# Supplementary Material

# to

# Boron-phil and boron-phob structure units in novel Borides $Ni_3Zn_2B$ and $Ni_2ZnB$: Experiment and First Principles Calculations

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**Tables:**

Table I: Phase compositions of samples prepared for the single crystal growth (number refers to the Fig. 1)

| No. | Phase | Ni:Zn | Approximate composition from EDX | | |
|---|---|---|---|---|---|
| | | | Ni | Zn | B |
| 1a | $\tau_4$ | 76.0:24.0 | 50.5 | 15.9 | 33.6 |
| | $\tau_5$ | - | - | - | - |
| | $\tau_6$ | 68.6:31.4 | 50.6 | 23.4 | 26.0 |
| | $Ni_2Zn_{11}$ | 27.6:72.4 | 27.6 | 72.4 | - |
| 1b | $\tau_5$ | 62.5:37.5 | 52.3 | 31.3 | 16.4 |
| | $Ni_2Zn_{11}$ | 30.0:70.0 | 30.0 | 70.0 | - |
| | rT-NiZn | 46.8:53.2 | 46.8 | 53.2 | - |
| | eutectic | 39.2:60.8 | 36.1 | 55.9 | 8.0 |
| 1c | $\tau_4$ | 75.3:24.7 | 51.7 | 15.2 | 33.1 |
| | $\tau_5$ | 60.6:39.4 | 50.4 | 32.8 | 16.7 |
| | $\tau_6$ | 67.9:32.1 | 51.1 | 24.2 | 24.7 |
| | $Ni_2Zn_{11}$ | 28.1:71.9 | 28.1 | 71.9 | - |
| | eutrectic | 39.9:60.1 | 36.4 | 54.7 | 8.9 |
| 1d | $\tau_5$ | 63.3:36.7 | 53.1 | 30.8 | 16.2 |
| | rT-NiZn | 47.7:52.3 | 47.7 | 52.3 | - |
| | $Ni_2Zn_{11}$ | - | - | - | - |

| | | | | | |
|---|---|---|---|---|---|
| 1e | $\tau_5$ | 61.5:38.5 | 53.0 | 33.1 | 13.8 |
| | $\tau_6$ | 68.6:31.4 | 53.0 | 21.9 | 25.2 |
| | $Ni_2Zn_{11}$ | - | - | - | - |
| | eutectic | 38.1:61.9 | 35.0 | 56.7 | 8.3 |
| 1f | $\tau_4$ | 75.3:24.7 | 50.4 | 16.5 | 33.1 |
| | $\tau_5$ | 62.2:37.8 | 54.0 | 29.5 | 16.5 |
| | $\tau_6$ | 68.4:31.6 | 51.3 | 23.6 | 25.1 |
| | $Ni_2Zn_{11}$ | - | - | - | - |

Table II: Interatomic bonding distances in $\tau_5$.

| Atom 1 | Atom 2 | $d_{1,2}$ [nm] | Atom 1 | Atom 2 | $d_{1,2}$ [nm] |
|---|---|---|---|---|---|
| Ni1 | B (2×) | 0.20632(1) | Zn1 | Ni3 (1×) | 0.25225(1) |
| CN=13 | Ni1 (1×) | 0.25194(1) | CN=12 | Ni3 (2×) | 0.25597(1) |
| | Zn2 (2×) | 0.25379(1) | | Ni2 (2×) | 0.25699(1) |
| | Ni3 (1×) | 0.25604(1) | | Ni1 (2×) | 0.25755(1) |
| | Zn1 (2×) | 0.25755(1) | | Zn2 (1×) | 0.25996(1) |
| | Zn2 (2×) | 0.26094(1) | | Zn1 (2×) | 0.26332(1) |
| | Ni1 (2×) | 0.26332(1) | | Zn1 (2×) | 0.26976(1) |
| | Ni2 (1×) | 0.26440(1) | Zn2 | Ni1 (2×) | 0.25379(1) |
| Ni2 | B (2×) | 0.20606(1) | CN=12 | Zn1 (1×) | 0.25996(1) |
| CN=13 | Zn1 (2×) | 0.25699(1) | | Zn2 (1×) | 0.26047(1) |
| | Zn2 (2×) | 0.26072(1) | | Ni2 (2×) | 0.26072(1) |
| | Ni3 (2×) | 0.26096(1) | | Ni1 (2×) | 0.26094(1) |
| | Ni2 (2×) | 0.26332(1) | | Zn2 (2×) | 0.26332(1) |
| | Ni1 (1×) | 0.26440(1) | | Ni2 (2×) | 0.26622(1) |
| | Zn2 (2×) | 0.26622(1) | B | Ni3 (2×) | 0.20545(1) |
| Ni3 | B (2×) | 0.20545(1) | CN=7 | Ni2 (2×) | 0.20606(1) |
| CN=13 | B (1×) | 0.21615(1) | | Ni1 (2×) | 0.20632(1) |
| | Ni3 (2×) | 0.24984(1) | | Ni3 (1×) | 0.21615(1) |
| | Zn1 (1×) | 0.25225(1) | | | |
| | Zn1 (2×) | 0.25597(1) | | | |
| | Ni1 (1×) | 0.25604(1) | | | |
| | Ni2 (2×) | 0.26096(1) | | | |
| | Ni3 (2×) | 0.26332(1) | | | |

