4)	0.0057(2)	0.0057(2)	0.0057(2)	0.0002(1)	0.0002(1)	0.0002(1)
Ni(3)	48*h*	0	0.17010(4)	0.17010(4)	0.0066(3)	0.0059(2)	0.0059(2)	0	0	0.0003(2)
B	24*e*	0.2668(7)	0	0	0.008(3)	0.006(2)	0.006(2)	0	0	0

Acknowledgment. The authors thank H. Rosner for helpful discussions.

References

1. Westgren, A.: Complex Chromium and Iron Carbides. Nature **132** (1933) 480.
2. Kuzma, Yu.; Voroshylov, Yu.: New compounds with the $W_2Cr_{21}C_6$ structure type. Sov. Phys. Crystallogr. **12** (1967) 297-298.
3. Stadelmaier, H.; Helms, B.: Ein Borid mit $Cr_{23}C_6$-Struktur im System Nickel-Zirkon-Bor. Metall. **19** (1965) 121-122.
4. Kuzma, Yu.; Lakh, V.; Voroshylov, Yu.; Stadnyk, B.: Crystal structure of the compounds $Zr_2Ni_{21}B_6$ and $Zr_2Co_{21}B_6$. Dopov. Akad. Nauk URSR. **6** (1966) 772-774.
5. Ganglberger, E.; Nowotny, H.; Benesovsky, F.: Neue Boride mit $Cr_{23}C_6$-Struktur. Monatsh. Chem. **96** (1965) 1144-1146.
6. Stepanchykova, H.; Kuz´ma, Yu.: The systems Sc-Ni-B. Visn. Lviv. Univ. Ser. Khim. **23** (1981) 48-51.
7. Lugscheider, E.; Reimann, H.; Pankert, R.: Mit 4a- und 5a-Metallen stabilisierte τ-Boride des Nickel. Metall. **36** (1982) 247-251.
8. Veremchuk, I.; Gumeniuk, R.; Prots, Yu.; Schnelle, W.; Burkhardt, U.; Rosner, H.; Kuzma, Yu.; Leithe-Jasper, A.: Crystallographic and physical properties of $RE_{2-x}Ni_{21}B_6$ (RE = Er, Yb and Lu). Solid State Sci. In press.
9. Pauling L.: The Chemical Bond. Cornell Univ. Press Ithaca, NY 1967. p. 150.
10. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures, Universität Göttingen 1997.
11. Akselrud, L. G.; Zavalii, P. Y.; Grin, Yu. N.; Pecharsky, V. K.; Baumgartner, B.; Wölfel, E.: Use of the CSD program package for structure determination from powder data. Mater. Sci. Forum **133-136** (1993) 335-340.
12. Dowty E.: ATOMS 5.1. Shape Software. 521 Hidden Valley Road, Kingsport, TN, 37663, USA 2000.