Crystallization of Massive Amorphous Boron

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Abstract: Wire-grown, massive amorphous boron heated in inert atmospheres at pressures of 10^{-5} to 10^{-6} torr was converted to the β-rhombohedral modification at 1000° or above. The extent of conversion depended on the time of treatment and was inhibited by the presence of 50 torr of argon or 30 torr of nitrogen. It is concluded that the conversion takes place by a surface diffusion mechanism. The stepwise development of a β-rhombohedral X-ray diffraction pattern suggests that massive amorphous boron may be a microcrystalline deposit of this particular modification of the element.

Massive amorphous boron has been described by Talley, *et al.*,[1] with particular attention to the material in the form of filaments. Others[2] have prepared the material by the same general procedure: reduction of a boron halide by hydrogen in the presence of a hot filament. The designation "amorphous" is based on the diffuse rings produced in X-ray diffraction by this form of boron. A typical powder diffraction pattern of an amorphous boron filament consists of diffuse halos with a line breadth of about $\Delta 2\theta = 5°$, at *d* spacings of 4.4, 2.5, 1.7, and 1.4 A.

Transformations from one crystal modification of boron to another have been discussed by Hoard[3] and Newkirk.[4] No reversible transformations have been reported. Johnston, *et al.*,[5] transformed an amorphous boron powder, prepared from decomposition of diborane at 700°, to a crystal modification now identified as β-rhombohedral, by heat treatment of the pelletized powder under reduced pressure for 10 min at 1700°. Amorphous boron filaments, prepared by Talley, *et al.*,[1] transformed to crystalline forms, one of which transmitted appreciable amounts of red light, on heat treatment at 1260°. Rossini, *et al.*,[6] have estimated the energy of transformation of amorphous to crystalline boron as 0.4 kcal/g-atom. Hoard[3] has stated that "a single polymorph, the β-rhombohedral modification, may turn out to be themodynamically stable over the whole range of temperatures (and more or less normal pressures)." The observations herein describe changes produced in massive amorphous boron filaments by heat treatments under reduced pressure and in the presence of inert gases.

Experimental Section

Boron filaments used for this study were prepared by Texaco Experiment Inc., Richmond, Va. Two types were examined: filaments made by reduction of boron trichloride by hydrogen in the presence of a heated tungsten wire; and filaments made by decomposition of a borane on a heated, carbon-coated silica filament. Additionally, tungsten-core filaments which were split longitudinally and from which the tungsten borides of the core had been removed by treatment with hot, 30% hydrogen peroxide were examined. The tungsten-core filaments were approximately 140 μ in diameter with a core about 13 μ in diameter. The silica-core filaments measured about 70 μ in diameter with a core about 15 μ in diameter. The purity of the boron portion of the filaments was typically greater than 99%. The tungsten-core boron filaments are commercially available. Conditions for preparation of the filaments are described by Talley, *et al.*,[1] who point out that the temperature of deposition should be about 1100° and should not exceed about 1200° to avoid deposition of polycrystalline boron. The samples used in this study were not subjected to further heat treatments prior to use. X-Ray diffraction patterns of the tungsten-core filaments showed the presence of crystalline phases of tungsten borides in addition to the previously mentioned diffuse halos of amorphous boron. The silica-core filaments gave only the diffuse halos characteristic of amorphous boron.

The filaments were heated in a Pyrex-glass chamber, 3 in. in diameter and 12 in. long, fitted with an O-ring-sealed, brass back plate with throughputs for electrical contacts, thermocouples, and gases. The chamber could be evacuated to pressures in the 10^{-5} to 10^{-6} torr range. Filaments were heated resistively using tantalum or stainless-steel contacts, or externally in a platinum-wound tube furnace. Temperature was measured with a disappearing filament type optical pyrometer for resistance heating and with a chromel–alumel thermocouple for furnace heating. To reduce the initial power requirements for heating silia-core and split filaments, and to avoid initial over-heating, the filaments were heated with the tube furnace until their resistance had dropped to a value which allowed smooth start-up and operation. The brightness temperatures reported have been corrected for an emittance of 0.65 for boron.[7]

The pressure of inert gases introduced into the reaction chamber was measured with a mercury manometer. Impurities were removed from them by passage through a train containing finely divided copper at 400°, ascarite, and magnesium perchlorate. No surface reactions, *i.e.*, oxidation or reaction with water vapor, were detected in samples heated in these atmospheres.