Table III: Distances between the center of the $Ni_2Zn_4$ octahedra and the nearest Ni/Zn atoms in $\tau_5$-$Ni_3Zn_2B$.

| Cage | Center | Ligand | Distances (nm) |
|---|---|---|---|
| 1 | (½,½,½) | Zn2 (4×) | 0.18519(1) |
| | | Ni2 (2×) | 0.18743(1) |
| 2 | (~0.4,½,~0.15) | Zn1 (2×) | 0.18501(1) |
| | | Zn2 (2×) | 0.18501(1) |
| | | Ni1 (1×) | 0.18321(1) |
| | | Ni2 (1×) | 0.18321(1) |
| 3 | (0,½,0) | Ni1 (4×) | 0.18222(1) |
| | | Zn2 (2×) | 0.18179(1) |
| 4 | (¼,¼,0) | Zn1 (2×) | 0.22992(1) |
| | | Zn1 (2×) | 0.13488(1) |
| | | Ni3 (2×) | 0.21537(2) |

Table IV: Interatomic distances in $\tau_6$-$Ni_2ZnB$

| Atom 1 | Atom 2 | $d_{1,2}$ [nm] | Atom 1 | Atom 2 | $d_{1,2}$ [nm] |
|---|---|---|---|---|---|
| Ni1 CN=14 | B (2×) | 0.20135(1) | Zn CN=12 | Ni1 (2×) | 0.25262(1) |
| | B (1×) | 0.21812(1) | | Ni1 (1×) | 0.25275(2) |
| | Ni1 (2×) | 0.24688(1) | | Zn (1×) | 0.25459(2) |
| | Zn (2×) | 0.25262(1) | | Ni2 (2×) | 0.26361(1) |
| | Zn (1×) | 0.25275(2) | | Ni2 (2×) | 0.26435(1) |
| | Ni2 (1×) | 0.25936(2) | | Zn (2×) | 0.26899(2) |
| | Ni2 (2×) | 0.26096(1) | | Zn (2×) | 0.28371(2) |
| | Ni2 (1×) | 0.27474(2) | B CN=8 | B (1×) | 0.18495(1) |
| | Ni1 (2×) | 0.28371(2) | | Ni1 (2×) | 0.20135(1) |
| Ni2 CN=15 | B (2×) | 0.21085(1) | | Ni2 (2×) | 0.21085(1) |
| | B (2×) | 0.21309(1) | | Ni2 (2×) | 0.21309(1) |
| | Ni2 (1×) | 0.25502(2) | | Ni1 (1×) | 0.21812(1) |
| | Ni1 (1×) | 0.25936(2) | | | |
| | Ni1 (2×) | 0.26096(1) | | | |
| | Zn (2×) | 0.26361(1) | | | |
| | Zn (2×) | 0.26435(1) | | | |
| | Ni1 (1×) | 0.27474(2) | | | |
| | Ni2 (2×) | 0.28371(2) | | | |

Table V: Distances between the center of the octahedral cage $Ni_2Zn_4$ and Ni/Zn atoms in $\tau_4$-$Ni_3ZnB_2$ (recalculated from ref. [7]) and $\tau_6$-$Ni_2ZnB$.

