Supplementary Information for

"Hierarchical and chemical space partitioning in new intermetallic borides $M\mathrm{Ni}_{21}\mathrm{B}_{20}$ (M = In, Sn)"

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Table S1. Interatomic distances (Å) in the structures of $SnNi_{21}B_{20}$ and $InNi_{21}B_{20}$

Atoms		$SnNi_{21}B_{20}$	$InNi_{21}B_{20}$	CN[a]
M[b]	–12Ni3	2.9350(4)	2.9179(4)	12
Ni1	–4B2	2.039(4)	2.021(4)	12
	–8Ni3	2.5703(3)	2.5646(3)	
Ni2	–4B2	2.162(5)	2.170(4)	16
	–4B1	2.164(4)	2.154(5)	
	–4Ni3	2.7176(9)	2.7169(9)	
	–4Ni2	2.719(2)	2.731(2)	
Ni3	–2B1	2.091(4)	2.096(4)	15
	–4B2	2.186(3)	2.183(3)	
	–2Ni1	2.5703(3)	2.5646(3)	
	–2Ni2	2.7176(9)	2.7169(9)	
	–1*M*	2.9350(4)	2.9179(4)	
	–4Ni3	2.9350(4)	2.9179(4)	
B1	–3B2	1.760(6)	1.764(5)	9
	–3Ni3	2.091(4)	2.096(4)	
	–3Ni2	2.164(4)	2.154(5)	
B2	–2B1	1.760(6)	1.764(5)	9
	–1Ni1	2.039(4)	2.021(4)	
	–2Ni2	2.162(5)	2.170(4)	
	–4Ni3	2.186(3)	2.183(3)	

[a] CN= coordination number; *M* = Sn or In

Table S2. Crystallographic data for $SnNi_{21}B_{20}$ and $InNi_{21}B_{20}$ at low temperatures from synchrotron diffraction data

Composition	$SnNi_{21}B_{20}$	$InNi_{21}B_{20}$
Space group	$Pm\bar{3}m$	
a (Å)	7.17585(2)	7.16608(9)
V (Å^3)	369.505(3)	368.00(2)
Calculated density/(g cm^{-3})	7.045	7.056
Z	1	
λ (Å)	0.40073	
2θ range (°)	1 to 40	
T/K	100	80
μ/mm^{-1}	8.598	8.424
Reflns in measured	19499	
Refined parameters	18	15
Refinement method	Full-profile Rietveld	
R_I; R_p	0.057; 0.086	0.064; 0.080

Table S3. Atomic coordinates, isotropic and anisotropic displacement parameters (in Å^2) for $SnNi_{21}B_{20}$ and $InNi_{21}B_{20}$ respectively at 100 K and 80 K from synchrotron diffraction data

Atom	site	x	y	z	B_{iso}/B_{eq}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$SnNi_{21}B_{20}$											
Sn	1*a*	0	0	0	1.33(2)	1.33(3)	B_{11}	B_{11}	0	0	0
Ni1	3*d*	0	0	1/2	1.18(3)	1.02(4)	B_{11}	1.50(6)	0	0	0
Ni2	6*f*	1/2	0.2319(2)	1/2	1.14(2)	1.04(3)	1.35(5)	B_{11}	0	0	0
Ni3	12*i*	0.28889(6)	*x*	0	1.16(2)	1.24(2)	B_{11}	0.99(4)	0.15(2)	0	0
B1	8*g*	0.2920(5)	*x*	*x*	1.33(7)	1.3(1)	B_{11}	B_{11}	–0.3(2)	B_{12}	B_{12}
B2	12*j*	1/2	0.2011(5)	*y*	1.0(1)	0.9(2)	1.1(1)	B_{22}	0	0	0.1(2)
$InNi_{21}B_{20}$											
In	1*a*	0	0	0	0.97(1)	0.97(2)	B_{11}	B_{11}	0	0	0
Ni1	3*d*	0	0	1/2	0.85(3)	0.79(3)	B_{11}	0.95(5)	0	0	0
Ni2	6*f*	1/2	0.2308(1)	1/2	0.77(2)	0.72(2)	0.86(4)	B_{11}	0	0	0
Ni3	12*i*	0.28725(5)	*x*	0	0.81(1)	0.90(2)	B_{11}	0.64(3)	0.07(2)	0	0
B1	8*g*	0.2921(5)	*x*	*x*	1.1(1)						
B2	12*j*	1/2	0.1990(4)	*y*	0.98(7)						

Table S4. Crystallographic data for $SnNi_{21}B_{20}$ at 293 K from single crystal diffraction data