After treatment the filaments were removed and examined by reflected light microscopy, generally at a magnification of 450 ×, and by X-ray diffraction using a 14.32-cm diameter powder camera.

Results and Discussion

The effect of heating tungsten-core, amorphous boron filaments under reduced pressure at various temperatures is summarized in Table I. No change occurred in filaments held at temperatures below about 950° for relatively long periods. Filaments heated at 1000° exhibited a crystalline surface, the extent of which depended on the time at the elevated temperature. The surface appearance changed quite rapidly at temperatures above 1000°. Parallel experiments with silica-core filaments and with tungsten-core filaments

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[1] C. P. Talley, L. E. Line, Jr., and Q. D. Overman, Jr., in "Boron Synthesis, Structure, and Properties," J. A. Kohn, W. F. Nye, and G. K. Gaule, Ed., Plenum Press, New York, N. Y., 1960, pp 94–104.

[2] A. W. Laubengayer, D. T. Hurd, A. E. Newkirk, and J. L. Hoard, *J. Am. Chem. Soc.*, **65**, 1924 (1943).

[3] J. L. Hoard, in "From Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, pp 42–52.

[4] A. E. Newkirk, in "Boron, Metallo-Boron Compounds, and Boranes," R. M. Adams, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 233–299.

[5] H. L. Johnston, H. N. Hersh, and E. C. Kerr, *J. Am. Chem. Soc.*, 73, 1112 (1951).

[6] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffee, National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952, p 313.

[7] C. P. Talley, private communication.

which were split and from which the tungsten borides of the core were removed, as described above, gave the same results.

Table I. Heat Treatments of Massive Amorphous Boron under Vacuum

Treatment			Results	
Temp, °C	Pressure, 10^{-6} torr	Time at temp	X-Ray diffraction	Microscopic appearance
850	40	16 hr	No change	No change
950	6	1 hr	No change	No change
1050	13	30 min	β-Rhombohedral[a]	Crystalline surface
1050	22	15 min	β-Rhombohedral[a]	Crystalline surface
1050	6.5	15 sec	Amorphous plus β-rhombohedral	Areas of dendritic growth
1150	14	30 min	β-Rhombohedral	Crystalline surface
1250	3.5	1 hr	β-Rhombohedral	Crystalline surface
1350	0.7	19 min	β-Rhombohedral	Crystalline surface

[a] Identification based on ASTM Card No. 11-618 and ref 11

The appearance of crystallinity on the surface of heated filaments was readily ascertained by microscopic examination. The filaments before heating had a characteristic "orange peel" appearance. After treatment which resulted in crystallization the filament surface had a polycrystalline appearance, the crystallite size depending on the temperature and the time of treatment. When treatment was insufficient to cause complete crystallization of the filament, areas of crystallinity could be seen superimposed on the original surface. In all cases the crystallites were elevated above the original surface of the filaments. Filaments heated at 1050° for short periods gave the characteristic X-ray diffraction pattern of amorphous boron although their surfaces had crystallized and some lines of the β-rhombohedral pattern had appeared. Since the easily distinguishable "orange peel" surface associated with amorphous boron was no longer evident and yet X-ray diffraction showed unequivocably the presence of the amorphous material, the obvious inference was that the surface of the filament had been converted to a crystalline modification while the bulk of the material was unchanged.