| Cage | Center | Ligand | Distances (nm) | |
|---|---|---|---|---|
| | | | $\tau_4$-$Ni_3ZnB_2$ | $\tau_6$-$Ni_2ZnB$ |
| 1 | (0,½,½) | Zn1 (4×) | 0.19396(5) | 0.19060(2) |
| | | Ni2 (2×) | 0.17688(7) | 0.18265(2) |
| 2 | (¼,¼,½) | Zn1 (2×) | 0.24420(6) | 0.24153(3) |
| | | Zn1 (2×) | 0.13346(6) | 0.13450(2) |
| | | Ni1 (2×) | 0.21851(7) | 0.21392(3) |

Table VI: Bader charge analysis of DFT results for $\tau_3$-$Ni_{21}Zn_2B_{20}$. Atomic position (pos.), Bader volume $V_b$ in Å$^3$, corresponding radius $R_b$ in Å, volume difference $\Delta V_b$ in Å$^3$ and ionic charge $\Delta q_{ion}$ in units of the proton charge defined as difference of the Bader charge of the selfconsistent calculations minus the charge of the superposed electron densities of the free atoms.

| **pos.** | **$V_b$** | **$R_b$** | **Ä$V_b$** | **Äq$_{ion}$** |
|---|---|---|---|---|
| Ni1 | 9.89 | 2.11 | -0.32 | 0.32 |
| Ni2 | 9.46 | 2.08 | -0.33 | 0.38 |
| Ni3 | 10.52 | 2.16 | -0.24 | 0.28 |
| Ni4 | 10.05 | 2.12 | 0.03 | 0.09 |
| Ni5 | 10.10 | 2.13 | 0.07 | 0.09 |
| Ni6 | 9.62 | 2.09 | -0.16 | 0.33 |
| Zn | 12.01 | 2.25 | -0.80 | 0.38 |
| B1 | 7.05 | 1.89 | 0.23 | -0.28 |
| B2 | 6.57 | 1.84 | 0.42 | -0.41 |
| B3 | 6.80 | 1.87 | 0.34 | -0.34 |

Table VII: Bader charge analysis of DFT results for $\tau_4$-$Ni_3ZnB_2$. Atomic position (pos.), Bader volume $V_b$ in Å$^3$, corresponding radius $R_b$ in Å, volume difference $\Delta V_b$ in Å$^3$ and ionic charge $\Delta q_{ion}$ in units of the proton charge defined as difference of the Bader charge of the selfconsistent calculations minus the charge of the superposed electron densities of the free atoms.

| **pos.** | **$V_b$** | **$R_b$** | **Ä$V_b$** | **Äq$_{ion}$** |
|---|---|---|---|---|
| Ni1 | 10.82 | 2.18 | 0.22 | 0.02 |
| Ni2 | 10.79 | 2.18 | 0.09 | 0.11 |
| Ni3 | 9.05 | 2.05 | -0.38 | 0.34 |
| Zn | 12.15 | 2.26 | -0.70 | 0.26 |
| B1 | 7.11 | 1.89 | 0.42 | -0.39 |
| B2 | 6.77 | 1.86 | 0.34 | -0.34 |

Table VIII: Bader charge analysis of DFT results for $\tau_5$- $Ni_3Zn_2B$. Atomic position (pos.), Bader volume $V_b$ in Å$^3$, corresponding radius $R_b$ in Å, volume difference $\Delta V_b$ in Å$^3$ and ionic charge $\Delta q_{ion}$ in units of the proton charge defined as difference of the Bader charge of the selfconsistent calculations minus the charge of the superposed electron densities of the free atoms.

| **pos.** | **$V_b$** | **$R_b$** | **ÄV$_b$** | **Äq$_{ion}$** |
|---|---|---|---|---|
| Ni1 | 11.36 | 2.21 | 0.45 | -0.10 |
| Ni2 | 11.51 | 2.22 | 0.39 | -0.06 |
| Ni3 | 10.56 | 2.16 | 0.13 | 0.05 |
| Zn1 | 11.86 | 2.25 | -0.64 | 0.24 |
| Zn2 | 11.99 | 2.25 | -0.66 | 0.24 |
| B | 7.32 | 1.91 | 0.33 | -0.38 |

Table IX: Bader charge analysis of DFT results for $\tau_6$-$Ni_2ZnB$. Atomic position (pos.), Bader volume $V_b$ in Å$^3$, corresponding radius $R_b$ in Å, volume difference $\Delta V_b$ in Å$^3$ and ionic charge $\Delta q_{ion}$ in units of the proton charge defined as difference of the Bader charge of the selfconsistent calculations minus the charge of the superposed electron densities of the free atoms.

