bien, alternativement, aux minima d'intensité sur le spectre X d'absorption.

Si ces coïncidences ne sont pas fortuites*, on peut en conclure que le spectre des électrons transmis décrit, d'une manière approchée, la densité des états d'excitation pour les électrons de conductibilité dans l'aluminium. Les pertes d'énergie discrètes ainsi observées par Ruthemann dans l'aluminium correspondraient à l'excitation d'électrons de la bande de conductibilité de ce métal vers les bandes inoccupées permises, de grande densité, révélées aussi par les structures d'absorption X, ce qui est très compréhensible. Une analyse plus fine du phénomène observé par Ruthemann devrait montrer le rôle de la distribution des électrons du métal dans la bande de conductibilité.

Dans d'autres expériences sur le collodion, il semble que Rutheman (1942) ait pu observer l'excitation d'électrons *K* du carbone, de l'oxygène et de l'azote.

Pour conclure, nous voyons que le dépouillement et l'analyse comparée des variations du coefficient d'absorption en fonction de la structure cristalline des métaux, est relativement facile dans le cas du système cubique. La localisation expérimentale des minima d'absorption a son importance dans le cadre de l'étude générale des solides; elle peut avoir son intérêt pour l'analyse fine de phénomènes divers où intervient la propagation des électrons dans ces cristaux.

Note sur épreuves, 25 *mars* 1952. Tomboulian & Pell (1951) ont repris l'analyse du spectre d'absorption *L* de l'aluminium jusqu' á 80 eV. de $L_{\text{II, III}}$. Si l'on en néglige le début, leur courbe Fig. 5 est en accord avec nos résultats, le minimum *S* 3 étant peut-être dédoublé.

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* L'accord est plutot moins bon avec des mesures annoncées comme plus précises par Ruthemann (1948) et Lang (1948).

Références

Cauchois, Y. (1948). *Les Spectres de Rayons X et la Structure Électronique de la Matière.* Paris: Gauthier-Villars.

Cauchois, Y. & Manesco, I. (1950). *J. Chim. phys.* **47**, 892.

Cauchois, Y. & Mott, N. F. (1949). *Phil. Mag.* (7), **40**, 1260.

Cauchois, Y. (1952). *Acta Cryst.* **5**, 348.

Das Gupta K. (1946). *Indian J. Phys.* **20**, 226.

Farineau, J. (1938). *Ann. Phys. Paris* (11), **10**, 20.

Johnston, J. E. (1939). *Proc. Camb. Phil. Soc.* **35**, 108.

Lang, W. (1948). *Optik*, **3**, 233.

Munier, J. H., Bearden, J. A. & Shaw, C. H. (1940). *Phys. Rev.* **58**, 537.

Ruthemann, G. (1941). *Naturwissenschaften*, **29**, 648.

Ruthemann, G. (1942). *Naturwissenschaften*, **30**, 144.

Ruthemann, G. (1948). *Ann. Phys.* Lpz., **2**, 113.

Sandström, A. (1935). *Nova Acta Soc. Sci. upsal.* (4), **9**, No. 11.

Sandström, A. (1941). *Ark. Mat. Astr. Fys.* 28A, No. 12.

Tomboulain, D. H. & Pell, E. M. (1951). *Phys. Rev.* **83**, 1196.

Acta Cryst. (1952). **5**, 356

An X-ray Study of Boron Nitride

By R. S. Pease

Atomic Energy Research Establishment, Harwell, Didcot, England

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The crystal structure, accurate unit-cell dimensions, and the thermal expansion of boron nitride are established. The presence of packing faults is shown, and the similarity of boron nitride to graphite in this and other respects is demonstrated. The nature of the B–N bond is discussed in terms of two possible models.

Introduction

The properties of boron nitride are interesting from several points of view. It has one of the simplest layer structures known and, as is shown below, it exhibits a unique form of layer packing. Geometrically, the structure is very similar to that of graphite, and the overall resemblance is strengthened by the fact that in the periodic table boron and nitrogen are adjacent to carbon. It is therefore notable that the electrical properties of boron nitride are wholly different from those of graphite.