Composition	$SnNi_{21}B_{20}$
Space group	$Pm\bar{3}m$
a (Å)	7.1834(1)
V (Å^3)	370.67(2)
Calculated density/(g cm^{-3})	7.023
Z	1
Radiation; λ (Å)	Mo K_{α}; 0.71073 Å
$2\theta_{max}$(°)	67.16
$N(hkl)_{measured}$	3035
$N(hkl)_{unique}$	185
$N(hkl)_{observed}$ ($F_{hkl} > 4\sigma(F)$)	178
R_{int}/R_{σ}	0.089/0.041
Refined parameters	16
R_F/wR_F^2	0.063/0.065
Extinction coefficient	–

Table S5. Atomic coordinates, isotropic and anisotropic displacement parameters (in Å^2) for $SnNi_{21}B_{20}$ at 293 K from single crystal diffraction data

Atom	site	x	y	z	B_{iso}/B_{eq}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	1a	0	0	0	1.48(3)	1.48(5)	B_{11}	B_{11}	0	0	0
Ni1	3d	0	0	$^1/_2$	1.13(5)	0.89(7)	B_{11}	1.6(2)	0	0	0
Ni2	6f	$^1/_2$	0.2324(3)	$^1/_2$	0.82(3)	0.74(4)	0.99(7)	B_{11}	0	0	0
Ni3	12i	0.2888(1)	x	0	1.05(3)	1.22(4)	B_{11}	0.71(6)	0.21(4)	0	0
B1	8g	0.296(1)	x	x	0.7(2)						
B2	12j	$^1/_2$	0.1967(9)	y	0.7(2)						

Table S6. Physical properties of MNi$_{21}$B$_{20}$ (M = Sn, In)

M	χ_0 (emu mol^{-1})	ρ_0 (μΩm)	ρ_{300} (μΩm)	RRR	γ (mJ mol^{-1} K^{-2})	β (J mol^{-1}K^{-4})	δ (J mol^{-1} K^{-6})	$\Theta_D(0)$ (K)
Sn	8.28(2)×10^{-4}	4.02(6) ×10^{-2}	1.65	41	76.9(1)	2.83(4)×10^{-4}	2.55(2) ×10^{-6}	661
In	5.90(2)×10^{-4}	3.20(6) ×10^{-2}	8.85×10^{-1}	27.7	59.3(1)	3.66(4) ×10^{-4}	1.99(4) ×10^{-6}	606

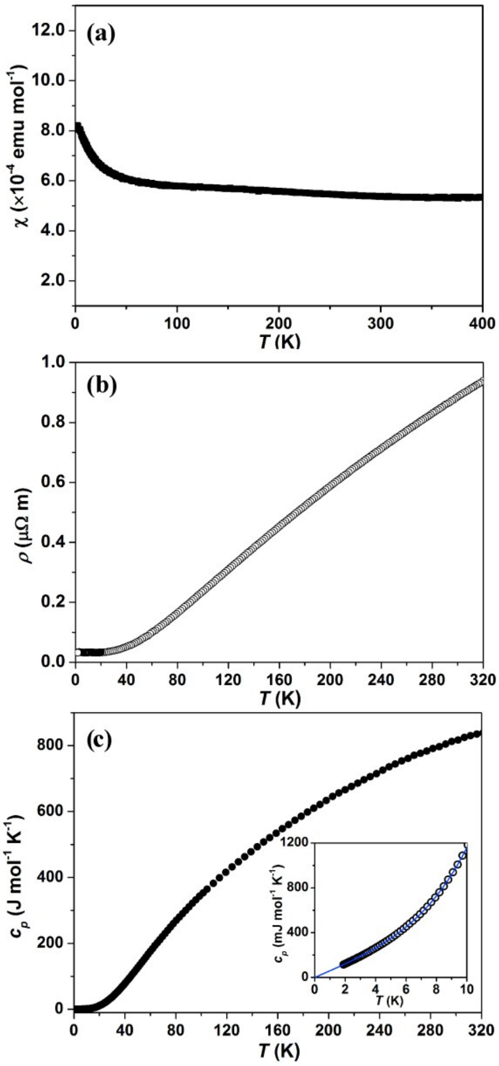

Figure S1. Physical properties of $InNi_{21}B_{20}$: (a) temperature-dependent magnetic susceptibility $\chi(T)$ in the external magnetic fields $\mu_0 H = 7.0$ T; (b) temperature-dependence of electrical resistivity $\rho(T)$; (c) temperature-dependence of heat capacity $c_p(T)$, and the inset shows its fitting by $c_p(T) = \gamma T + \beta T^3 + \delta T^5$ from 2.0 K to 10K.