| **pos.** | **$V_b$** | **$R_b$** | **ÄV$_b$** | **Äq$_{ion}$** |
|---|---|---|---|---|
| Ni1 | 10.78 | 2.18 | 0.09 | 0.10 |
| Ni2 | 10.76 | 2.17 | 0.22 | 0.02 |
| Zn | 12.21 | 2.27 | -0.70 | 0.26 |
| B | 6.99 | 1.88 | 0.38 | -0.38 |

Table X. Comparison of experimental single crystal and DFT calculated lattice and atom parameters for $\tau_3$ to $\tau_6$ (all structures standardized with program *Structure Tidy* [23]).

| **Parameter/compound** | **$\tau_3$-$Ni_{21}Zn_2B_{20}$ - SC data** | **DFT data** |
|---|---|---|
| *a* [nm]; *c* [nm] | 0.72103(1); 1.42842(5) | 0.718896; 1.426445 |
| **16 Ni1** in 16*n* (0, *y*, *z*) | *y*=0.30020(5), *z*=0.10062(3) | *y*=0.299922, *z*=0.100786 |
| **8 Ni2** in 8*j* (*x*, ½, 0) | *x*=0.24032(8) | *x*=0.239928 |
| **8 Ni3** in 8*f* (¼, ¼, ¼) | | |
| **4 Ni4** in 4*d* (0,½,¼) | | |
| **2 Ni5** in 2*a* (0, 0, 0) | | |
| **4 Ni6** in 4*e* (0,0,*z*) | *z*=0.36216(5) | *z*=0.361496 |
| **4 Zn** in 4*e* (0, 0, *z*) | *z*=0.19029(5) | *z*=0.189985 |
| **16 B1** in 16*n* (0, *y*, *z*) | *y*=0.2984(4); *z*=0.3453(2) | *y*=0.299797; *z*=0.345918 |
| **16 B2** in 16*m* (*x*, *x*, *z*) | *x*=0.2929(3), *z*=0.1059(2) | *x*=0.293361, *z*=0.105781 |
| **16 B3** in 16*l* (*x*, *x*, 0) | *x*=0.2025(4) | *x*=202205 |

| **Parameter/compound** | **$\tau_5$-$Ni_3Zn_2B$ single crystal data** | **DFT data** |
|---|---|---|
| *a* (SC) [nm] | 0.95101(4) | 0.950651 |
| *b* (SC) [nm]; β (SC) [°] | 0.2892(4); 101.097(3) | 0.288048; 101.402 |
| *c* (SC) [nm] | 0.84366(3) | 0.844890 |
| **4 Ni1** in 4*i* (*x, 0, z*) | *x* =0.21879(5), *z*=0.25127(6) | *x* =0.218009, *z*=0.251072 |
| **4 Ni2** in 4*i* (*x, 0, z*) | *x* =0.49680(5), *z*=0.28968(6) | *x* =0.494699, *z*=0.288199 |
| **4 Ni3** in 4*i* (*x, 0, z*). | *x* =0.63894(5), *z*=0.00305(6) | *x* =0.638427, *z*=0.002498 |
| **4 Zn** in 4*i* (*x, 0, z*) | *x* =0.13845(5), *z*=0.52534(5) | *x* =0.138285, *z*=0.524851 |
| **4 B1** in 4*i* (*x, 0, z*) | *x* =0.1550(5), *z*=0.8151(5) | *x* =0.156015, *z*=0.815686 |
| **4 B2** in 4*i* (*x, 0, z*) | *x* =0.0145(5), *z*=0.1119(5) | *x* =0.014606, *z*=0.111747 |

[a]crystal structure data are standardized using the program Structure Tidy[20].
[b]nominal composition of the alloy from which a single crystal was isolated.
[c]anisotropic atomic displacement parameters $U_{ij}$ in [$10^2$ $nm^2$].

