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RICE UNIVERSITY

X-RAY DIFFRACTION STUDY OF THE STRUCTURE OF BORON
 IN VAPOR-DEPOSITED BORON FIBERS

by

JAYANT V. BHAROWAJ

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS

DECEMBER, 1979
X-RAY DIFFRACTION STUDY OF THE STRUCTURE
OF BORON IN VAPOR-DEPOSITED BORON FIBERS

ABSTRACT

Jayant V. Bhardwaj

The structure of vapor-deposited fiber boron is studied using x-ray diffraction and computer modeling. The diffraction pattern displays broad peaks which have been interpreted in previous studies to arise from a microcrystalline material having an average crystallite size of about 30 Å.

This study was initiated by quantitatively investigating the microcrystalline models suggested by workers. The Debye equation was used to compute the intensity scattered by randomly oriented crystallites. Crystallites with diameters up to 26 Å were considered. An additional computer program was written to calculate the different interatomic distances and their multiplicities, and to compute their contributions to the various peaks. This method of analysis was utilized to drive the atoms in the microcrystal towards positions which gave a more favorable fit of the computed intensity profile to the experimentally obtained profile.

Chapter I describes boron, the production of boron fiber and its properties and includes a survey of previous work. Chapter II addresses the experimental techniques used to obtain the diffraction pattern. In Chapter III, the methods utilized the model and compute the interference patterns are described. Chapter IV summarizes and discusses the results which indicate that a complex atomic arrangement is present, involving
distorted nearest-neighbor distances, partial icosahedra and individual atoms. Some of the icosahedra display orientations present in alpha-rhombohedral boron, while others display those observed in tetragonal boron. The average size of the region of local atomic ordering is approximately 20 Å.
ACKNOWLEDGMENTS

I am deeply grateful to my advisor, Dr. Aaron D. Krawitz who exercised the right amount of control and freedom, especially in the initial stages, to make this work fruitful and enjoyable. I would like to thank NASA for supporting portions of this work and for supplying the fibers; Rice University for offering me a Fellowship; the Mechanical Engineering Department for providing liberal access to the PDP 11/03 minicomputer; and Al Ehlert for being there whenever the equipment broke down.

I acknowledge here my debt to my farsighted parents for providing me with the opportunity and for being patient when I faltered; and to my brother Vas, who helped.

I would like to dedicate this work to my wife, Helen, who patiently proofread and typed the manuscript, and without whose emotional, physical and even financial support, this task would have been Herculean.
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I. INTRODUCTION

A. Background

The idea of combining different materials macroscopically to obtain the best qualities of both constituents is quite old. For example, straw was used by ancient Israelites to strengthen mud bricks. More recently, fiber-reinforced composite materials are considered to be one of the major technological developments of the century. The high strength-to-density (specific strength) and stiffness-to-density (specific modulus) ratios of these materials make them ideally suited for the aircraft and aerospace industry. The same advantages of lighter structures, bigger payloads, longer operating ranges and fuel economy have motivated several other industries to commit themselves to greater use of composites in such diverse applications as truck drive-shafts and tennis racquets\(^1,2,3\). Various composite materials have been developed using different fiber and matrix constituents. Of these, boron fibers are one of the more versatile and have been utilized with both polymeric and metallic matrices. They are, however, expensive to produce, and thus are limited to applications in which they are cost-effective.

Boron fibers are made in a continuous process by decomposing boron trichloride with hydrogen in a reaction chamber and vapor-depositing elemental boron onto a moving resistance-heated tungsten wire substrate. The fiber thus obtained has a high strength and elastic modulus. The strength of a boron fiber stems from a favorable residual stress distribution which is compressive at the skin and the core of the fiber and tensile in-between\(^4\). Attempts to improve the cost-effectiveness by increasing production speeds has led to less favorable residual stress
distributions and poor quality fibers. Several efforts have been made to understand the fundamental nature of this stress distribution and the process parameters affecting it. The primary causes are now considered to be the volume expansion of the core due to boron diffusion and tungsten boride formation; the thermal expansion mismatch between the boride core and the deposited boron; the quenching at the exit end of the reactor and the elongation in the boron during deposition.