Boron nitride is one of the very few boron compounds known to have a simple crystal structure, and it is thus of importance to the study of the stereochemistry of boron, particularly as the structure of the element itself is unknown. Furthermore, the nature of the B–N bond in boron nitride is at present the subject of conflicting views.

This paper reports X-ray work which has been carried out to establish the correct crystal structure (Pease, 1950); accurate values of the unit cell dimensions; the thermal expansion; and the similarity of boron nitride to graphite in respect of crystallite size and shape, packing faults and Debye temperature. The problem of the bond nature is discussed, but the available evidence appears to be insufficient to decide between the conflicting views.

The material

Commercially prepared boron nitride was obtained from Messrs. B. D. H. Ltd. This was found to be very poorly crystalline. Recrystallization was achieved by heating the material at 2050° C. for two hours or so in a stream of nitrogen.

The general appearance of the recrystallized material was in excellent accord with Goldschmidt's description (1926). The specific gravity was measured by the displacement method, and found to be $2{\cdot}29 \pm 0{\cdot}03$ in adequate agreement with Goldschmidt's figure of $2{\cdot}255 \pm 0{\cdot}02$ and with a theoretical value of 2·270 obtained from the unit-cell dimensions given below.

Chemical analysis was employed to measure the impurity content. Traces of magnesium, carbon, silicon and a variety of metallic elements, amounting in all to less than 0·6% by weight, were detected.

X-ray measurements

Of necessity the X-ray examination was confined to powder specimens; Cu K and Mn K radiations were employed. Fig. 1 (*a*)–(*d*) shows photographs taken with extruded specimens of approximately $\frac{1}{3}$ mm. diameter. A comparison of Fig. 1 (*a*) and (*b*) shows the decisive importance of recrystallization for the accurate measurement of intensities and spacings. The photograph at Fig. 1 (*c*) was given by graphite, and the similarity to the boron nitride photographs is readily visible.

The interplanar spacings were obtained by determining the line positions relative to the camera knife edges with a measuring microscope. The camera temperature was stabilized at $35° \pm 0{\cdot}5°$ C. for the relevant exposures.

Line profiles and integrated intensities were determined by microphotometry of the films. To guard against possible error due to preferred orientation in the extruded specimens, integrated intensities were also measured on a Geiger-counter spectrometer, using slabs of non-oriented powder compact. The spectrometer could be used only on lines with θ less than 45°; the agreement between the two sets of intensities for these lines was within experimental error.

The unit cell

The reflexions can all be indexed on the basis of a hexagonal unit cell. The dimensions of this have been determined from the observed interplanar spacings using an extrapolation technique similar to that recently described by Henry, Lipson & Wooster (1951, p. 193). The principal high-angle reflexions used for determining a were the Cu $K\alpha_1\alpha_2$ 120, 122, Cu $K\beta$ 300 and 302, the last being reflected at $\theta = 80{\cdot}5°$. For the determination of c, the 006 reflexion of Mn $K\alpha$ at $\theta = 71°$ is the best available; it was used in conjunction with a number of lower-angle lines, and the $hk0$ extrapolation plots.

The dimensions at 35° C., assuming Cu $K\alpha_1 = 1{\cdot}54051$ Å, are

$$a = 2{\cdot}50399 \pm 0{\cdot}00005, \quad c = 6{\cdot}6612 \pm 0{\cdot}0005 \text{ Å};$$

the quoted errors being observed standard deviations.

The absence of large systematic errors was confirmed using the same equipment and technique to determine the a dimension of well-crystallized graphite. The value obtained at 15° C., $2{\cdot}46140 \pm 0{\cdot}00010$ Å, agrees well with the value $2{\cdot}46138 \pm 0{\cdot}00010$ Å given by Bacon (1950*a*).

