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Crystal Structure Refinements of Ni_3B, o-Ni_4B_3 and m-Ni_4B_3

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The crystal structures of the nickel borides Ni_3B, o-Ni_4B_3, and m-Ni_4B_3 previously determined by two-dimensional Fourier methods have now been refined from three-dimensional intensity materials using the least-squares method. The least-squares refinement has resulted in much more reliable Ni—B and B—B distances as compared with those originally reported.

In earlier investigations of the nickel borides by one of the present authors,[1,2] the compound Ni_3B and two further borides with the ideal crystallographic formula Ni_4B_3 were studied. The two latter compounds were denoted o-Ni_4B_3 and m-Ni_4B_3 in accordance with their crystallographic symmetries: orthorhombic and monoclinic, respectively. Although a critical examination of composition and modes of formation was not made, it was observed that m-Ni_4B_3 has a higher boron content than o-Ni_4B_3. Small variations in the unit cell dimensions indicated a moderate range of homogeneity for o-Ni_4B_3, while for Ni_3B and m-Ni_4B_3 no lattice parameter variations were observed.

The nickel-boron system was recently re-investigated by Schöbel and Stadelmaier [3] using thermo-analytic, metallographic, and X-ray diffraction methods. The three compounds Ni_3B, o-Ni_4B_3, and m-Ni_4B_3 were all found to melt congruently, Ni_3B at 1166°C, o-Ni_4B_3 of composition 41.4 at% B at 1025°C, and m-Ni_4B_3 of composition 43.6 at% B at 1031°C. (The ideal formula Ni_4B_3 corresponds to 42.9 at% B).

Table 1. Structure data for Ni_3B.

Space group *Pnma*; $Z = 4$; $a = 5.2105$ Å; $b = 6.6174$ Å; $c = 4.3904$ Å; $\sigma(a) = 0.0005$ Å; $\sigma(b) = 0.0006$ Å; $\sigma(c) = 0.0004$ Å.

Atom	Position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Ni 1	8 *d*	0.1797	0.0005	0.0622	0.0007	0.3449	0.0006	0.32	0.03
Ni 2	4 *c*	0.0262	0.0007	—	—	0.8700	0.0009	0.37	0.05
B	4 *c*	0.8960	0.0071	—	—	0.4285	0.0081	0.81	0.42

Final R-value for the 219 observed reflexions: 0.078.

Table 2. Structure data for o-Ni_4B_3.

Space group $Pnma$; $Z = 4$; $a = 11.9540$ Å; $b = 2.9815$ Å; $c = 6.5684$ Å; $\sigma(a) = 0.0008$ Å; $\sigma(b) = 0.0003$ Å; $\sigma(c) = 0.0005$ Å.

Atom	Position	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Ni 1	4 c	0.1484	0.0003	0.9912	0.0005	0.37	0.05
Ni 2	4 c	0.4497	0.0003	0.7490	0.0005	0.27	0.05
Ni 3	4 c	0.2002	0.0003	0.3788	0.0005	0.27	0.04
Ni 4	4 c	0.3756	0.0003	0.1675	0.0005	0.30	0.05
B 1	4 c	0.4685	0.0020	0.4328	0.0034	−0.04	0.27
B 2	4 c	0.0356	0.0022	0.4815	0.0042	0.35	0.35
B 3	4 c	0.2565	0.0027	0.6792	0.0052	0.93	0.47

Final R-value for the 261 observed reflexions: 0.083.

Table 3. Structure data for m-Ni_4B_3.

Space group $C2/c$; $Z = 4$; $a = 6.4282$ Å; $b = 4.8795$ Å; $c = 7.8190$ Å; $\beta = 103.315°$; $\sigma(a) = 0.0005$ Å; $\sigma(b) = 0.0004$ Å; $\sigma(c) = 0.0006$ Å; $\sigma(\beta) = 0.008°$.