| **Parameter/compound** | **$\tau_5$-$Ni_3Zn_2B$ single crystal data** | **DFT data** |
|---|---|---|
| *a*(SC) / *a*(XPD-Si standard) (nm) | 1.68942(8) / 1.6934(2) | 1.696467 |
| *b*(SC) / *b*(XPD-Si standard) (nm) | 0.26332(1) / 0.26448(1) | 0.263834 |
| *c*(SC) / *c*(XPD-Si standard) (nm) | 0.61904(3) / 0.62152(3) | 0.619690 |
| *β*(SC) / *β*(XPD-Si standard) (°) | 111.164(2) / 111.170(4) | 111.344 |
| **4 Ni1** in 4i (x,0,z); **occ.** | x= 0.07909(2); z = 0.10781(5) | x= 0.079453; z = 0.110651 |
| **4 Ni2** in 4i (x,0,z); **occ.** | x= 0.11705(2); z = 0.56127(5) | x= 0.116902; z = 0.559792 |
| **4 Ni3** in 4i (x,0,z); **occ.** | x= 0.24022(2); z = 0.32068(5) | x=0.239784; z = 0.320496 |
| **4 Zn1** in 4i (x,0,z); occ. | x= 0.32445(2); z = 0.05714(5) | x= 0.324597; z = 0.058113 |
| **4 Zn2** in 4i (x,0,z); occ. | x= 0.48766(2); z = 0.27981(5) | x= 0.487293; z = 0.279410 |
| **B** in 4i (x,0,z); occ. | x= 0.3476(2); z = 0.6437(5) | x= 346310; z = 0.640957 |

| **Parameter/compound** | **$\tau_6$-$Ni_2ZnB$ single crystal data** | **DFT data** |
|---|---|---|
| *a*(SC) / *a*(XPD-Si standard) (nm) | 0.95296(7) / 0.9549(6) | 0.954008 |
| *b*(SC) / *b*(XPD-Si standard) (nm) | 0.28371(2) / 0.28466(3) | 0.28435 |
| *c*(SC) / *c*(XPD-Si standard) (nm) | 0.59989(1) / 0.6006(3) | 0.601324 |
| *β*(SC) / *β*(XPD-Si standard) (°) | 93.009(4) / 93.01(5) | 92.996 |
| **4 Ni1** in 4i (x,0,z) | x= 0.45925(3); z = 0.19908(4) | x= 0.460496; z = 0.196963 |
| **4 Ni2** in 4i (x,0,z) | x= 0.72930(3); z = 0.16342(4) | x= 0.728978; z = 0.163505 |

| | | |
|---|---|---|
| **4 Zn** in 4i (x,0,z) | x= 0.13083(3); z = 0.46672(4) | x= 0.130741; z = 0.467678 |
| **4 B** in 4i (x,0,z) | x= 0.0931(2); z = 0.0515(4) | x= 0.094038; z = 0.049909 |

**Figures:**

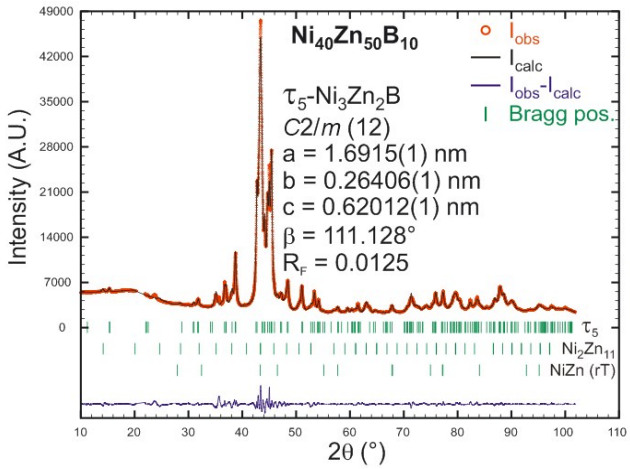


Figure I: Rietveld refinement of sample $Ni_{40}Zn_{50}B_{10}$ which contains three phases $\tau_5$-$Ni_3Zn_2B$, $Ni_2Zn_{11}$, and the room temperature modification rT-NiZn.