The structure

The unit cell is bimolecular. Reflexions with $h+2k=3n$ and l odd are all absent. From these facts and the values of F_{00l} it is easily shown that the structure is of a simple layer type, with an interplanar spacing of $\frac{1}{2}c$; each layer consists of a flat, or nearly flat network of B_3N_3 hexagons. There are four possible ways in which these layers may be packed. Three of the possibilities are simply different arrangements of boron and nitrogen atoms at sites occupied by carbon atoms in graphite; one of these, which will be called structure A, has been accepted up to the present as correct (Hassel, 1926; Brager, 1937, 1939). The fourth possible way, structure B, is shown at Fig. 2; the atomic sites can be written:

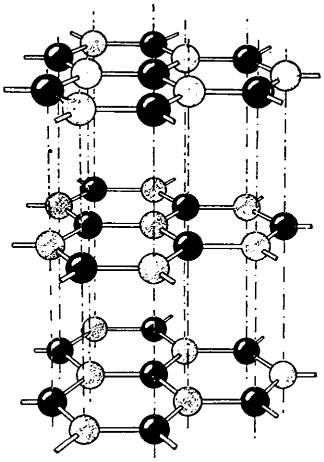

Fig. 2. The structure of boron nitride (structure *B*).

$$\text{N:} \quad (0, 0, 0) \text{ and } (\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{2}).$$
$$\text{B:} \quad (0, 0, \tfrac{1}{2}) \text{ and } (\tfrac{1}{3}, \tfrac{2}{3}, 0).$$

