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Crystal Structure of Ni_3B and Co_3B

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Ni_3B and Co_3B are isostructural with cementite (Fe_3C). A single-crystal structure determination of Ni_3B has been made. Some properties of the cementite structure are discussed.

X-Ray investigations of the Co-B and Ni-B systems have revealed the existence of two isomorphous borides Co_3B and Ni_3B. Co_3B has not been reported in earlier work on the Co-B system [1-3]. Ni_3B has previously been found by Andersson and Kiessling [4] but no X-ray data were published. The powder diffraction lines of Co_3B and Ni_3B, which could be indexed with orthorhombic unit cells (Table 1), showed close resemblance to the cementite (Fe_3C) powder pattern [5].

The first X-ray investigation of cementite was carried out by Westgren and Phragmén [6,7], who determined the orthorhombic unit cell using powder and single-crystal methods. From Westgren's and Phragmén's data Hendricks [8] deduced the space group ($P\,b\,n\,m$) and the iron positions. Different positions of the carbon atoms were proposed by Hendricks and by Westgren [9]. Westgren's structure proposal was later confirmed by Lipson and Petch [10] who settled the carbon positions with threedimensional Fourier methods using accurate intensity measurements from powder photographs. However, Lipson's and Petch's intensity material was rather limited (26 independent reflexions, in four cases with overlaps) and since no actual single-crystal determination of the cementite structure has been made, it seemed desirable to determine the structure of Co_3B or Ni_3B with the single-crystal technique.

EXPERIMENTAL

The borides were prepared from elementary boron (97.5 %), nickel powder (99.8 %) and cobalt powder (99.2 %, containing 0.45 % nickel) either by arcmelting or by sintering at 900°—1 000°C in evacuated and sealed silica tubes. X-Ray powder photographs were taken in Guinier-type focusing cameras with Cr-$K\alpha$ or Cu-$K\alpha$ radiation, using CaF_2 as standard. Ni_3B was chosen for the single-crystal work, and small crystal fragments were picked from crushed melts. The zero-layer line around the b-axis and the layer-lines 0—8 around the c-axis were recorded with Mo-K radiation in a multiple-film Weissenberg camera with thin iron foils between successive films. About 250 nonequivalent intensities were visually estimated by comparison with a standard intensity scale. Relative $|F|^2$.

values were calculated with the aid of Lu's curves [11]. An empirical correction for thermal movement and Θ-dependent absorption was obtained by plotting log F_o/F_c against $\sin^2\Theta$. Fourier summations were made on the Hägg-Laurent machine [12].

DETERMINATION OF THE STRUCTURE

All reflexions were consistent with space group $P\,b\,n\,m$. Starting with the assumption that the signs of the corresponding structure factors in Fe_3C and Ni_3B were the same, correct signs of all Ni_3B reflexions were determined by successive refinements of the electron density projections $\varrho\,(xz)$ and $\varrho\,(xy)$. The nickel positions obtained from the projections were further refined with electron density maps in the $(x\ y\ 1/4)$ plane using the entire intensity material. By difference synthesis in the same plane the positions of the boron atoms were found. After the last refinement, the reliability index was 0.11.

The result of the structure determination is collected in Table 2. Interatomic distances are listed in Table 3.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The cementite structure has been discussed by several authors [8-10,13,14]. The packing of the metal atoms is rather complicated and attempts have been made to interpret the structure in terms of deformed austenite or martensite structures. In view of the result of the Ni_3B structure determination, a comparison of the cementite structure with boride structures might also be justified.

As pointed out by Lipson and Petch, the cementite structure is built up of successive metal atom layers parallel with {103}. The layers are composed of a slightly corrugated array of interconnected squares and triangles with

Table 1. Unit cell dimensions of Co_3B and Ni_3B in Å. (Estimated accuracy ± 0.05 %).

	Co_3B	Ni_3B
a	4.408	4.389
b	5.225	5.211
c	6.629	6.619

Table 2. Atomic parameters in Ni_3B (space group $P\,b\,n\,m$). (Estimated accuracy of the Ni parameters ± 0.002).

	x	y	z
Ni_I in 8 d	0.347	0.178	0.061
Ni_{II} in 4 c	−0.136	0.028	—
B in 4 c	0.43_3	0.11_0	—

Table 3. Interatomic distances in Ni_3B in Å.