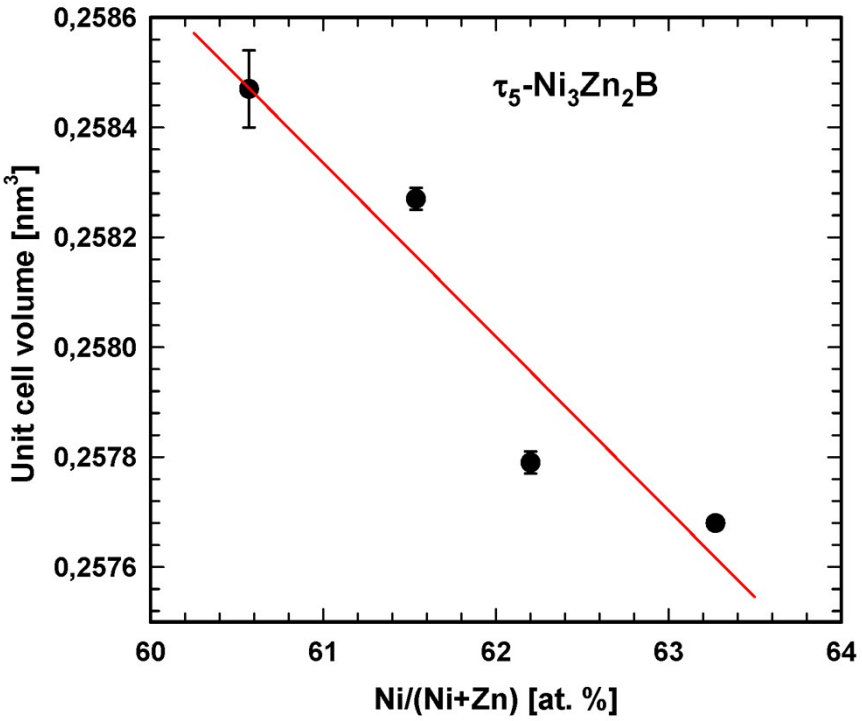


Figure II: Compositional dependence unit cell volume (from Rietveld refinement) of $\tau_5$-$Ni_3Zn_2B$; the solid line represents the linear fit according to Vegard‘s law.

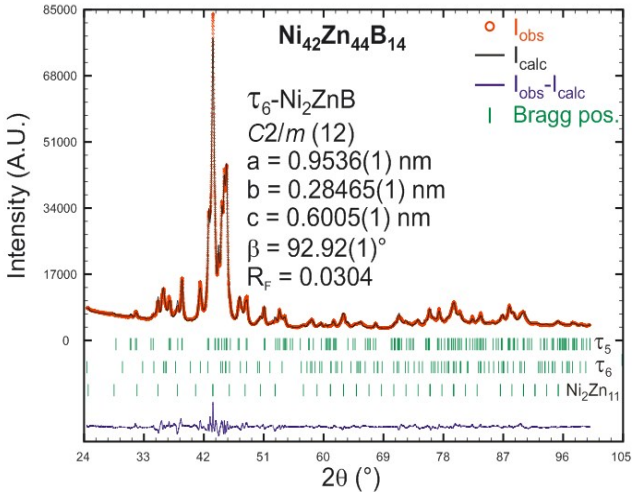


Figure III. Rietveld refinement of a three-phase alloy with nominal composition of $Ni_{42}Zn_{44}B_{14}$ (in at.%), containing $\tau_5$, $\tau_6$, and $Ni_2Zn_{11}$.

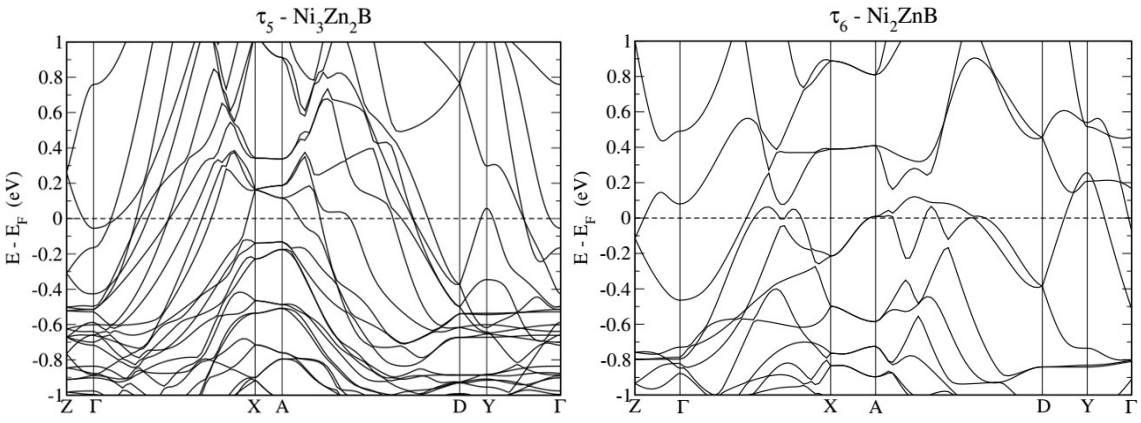


Figure IV. Electronic band structure of (a) $\tau_5$-$Ni_3Zn_2B$ and (b) $\tau_6$-$Ni_2ZnB$ along high symmetry directions. The coordinates of the symmetry points in reciprocal lattice units are Z(½,0,0), Γ(0,0,0) X(0,½,0), A(½,½,0), D(½,0,½), Y(0,0,½).