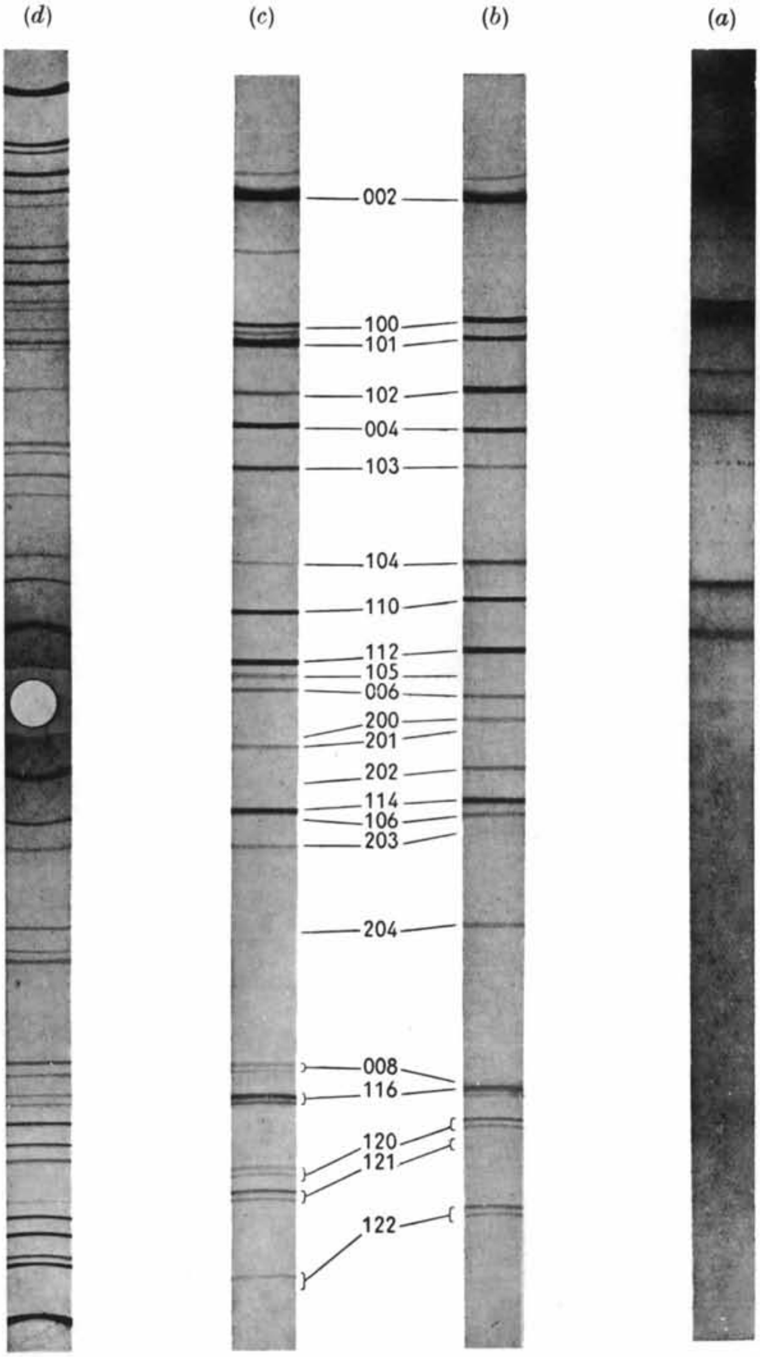

Fig. 1 (*a*) Commercially supplied BN. Cu $K\alpha$ radiation; 19 cm. camera. (*b*) Recrystallized BN. Cu $K\alpha$ radiation; 19 cm. camera. (*c*) Well-crystallized graphite. Cu $K\alpha$ radiation; 19 cm. camera. (*d*) Recrystallized BN. Monochromatized Cu $K\beta$ radiation; 9 cm. camera.

The observed values of F^2_{hkl}, together with those calculated for structures A and B, are given in Table 1. The calculated values are based on atomic scattering powers given in the *International Tables*, and contain no allowance for temperature factor.

Table 1. *Observed and calculated* F^2_{hkl}

hkl	F^2_c (A)	F^2_c (B)	F^2_o
100	49	58	75±7
101	23	12	16±2
102	33	44	45±5
103	16	4·7	4·6±0·8
104	15	27	23±3
105	13	1·4	~ 1
106	8	18	12±4
107	9	0·2	< 1
108	3	13	~ 10
200	11	22	17±2
201	12	1·0	~ 1
202	9	20	15±4
203	10	0·6	~ 1
204	5·6	16	~ 8
205	9	0·5	< 1
206	3	13	~ 10
120	5·3	14	12·5±1·5
121	9·0	0·2	~ 0·5
122	5·6	13	9±1
123	9·0	0·2	< 0·5
124	5·7	10	5±0·5
002	390		560±100
004	150		158±10
006	86		60±10
008	59		26±6
110	100 (Standard)		100
112	90		80±8
114	72		55±5
116	58		30±5
300	47		36±2
302	47		31±2

From this, it is evident that the assumption of structure A involves large discrepancies between F_o and F_c. The largest, which occur with l odd, are readily visible in a comparison of the photographs of boron nitride and graphite. They cannot be reduced at all by assuming that the layers are puckered; and are well outside the normal range of temperature effects. Both of the other two graphite-like structures give a considerably worse fit.

In contrast, structure B involves relatively small discrepancies, and gives a reliability index of 0·16 for lines with $h+2k \neq 3n$. The intensities of lines with $h+2k = 3n$ are independent of the four alternative structures, and consequently provide an empirical standard by which to judge the agreement between calculated and observed. The reliability index for these latter lines is 0·18. Thus structure B must be accepted as correct.

Such discrepancies as exist between F_c and F_o for structure B appear to be explicable along familiar lines. As regards the $00l$ reflexions, the discrepancies are largely due to the omission of any allowance for the temperature factor. Fig. 3 gives a plot of $\log_e (F_o/F_c)^2$ against l^2, showing a linear relationship within experimental error. The slope of the line corresponds to a Debye temperature of 410° K., which is of the same order as the value 530° K. found by Bacon (1950*b*) for the only comparable substance, graphite.