Atom	Position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Ni 1	8 f	0.0442	0.0003	0.2481	0.0005	0.4835	0.0002	0.15	0.02
Ni 2	8 f	0.2024	0.0003	0.5695	0.0005	0.2864	0.0002	0.08	0.02
B 1	8 f	0.2324	0.0021	0.9230	0.0036	0.4396	0.0016	0.08	0.12
B 2	4 e	—	—	0.9358	0.0058	—	—	0.41	0.23

Final R-value for the 583 observed reflexions: 0.108.

Table 4. Interatomic distances (Å) and their standard deviations in Ni_3B. Distances shorter than 3.4 Å listed.

		Dist.	S.d.			Dist.	S.d.
Ni 1 —	B	1.966	0.029	Ni 2 —	2 Ni 1	2.512	0.004
	B	2.063	0.029		2 Ni 1	2.524	0.004
	B	2.327	0.017		B	2.544	0.036
	2 Ni 1	2.456	0.003		2 Ni 1	2.555	0.004
	Ni 1	2.458	0.005		2 Ni 1	2.575	0.004
	Ni 1	2.486	0.009		2 Ni 1	2.739	0.004
	Ni 2	2.512	0.004		2 Ni 2	2.810	0.003
	Ni 2	2.524	0.004				
	Ni 2	2.555	0.004	B —	2 Ni 1	1.966	0.029
	Ni 2	2.575	0.004		Ni 2	2.054	0.036
	2 Ni 1	2.735	0.001		2 Ni 1	2.063	0.029
	Ni 2	2.739	0.004		Ni 2	2.120	0.037
					2 Ni 1	2.327	0.017
Ni 2 —	B	2.054	0.036		Ni 2	2.544	0.036
	B	2.120	0.037		2 B	3.040	0.037

The crystal structures of the three borides were determined by Rundqvist [1,2] on the basis of three-dimensional single-crystal intensity data, but owing to the lack of adequate computing facilities, the refinements of the structures were carried out by means of two-dimensional Fourier methods only. In view of the new phase-analytical information available on the nickel borides it was thought worthwhile to bring the corresponding crystallographic information

Table 5. Interatomic distances (Å) and their standard deviations in o-Ni_4B_3. Distances shorter than 3.2 Å listed.

		Dist.	S.d.
Ni 1 —	2 B 1	2.079	0.016
	B 1	2.208	0.023
	2 B 3	2.245	0.025
	B 3	2.421	0.034
	2 Ni 3	2.458	0.004
	2 Ni 2	2.543	0.004
	2 Ni 4	2.613	0.004
	Ni 3	2.620	0.005
	Ni 2	2.852	0.005
	Ni 4	2.952	0.005
	2 Ni 1	2.981	0.000
Ni 2 —	B 2	2.046	0.027
	B 1	2.089	0.022
	2 B 2	2.142	0.020
	2 B 1	2.146	0.016
	B 3	2.356	0.032
	2 Ni 3	2.482	0.004
	2 Ni 1	2.543	0.004
	2 Ni 4	2.624	0.004
	Ni 1	2.852	0.005
	Ni 4	2.888	0.005
	2 Ni 2	2.981	0.000
Ni 3 —	2 B 3	2.052	0.023
	B 2	2.081	0.026
	B 3	2.085	0.034
	2 Ni 1	2.458	0.004
	2 Ni 2	2.482	0.004
	Ni 4	2.515	0.005
	2 Ni 4	2.577	0.004
	Ni 1	2.620	0.005
	2 Ni 2	2.981	0.000
Ni 4 —	B 1	2.066	0.022
	B 2	2.148	0.026
	2 B 3	2.172	0.024
	2 B 2	2.201	0.020
	Ni 3	2.515	0.005
	2 Ni 3	2.577	0.004
	2 Ni 1	2.613	0.004
	2 Ni 2	2.624	0.004
	Ni 2	2.888	0.005
	Ni 1	2.952	0.005
	2 Ni 4	2.981	0.000
B 1 —	2 B 1	1.889	0.027
	Ni 4	2.066	0.022
	2 Ni 1	2.079	0.016
	Ni 2	2.089	0.022
	2 Ni 2	2.146	0.016
	Ni 1	2.208	0.023
	B 2	2.837	0.035
	2 B 1	2.981	0.000
	B 3	3.008	0.040
B 2 —	2 B 2	1.733	0.026
	Ni 2	2.046	0.027
	Ni 3	2.081	0.026
	2 Ni 2	2.142	0.020
	Ni 4	2.148	0.026
	2 Ni 4	2.201	0.020
	B 1	2.837	0.035
	B 3	2.942	0.042
	2 B 2	2.981	0.000
B 3 —	2 Ni 3	2.052	0.023
	Ni 3	2.085	0.034
	2 Ni 4	2.172	0.024
	2 Ni 1	2.245	0.025
	Ni 2	2.356	0.032
	Ni 1	2.421	0.034
	B 2	2.942	0.042
	2 B 3	2.981	0.000
	B 1	3.008	0.040