The geometry of the sample prevented successful grazing-angle, X-ray study. These results suggest that the observed changes took place, or at least were initiated, by a surface mechanism. Further support for the conclusion that surface diffusion or vapor transport was the mechanism by which the transformations occurred is given by the results of heat treatments at 1000° in inert-gas atmospheres. Crystal growth was inhibited by the presence of 50 torr of argon or 30 torr of nitrogen under conditions which caused crystal growth under reduced pressures of these gases. The inhibition of crystal growth by different pressures of argon and nitrogen may be a reflection of the different thermal conductivities of the two gases. The surface temperature of the filaments may have been reduced just sufficiently to reduce the mobility of the surface atoms. The results are parallel to the report of Coleman and Sears[8] who found that the growth of zinc whiskers by vapor deposition was controlled by the presence of inert gases. Additionally, Markovskii[9] has said that boron begins to sublime at 1200° under reduced pressure, and Searcy and Meyers[10] have reported its vapor pressure at 1842° as 2.6×10^{-4} torr. Mobility of the surface atoms is indicated by these properties, but the low vapor pressure of boron at the transformation temperature probably precludes a vapor transport mechanism. These various lines of evidence support the conclusion that massive amorphous boron is converted on heating to a readily identifiable crystalline form by a surface diffusion mechanism.

The possibility that crystallization of the boron was nucleated at the core of the filaments because, with resistance heating, the core might become substantially hotter than the surface was eliminated by the heat treatments of filaments from which the core was removed from the boron before heating. The small size of the filaments also precluded any substantial temperature gradient between the core region and the boron deposit.

No crystal modification of boron other than the β-rhombohedral was found in numerous experiments regardless of the temperature to which the filaments were heated. This somewhat surprising result, in view of the temperature ranges for stability of the various

Table II. *d* Spacings (A) from X-Ray Diffraction Patterns of Boron[a] Filaments

A (untreated)	B (950°, 30 min)	C (950°, 30 min)	D (1000°, 5 min)	E (950°, 45 min)	F (1200°, 1.5 min)
					7.89
					5.47
			5.03	5.03	5.03
4.4 br	4.4 br	4.4 br	4.64	4.66	4.62
					4.44
					4.27
				3.93	3.97
					3.70
					3.54
					3.41
					2.94
			2.83	2.84	2.85
					2.74
	2.58	2.57	2.55	2.57	2.58
2.5 br	2.5 br				2.47
	2.39	2.39		2.40	2.40
					2.32
					2.20
				2.03	2.03
			1.74	1.75	1.76
				1.72	1.71
					1.67
				1.55	1.55
					1.46
		1.45	1.45	1.45	1.45
					1.43
1.4 br	1.4 br	1.41	1.41	1.42	1.42
					1.38
		1.35	1.35	1.34	1.35
		1.32	1.33		1.32
					1.30

[a] Silica core.

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[8] R. V. Coleman and G. W. Sears, *Acta Met.*, **5**, 131 (1957).

(9) L. Ya. Markovskii in "Boron, Its Compounds and Alloys," G. V. Samsonov, Ed., AEC-tr-5032 (Book I), U. S. Atomic Energy Commission, Washington, D. C., 1962, p 55; a translation of G. V. Samsonov, L. Ya. Markovskii, A. F. Zhigach, and M. G. Valyashko, "Boron, ego Soedineniya," Akademiya Nauk Ukrain'skoi SSR, Kiev, 1960.

(10) A. W. Searcy and C. E. Meyers, *J. Phys. Chem.*, **61**, 957 (1957).