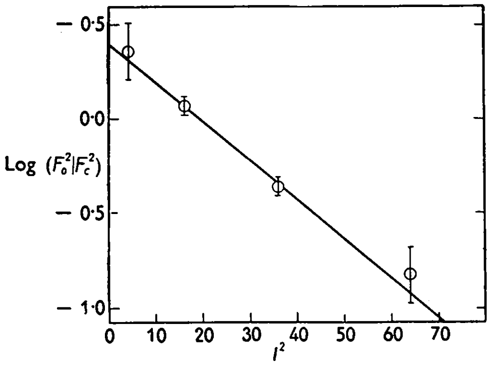

Fig. 3. Plot of $\log_e (F_o/F_c)^2$ versus l^2 for the $00l$ reflexions.

The interpretation is confirmed by a measurement of the ratio F_{006}/F_{004} at 300° C.; the value obtained is in good agreement with that predicted from the room-temperature results.

With the aid of the results at Fig. 3, the value of F_{008} shows that the layers are flat to within 0·01c. This is so small that simple considerations of symmetry suggest that, apart from thermal puckering, the layers are geometrically plane.

For the $hk0$ lines, the discrepancies do not follow a Debye–Waller temperature factor. Moreover, the relative intensities do not vary appreciably with temperature. It seems very probable that, as in graphite where the same situation is encountered (Franklin, 1950), the temperature corrections are small compared with errors in the theoretical values of the atomic scattering powers.

Neither of the previous investigators of the boron nitride structure (Hassel, 1926; Brager, 1937, 1939) appears to have considered the possibility of structure B. In their results, the major discrepancies between F_o and F_c arising from the assumption of structure A are largely obscured, partly by the small number of reflexions used, and partly by indexing and other errors. When the reflexions are correctly indexed, their values of F_o are in substantial agreement with those used herein.

Packing faults

In graphite there are packing faults consisting of random displacements of the layers perpendicular to the c axis (Hoffman & Wilm, 1936). At the faults the periodicity of the hkl lines is destroyed, but that of the $hk0$ and $00l$ lines is unaffected. As a result, the diffraction breadths for the hkl lines are larger than those expected from the breadths of the $hk0$ and $00l$ lines on the basis of a perfect plate-like crystallite.

Broadening of this kind is observed on the boron nitride photographs. Fig. 4 shows the profiles of the

α 006, 200 and β 114 lines of a Mn K radiation photograph; the α_1 component is shown by the broken line where it differs appreciably from the main trace. The 114 line is evidently much broader than either of the other lines. This is very suggestive of packing faults, and the breadths of other reflexions have been investigated.

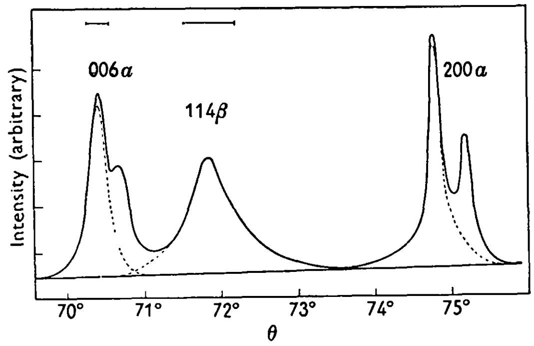

Fig. 4. Line profiles of Mn $K\alpha$ (006), (200) and $K\beta$ (114) reflexions.

The geometrical broadening was obtained from the total breadths of the $hk0$ lines, since these lines are so sharp at high angles that the diffraction broadening must be negligible. Diffraction breadths of the other lines were obtained from total breadths on the assumption of gaussian profiles. Where necessary, the $K\alpha_1\alpha_2$ doublet was resolved graphically (Pease, 1948). The diffraction breadths were interpreted in terms of a plate-like crystallite of infinite extent and thickness t.

It was found that the breadths of the hkl lines all correspond to a thickness of 300±50 Å, whereas those of the $00l$ lines correspond to a thickness of about 1200±300 Å. The results are illustrated in Fig. 5. The diameter of the particle was roughly estimated from optical examination, and from the maximum possible diffraction breadths of the $hk0$ lines. The dimensions obtained are very similar to those found for crystallites of well-crystallized graphite.