up to present standards of accuracy. In the following, the results are given from complete threedimensional least-squares structure refinements of Ni_3B, o-Ni_4B_3, and m-Ni_4B_3.

The unit cell dimensions were refined by the least-squares method from powder diffraction data obtained earlier.[1,2] The single-crystal intensity data from the earlier work [1,2] were used directly for the least-squares refinements of atomic positions and individual isotropic temperature factors. The computations were carried out on a CDC 3600 machine using a programme originally written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A. and modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden. Atomic scattering factors were taken from Ref. 4.

Table 6. Interatomic distances (Å) and their standard deviations in m-Ni_4B_3. Distances shorter than 3.2 Å listed.

		Dist.	S.d.			Dist.	S.d.
Ni 1 —	B 1	2.071	0.016	Ni 2 —	Ni 1	2.568	0.003
	B 1	2.132	0.014		2 Ni 2	2.610	0.001
	B 1	2.145	0.016		Ni 1	2.635	0.003
	B 1	2.170	0.014		Ni 1	2.802	0.003
	B 2	2.345	0.018		Ni 1	2.808	0.003
	B 2	2.345	0.011		Ni 1	3.074	0.003
	Ni 1	2.514	0.005				
	Ni 2	2.515	0.003	B 1 —	B 2	1.848	0.013
	Ni 2	2.530	0.003		B 1	1.922	0.033
	Ni 1	2.549	0.005		Ni 2	2.038	0.013
	Ni 2	2.568	0.003		Ni 1	2.071	0.016
	Ni 1	2.599	0.004		Ni 2	2.083	0.016
	Ni 2	2.635	0.003		Ni 2	2.086	0.012
	Ni 2	2.802	0.003		Ni 1	2.132	0.014
	Ni 2	2.808	0.003		Ni 1	2.145	0.016
	Ni 2	3.074	0.003		Ni 1	2.170	0.014
					B 2	3.161	0.021
Ni 2 —	B 1	2.038	0.013				
	B 1	2.083	0.016	B 2 —	2 B 1	1.848	0.013
	B 1	2.086	0.012		2 Ni 2	2.102	0.009
	B 2	2.102	0.009		2 Ni 2	2.191	0.023
	B 2	2.191	0.023		2 Ni 1	2.345	0.018
	Ni 1	2.515	0.003		2 Ni 1	2.345	0.011
	Ni 1	2.530	0.003		2 B 1	3.161	0.021
	Ni 2	2.533	0.004				

The results of the refinements are given in Tables 1, 2, and 3. Interatomic distances are listed in Tables 4, 5, and 6.

The new values obtained are in good agreement with the previously reported results. (Due to printing errors, the minus signs of $x_{Ni\ 2}$ and y_B for Ni_3B in Ref. 1 and of $y_{B\ 1}$ and $y_{B\ 2}$ for m-Ni_4B_3 in Ref. 2 are missing. The interatomic distances given in Refs. 1 and 2 are based on the correct parameter values.) The use of three-dimensional intensity material has led to a considerable improvement of the boron parameters, resulting in much more reliable Ni—B and B—B distances as compared with the values originally reported.

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