other reported crystal modifications,[4] suggests that the massive amorphous boron deposit is possibly a microcrystalline deposit of β-rhombohedral boron. Some evidence for this hypothesis is presented in the series of X-ray diffraction patterns of heated silica-core filaments summarized in Table II. Since the X-ray diffraction pattern of boron in these filaments was not partially obscured by the lines due to tungsten borides in the core, a clear picture of the initial stages of development of crystalline boron was obtained. In pattern A the diffuse halos at *d* spacings of 4.4, 2.5, and 1.4 A are characteristic of massive amorphous boron. In pattern B sharp lines at *d* spacings of 2.58 and 2.40 A, clearly associated with the 2.5-A halo and part of the β-rhombohedral pattern[11] illustrated in pattern F as obtained in this work, have appeared as a result of heating the filament at 950° for 30 min. A differentiation of the 1.4-A halo is apparent in pattern C, and sharp lines in the vicinity of the 4.4-A halo appear in the filament heated at 1000° for 5 min. The stepwise development of the β-rhombohedral diffraction pattern is clearly indicative of recrystallization and grain growth and suggests that the massive amorphous boron may be a microcrystalline deposit of β-rhombohedral boron.

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[11] J. L. Hoard and A. E. Newkirk, *J. Am. Chem. Soc.*, **82**, 70 (1960).

The Interaction of Iodine with Aminoboranes

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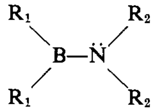
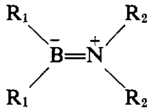
Abstract: The spectra of solutions containing mixtures of piperdinodimethylborane, (dimethylamino)dimethylborane, or (dimethylamino)di-*n*-propylborane with iodine in carbon tetrachloride exhibit absorption bands in the near-ultraviolet region that are not characteristic of either of the components and are assigned to complexes. The intensities of these bands depend upon the mole ratio of the components. The values of the equilibrium constants and heats of formation of these complexes, determined from spectral data, indicate that the aminoboranes act as amine donors rather than π donors toward iodine in these complexes.

Although the B–N bond in aminoboranes (I) is isoelectronic with the carbon–carbon double bond, there is only indirect evidence that electron delocalization (II) occurs in these systems. The position of the B–N stretching mode in the infrared spectra of aminoboranes is dependent upon the nature of the substituents and occurs over a wide range of frequencies (1300–1500 cm^{-1}).[2] Several attempts have been made to relate the degree of double bond character of the B–N bond to the frequency of this absorption;[2] the absorption at lower energies has been assigned to a B–N single bond suggesting that the electron pair is localized (I) in this type of compound. In addition, many aminoboranes are dimeric,[2b,d] the dimers presumably forming by intermolecular N–B bonding (III). In the case of (dimethylamino)dimethylborane (II, $R_1 = R_2 = CH_3$) the B–N stretching vibration occurs[3] at 1530 cm^{-1} and the compound is monomeric.[4] Thus theoretically it would appear that aminoboranes could act as either π-electron donors (II) or amine-type donors (I) when they interact with Lewis acids. In either case it might be expected that aminoboranes would form complexes with iodine in solution since both olefins (eq 1)[5] and amines (eq 2)[6] form complexes under these conditions. Therefore, the interaction between aminoboranes and iodine was studied in an attempt to elucidate the nature of the B–N bond in these compounds.



I



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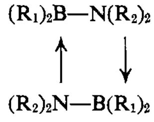
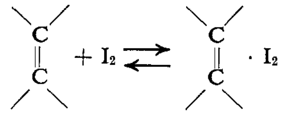


III



(1)

$$R_3N{:} + I_2 \rightleftarrows R_3N{:}I_2 \qquad (2)$$

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[1] Welch Foundation Fellow, 1961–1962; Dow Chemical Co. Fellow, 1962–1963.

[2] (a) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 5553 (1959); (b) K. Niedenzu and J. W. Dawson, *ibid.*, **82**, 4223 (1960); (c) G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962); (d) G. E. Coates and J. G. Livingston, *ibid.*, 1000 (1961).

[3] H. J. Becher and J. Goubeau, *Z. Anorg. Allgem. Chem.*, **268**, 133 (1952).

[4] G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

[5] J. G. Traynahm and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

[6] (a) C. Reed and R. S. Mulliken, *ibid.*, **76**, 3869 (1954); (b) S. Nagakura, *ibid.*, **80**, 520 (1958).