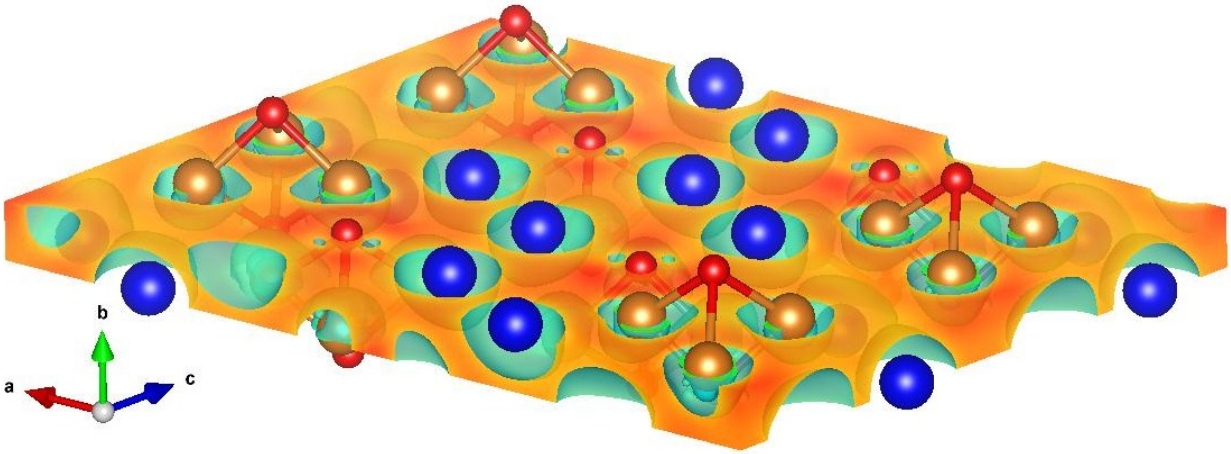


Figure V: Differences of self consistent minus superposed free atom charge density for $\tau_5$-$Ni_3Zn_2B$ as in Fig. 25 but with rotated axis. Colouring of atoms: Ni gold, Zn blue, B red. Graphic produced by VESTA.[46]

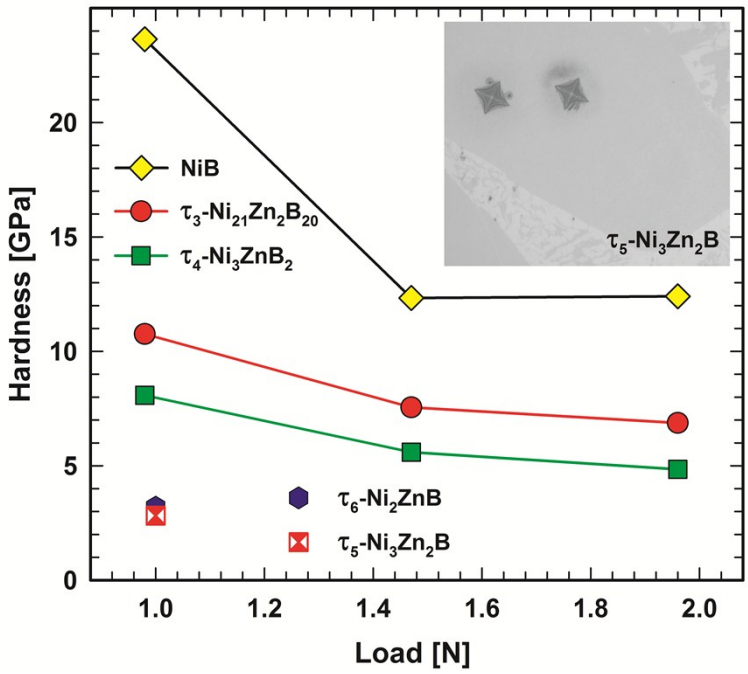


Figure VI. Vickers hardness of various $Ni_xZn_yB_z$ borides from microhardness measurements (as a function of load) and from nano-indentation. Insert: $H_V$ impressions in a grain of $\tau_5$. Data for NiB, $\tau_3$, and $\tau_4$ are from ref. [9].