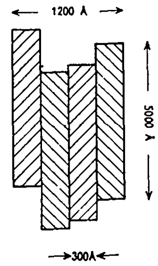

Fig. 5. Typical crystallite of BN.

No additional reflexions due to a rhombohedral structure similar to β-graphite were observed on the boron nitride photographs. But the layer packing of boron nitride differs from that of graphite in just that way which excludes the possibility of a rhombohedral modification.

Thermal expansion

The thermal expansion coefficients have been determined in the range 0–800° C., using a Unicam 19 cm. high-temperature camera.

For the control and measurement of specimen temperature, two ring thermocouples of Pt/Pt–13 % Rh. were placed round the ends of the specimen, just clear of the X-ray beam. They were calibrated in terms of specimen temperature by placing a third thermocouple in the position of the specimen. This third thermocouple was constructed with a large blackened head and 0·001 in. diameter leads in order to record the true radiation temperature in the specimen position. A pressure of less than 5 μ of Hg was maintained in the camera during the exposures. The mean specimen temperature of each exposure was obtained to within ±5° C.

The unit-cell dimensions were determined in the manner already mentioned from photographs taken with turned specimens and unfiltered Cu K radiation. The results are presented at Figs. 6 and 7. Each point represents one exposure.

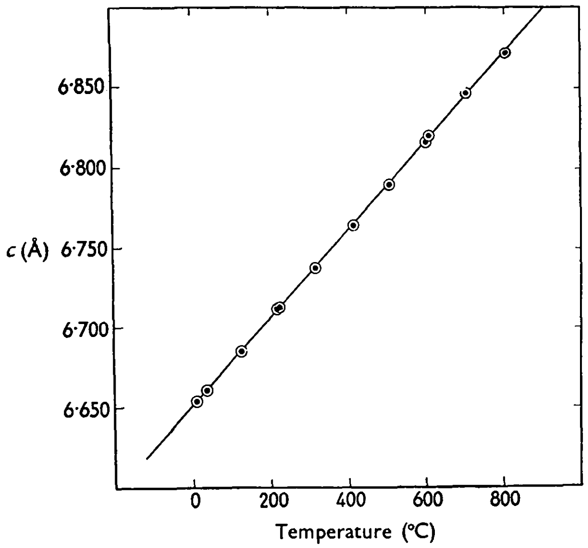

Fig. 6. Variation of c dimension with temperature.

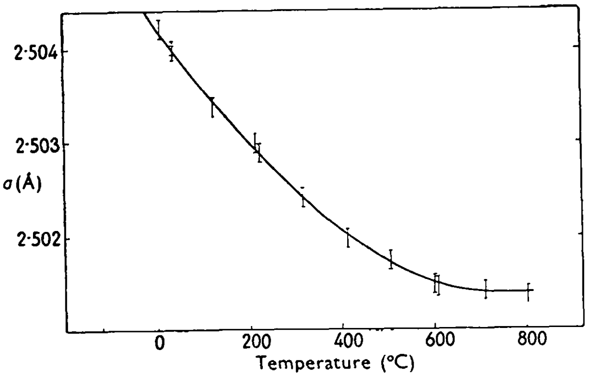

Fig. 7. Variation of a dimension with temperature.

Within experimental error the c dimension expands linearly over the range investigated, and can be expressed in Ångström units to within 0·001 Å by the expression

$$c = 6{\cdot}6516 + 2{\cdot}74 \times 10^{-4}t\,,$$

where t is the temperature in degrees centigrade. The mean coefficient is $40{\cdot}5 \times 10^{-6}$ deg.$^{-1}$.

The a dimension contracts as the temperature is raised, but the contraction is not linear, and ceases at about 800° C. The parabolic expression

$$a = 2{\cdot}50424 - 7{\cdot}42 \times 10^{-6}t + 4{\cdot}79 \times 10^{-9}t^2$$

fits the experimental data to within 0·0001 Å; it gives an expansion coefficient of $-2{\cdot}9 \times 10^{-6}$ deg.$^{-1}$ at 20° C., falling to zero at 770° C.