Ni_I −11 Ni	2.43, 2.46 (2), 2.50 (2), 2.55, 2.57, 2.58, 2.71, 2.74 (2).
Ni_{II}−12 Ni	2.50 (2), 2.55 (2), 2.57 (2), 2.58 (2), 2.71 (2), 2.79 (2).
B − 9 Ni	1.99 (2), 2.02, 2.07 (2), 2.09, 2.30 (2), 2.59.

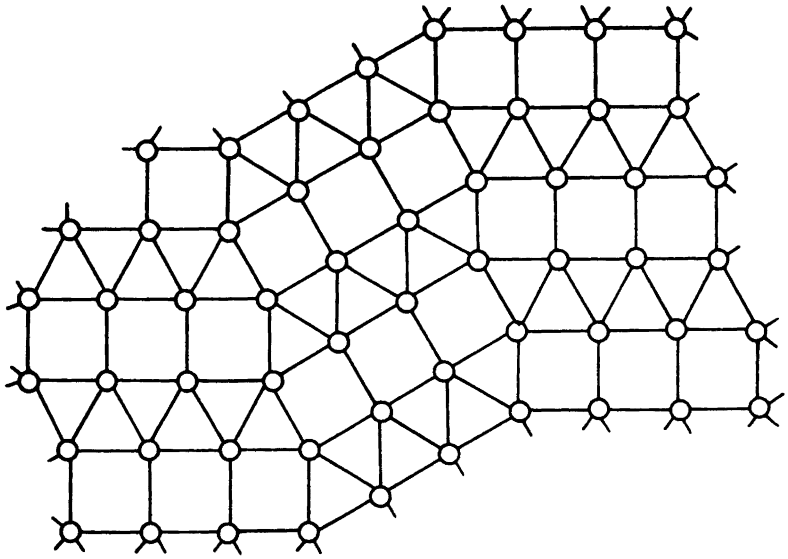

Fig. 1. Nickel atom layers parallel with {103} in Ni_3B.

metal atoms in the corners (Fig. 1). It is seen From Figs. 1, 2 and 3, that these layers may be regarded as an intermediate between the slightly corrugated atom layers parallel with $\{10\bar{1}1\}$ in hexagonal close-packed structures and the metal atom layers parallel with {001} in Ni_2B and Co_2B. These borides both have the $CuAl_2$ structure, which has been discussed by Black [15].

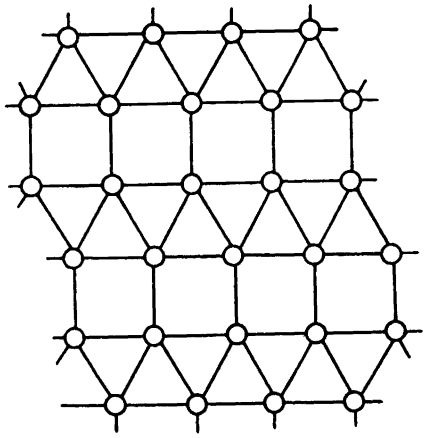

Fig. 2. Atom layers parallel with $\{10\bar{1}1\}$ in hexagonal close-packed structures.

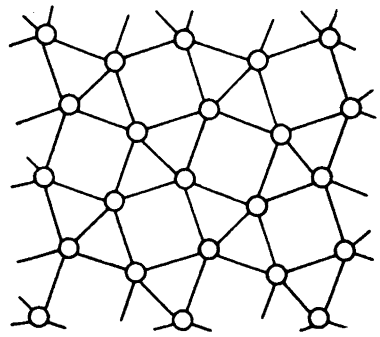

Fig. 3. Metal atom layers parallel with {001} in Me_2B-borides with the $CuAl_2$ structure.

The resemblance to other boride structures becomes more evident when the environment of the boron atoms in Ni_3B is considered. As seen from Table 3, the boron atoms are surrounded by nine nickel atoms. The six closest neighbours are situated in the corners of a triangular prism, the remaining three are situated at larger distances outside the rectangular sides of the prism. The triangular prismatic coordination around the boron atoms has been found in several types of transition metal borides [16]. The mean distance between the boron atoms and the six closest nickel atoms is 2.04 Å. Assuming the nickel radius to be 1.25 Å, the boron atom radius is only 0.79 Å, approaching the value 0.77 Å of the carbon atom radius in cementite. According to Kiessling [16] the normal boron radius is 0.86 Å.