The order of magnitude of these results is entirely consistent with the layer-like nature of the structure. The large expansion in the c direction indicates a weak inter-layer binding; the negative coefficient of the a dimension indicates that the bonds within the layer are so strong that up to 770° C. the true expansion of the bond is more than counteracted by the effects of layer puckering due to thermal agitation.

The thermal expansion coefficients of graphite in the same range of temperatures are $28{\cdot}2 \times 10^{-6}$ deg.$^{-1}$ for the c dimension, and $-1{\cdot}5 \times 10^{-6}$ deg.$^{-1}$ falling to zero at about 400° C., for the a dimension (Nelson & Riley, 1945). Both figures are substantially less than those given above for boron nitride, and in roughly the same proportion. In the light of Nelson & Riley's theoretical work, this fact suggests that thermal puckering of the layers is more severe in boron nitride, but that the interatomic forces within the layers are of about the same magnitude.

Supporting evidence is provided by the specific heat of boron nitride (Magnus & Danz, 1926) which is greater than that of graphite in this range of temperatures. This is also consistent with the lower value of the Debye temperature for thermal vibrations perpendicular to the layers, found for boron nitride.

Discussion

The structure

The structure (Fig. 2) deduced herein for boron nitride has not been found for any other substance. It is, however, formally related to the zincite structure in the same way as the structure of graphite is related to that of diamond. This is of significance in so far as the nitrides of other elements of the same sub-group (AlN, GaN, InN) have the zincite structure.

Graphite is the only close analogue of boron nitride. The geometrical difference between them lies in the nature of the layer packing. In boron nitride the hexagonal rings of atoms are packed directly on top of each other, whereas in graphite a form of close packing exists, in which half the atoms lie between the centres of the hexagonal rings of adjacent layers. Unlike the C–C bond of graphite, the B–N bond has an electrical dipole moment; the difference of packing may well be due to the interlayer interaction of these dipoles, which favours the observed type of packing above all others. The similarity of the two substances in respect of most properties indicates that the packing difference is of secondary importance, and that the magnitudes of the interatomic forces in the two substances are very similar.

The structure contains only one type of strong bond, the B–N bond joining each atom to its three coplanar nearest neighbours. The length of this bond is 1·446 Å. The sum of the single-bond covalent radii of boron and nitrogen (Pauling, 1945) is 1·58 Å.

The bond nature

Views as to the nature of the B–N bond in boron nitride are conflicting. On the one hand many workers have followed Levy & Brockway (1937) in supposing that the short bond length indicates a part-double-bond, involving resonant electrons, similar to that in graphite. On the other hand Hückel (1948, p. 586) has argued that the whiteness and low electrical conductivity of boron nitride belie the presence of resonating electrons, and that the bond must therefore be single. On the former view the electrical properties were unexplained and, on the latter, the short bond length.

In most substances the nature of a bond may be determined from the bond length. In boron compounds this procedure is unreliable, because the boron atom may be capable of existing without a completed octet of electrons around it, in which state its effective radius is smaller. Thus when the boron atom is triangularly co-ordinated, the short bond which is always observed, can be attributed either to a part-double bond in conjunction with the octet radius, or to a single bond in conjunction with the sextet radius. Although the bond lengths observed are consistent in most cases with a part-double bond, there is at present no estimate of the sextet radius available, so that the possibility of a predominantly single bond cannot be excluded on the grounds of bond length alone.

Since boron nitride is the one known boron compound with a clear-cut co-ordination number and an accurate value for the bond length, it is of particular interest to establish the bond type in this case.

No direct evidence as to the actual location of the p_z electron pair is available. X-ray data for a Fourier synthesis cannot be obtained from the powder samples owing to excessive overlapping of the high-order reflexions, and no single crystals of sufficient size for X-ray work have been obtained. The X-ray scattering powers of the atoms are different on the two models, but, even at the lowest Bragg angles at which reflexions are available, the differences that could be expected are small compared with the uncertainties in the theoretical values.

The only definite prediction which can be tested is a comparison with the B–N bond length in the benzene analogues $B_3N_3H_6$. The single-bond model requires that this length shall be the same as that in boron nitride, whereas the part-double-bond model requires that it shall be 0·035 Å shorter. The observed length is $1{\cdot}44 \pm 0{\cdot}02$ Å (Bauer, 1938), which is the same as in boron nitride. Unfortunately the predicted change only just exceeds the experimental error, so that this evidence is not conclusive.

Circumstantial evidence is as follows. The magnitudes of the interatomic forces in boron nitride have been shown to be very similar to those in graphite, where the part-double-bond model is correct. But this similarity is more than offset by the difference in the electrical properties of the two substances. In marked contrast with the metallic lustre and conductivity of graphite, boron nitride is white, and has exceptionally good insulating properties, which at high temperatures are better than those of most refractory oxides (Podzus, 1918). The diamagnetic susceptibility has been given as 0×10^{-6} c.g.s. e.m.u. $g.^{-1}$ (Meyer, 1898). This figure has been checked on the recrystallized material, and a value of $-0{\cdot}4 \pm 0{\cdot}1 \times 10^{-6}$ c.g.s. e.m.u. $g.^{-1}$ obtained (Dawson, 1950). This is wholly different from the exceptionally large value found in graphite ($\sim -10 \times 10^{-6}$ e.m.u. c.g.s. $g.^{-1}$), which is associated with the large orbits of the resonating p_z electrons. These differences between graphite and boron nitride are readily explicable if the single-bond model is correct, but a rigorous theoretical interpretation might also account for them on the part-double-bond model, particularly as the condition for metallic bonding (Pauling, 1949) does not exist in either substance.

Thus the matter cannot be decided at present. Moreover, the actual electronic distribution may well be intermediate between those given by the two models. However, it is clear that all the above evidence is readily explicable in terms of the single-bond model, and that this is by no means true of the part-double-bond model. To this extent, the single-bond model is the more acceptable.

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References

Arnfelt, H. (1932). *Ark. Mat. Astr. Fys.* B, No. 2, p. 23.
Bacon, G. E. (1950*a*). *Acta Cryst.* **3**, 137.
Bacon, G. E. (1950*b*). *Nature, Lond.* **166**, 794.
Bauer, S. H. (1938). *J. Amer. Chem. Soc.* **60**, 524.
Brager, A. (1937). *Acta Physicochimica U.S.S.R.* **7**, 699.
Brager, A. (1939). *Acta Physicochimica U.S.S.R.* **11**, 617.
Dawson, J. K. (1950). Private communication.
Goldschmidt, V. M. (1926). *Norsk geol. Tidsskr.* **9**, 258.
Franklin, R. E. (1950). *Nature, Lond.* **165**, 71.
Hassel, O. (1926). *Norsk geol. Tidsskr.* **9**, 266.
Henry, N. F., Lipson, H. & Wooster, W. A. (1951). *The Interpretation of X-ray Diffraction Photographs.* London: Macmillan.
Hoffman, U. & Wilm, D. (1936). *Z. Elektrochem.* **42**, 504.
Hückel, W. (1948). *Anorganische Strukturchemie.* Stuttgart: Emke.
Levy, H. & Brockwey, L. O. (1937). *J. Amer. Chem. Soc.* **59**, 2085.
Magnus, A. & Danz, H. (1926). *Ann. Phys., Lpz.* **81**, 407.
Meyer, S. (1899). *Ann. Phys. Lpz.* **69**, 236.
Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc., Lond.* **57**, 477.
Pauling, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.
Pauling, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
Pauling, L. (1949). *Proc. Roy. Soc.* A, **196**, 343.
Pease, R. S. (1948). *J. Sci. Instrum.* **25**, 353.
Pease, R. S. (1950). *Nature, Lond.* **165**, 722.
Podzus, E. (1918). *Elektrotech. Z.* **39**, 229. (*Chem. Abstr.* (1919). **13**, 210.)