Besides Fe_3C, very few compounds with the cementite structure have hitherto been reported. Meyer and Kohlhaas [17,18] claimed the existence of cobalt cementite and nickel cementite, but Jacobson and Westgren [19] could not confirm the cementite structure of Ni_3C. Kuo and Persson [20] have prepared manganese cementite (Mn_3C).

The possibility of substituting some other element for carbon in Fe_3C while retaining the structure was discussed by Petch [13] from size-factor considerations. Since the atomic radii of B, C and N are, respectively, 0.86, 0.76 and 0.71 Å it might be expected that nitrogen should replace carbon easily whereas boron should experience difficulties. Analogously, carbon should replace boron in Co_3B and Ni_3B. In fact, it has been found that Co_3B dissolves carbon to a limited extent, probably less than 20 % at 1 000° as found from measurements of the contraction of the Co_3B unit cell in ternary Co-B-C alloys. The solubility of carbon in Ni_3B is probably very small, since no significant contraction of the Ni_3B unit cell in ternary Ni-B-C alloys has been detected.

However, in Fe_3C, no solubility of nitrogen has been found [21] whereas an extended solubility of boron exists [22,23]. The boron solubility limit in Fe_3C has been determined by Nicholson [23] who found it possible to replace up to 80 % of the carbon by boron at 1 000°C. Recently, Aronsson (private communication) has prepared a ternary phase $Fe_3(B, Si)$ with cementite structure.

From the foregoing it is evident that simple size-factor considerations cannot be used to predict the existence of new compounds with the cementite structure. An attempt to explain the stability of boron-substituted Fe_3C has been made by Massalski [24] and Nicholson. They assume that the cementite structure is critically adjusted to the electronic environment produced by carbon atoms in interstitial positions. When boron is substituting for carbon in these positions, a similar electronic environment can be maintained if one electron is donated from the 3d shell of iron. This theory is supported by the results of magnetic measurements made by Nicholson.

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REFERENCES

1. Bjurström, T. *Arkiv Kemi, Mineral. Geol.* **11** *A* (1933) 5.
2. Köster, W. and Mulfinger, W. *Z. Metallkunde* **30** (1938) 348.

3. Chizhevskiy, N. P. and Schmelev, B. A. *Trudy Moskov. Inst. Staliim. I. V. Stalina* **17** (1940) 3.
4. Andersson, L.-H. and Kiessling, R. *Acta Chem. Scand.* **4** (1950) 160.
5. Rundqvist, S. *Nature* **181** (1958) 259.
6. Westgren, A. and Phragmén, G. *J. Iron Steel Inst.* **105** (1922) 241.
7. Westgren, A. and Phragmén, G. *Ibid.* **109** (1924) 159.
8. Hendricks, S. B. *Z. Krist.* **74** (1930) 534.
9. Westgren, A. *Jernkontorets Ann.* **87** (1932) 457.
10. Lipson, H. and Petch, N. J. *J. Iron Steel. Inst.* **142** (1940) 95.
11. Lu, Chia-Si *Rev. Sci. Instr.* **14** (1943) 331.
12. Hägg, G. and Laurent, T. J. *J. Sci. Instr.* **23** (1946) 155.
13. Petch, N. J. *J. Iron Steel Inst.* **149** (1944) 143.
14. Hume-Rothery, W., Raynor, G. V. and Little, A. T. *Ibid.* **145** (1942) 143.
15. Black, P. J. *Acta Met.* **4** (1956) 172.
16. Kiessling, R. *Acta Chem. Scand.* **4** (1950) 209.
17. Meyer, W. Fr. *Metallwirtsch.* **17** (1938) 413.
18. Kohlhaas, R. and Meyer, W. Fr. *Ibid.* **17** (1938) 786.
19. Jacobson, B. and Westgren, A. *Z. physik. Chem.* **20** *B* (1933) 361.
20. Kuo, K. and Persson, L. E. *J. Iron Steel Inst.* **178** (1954) 39.
21. Jack, K. H. *Proc. Roy. Soc. London* **195** *A* (1948) 34.
22. Vogel, R. and Tamman, G. *Z. anorg. Chem.* **123** (1922) 225.
23. Nicholson, M. E. *J. Metals* **9** (1957) 1.
24. Massalski, T. B. *Theory of Alloy Phases* (1956) 97—98 (Am. Soc. for Metals, Cleveland, Ohio).

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