Boron elongation during deposition could be the predominant cause of the unfavorable residual stress distributions obtained at increased production speeds. However, boron elongation is one of the least understood fundamental properties of the material. First observed by Talley, it appears to be controlled by structural rearrangements in the fiber. Mehalso suggested that each layer of boron is deposited with less than maximum density, incorporating many defects. With continued deposition at high temperature, the boron atoms diffuse inward, resulting in the densification and consequential volume expansion of the inner layers of the boron mantle. The driving force for this diffusion is the overall lowering of the energy of the system as boron atoms seek positions of lowest potential energy. Evidence for this model is given by the observation that greater boron elongations are obtained at lower deposition temperatures. It may be explained that boron atoms have greater mobility at higher deposition temperatures and attain lower potential energy positions with alacrity, thus lowering the concentration of defect deposition and the consequent elongation. Supporting evidence for the model was given by DiCarlo, whose recent measurements suggest a radial density variation with a less than average density in the surface layers. However, Wawner found no difference in
the electron diffraction patterns obtained from the inner and the sur-
face layers of the boron fiber. Both regions showed identical patterns
of diffuse "amorphous" haloes, suggesting that there were no discernible
differences in atomic structure. An investigation of the structure of
amorphous fiber boron was certainly forthcoming and necessary. Curios-
ity regarding its nature was further heightened by its strongly
anelastic behavior, which indicated some degree of crystallinity\textsuperscript{Sa}
by
displaying strong internal friction peaks with fairly well-defined
activation energies.

Glass-like amorphous materials do not have atomic arrangements of
long-range periodicity as displayed by crystalline materials. Instead,
atoms are arranged in a random fashion in space, conserving only their
nearest-neighbor distances. Diffraction patterns of liquids and glasses
show very broad haloes which decrease in intensity with increasing angle
of incidence of the x-ray beam on the sample. In the case of fiber
boron, the large amount of structure present at the higher angles of
incidence (Fig. 12) indicates a degree of ordering which rules out a
glass-like amorphous structure. Broad diffraction patterns such as
those of fiber boron often represent scattering from materials with very
fine-sized grains, of the order of tens of Angstroms, called micro-
crystalline materials. Boron is known to crystallize into various
temperature-dependent polymorphs, having a nearly regular icosahedral
grouping of twelve atoms (Fig. 1) as a common structural element.
Previous workers have postulated faulted structures\textsuperscript{10} or microcrystals\textsuperscript{11}
of these polymorphs to account for the observed broad haloes. These
models, however, have been inadequate to explain many of the experi-
mental observations.
It is the purpose of this study to elucidate the structure of amorphous fiber boron. The study was initiated by quantitatively investigating the microcrystalline models suggested by workers. The results indicate that a more complex atomic arrangement is present, involving distorted nearest-neighbor distances, partial icosahedra and individual atoms. Some of the regions have icosahedra with bonds along the five-fold axes, as displayed by alpha-rhombohedral boron. Other regions have icosahedra with extra atoms between them, as observed in tetragonal boron.

Chapter I describes boron, the production of boron fiber and its properties, and includes a survey of previous work. Chapter II addresses the experimental techniques used to obtain the diffraction pattern. In Chapter III the methods utilized to model and compute the interference pattern are described. Chapter IV summarizes and discusses the results.
B. Polymorphs

There are three well-known polymorphs of pure boron: the low-temperature alpha-rhombohedral form; the tetragonal form; and the high-temperature beta-rhombohedral form. All of the models utilize a common structural element, a nearly regular icosahedral grouping of twelve atoms (Fig. 1). Each icosahedron has twelve external bonds directed along the five-fold axes\textsuperscript{15}. Consequently, each boron atom has a preferred co-ordination of six nearest-neighbors, with a pentagonal pyramid as the co-ordination polyhedron (Fig. 2). The three polymorphs are:

1) **Alpha-rhombohedral boron.** The alpha-rhombohedral unit cell, $a_o = 5.05\AA$, $\alpha = 58.06^\circ$, space group R3m, contains one icosahedron at each of its lattice sites\textsuperscript{16}; see Fig. 3. Intra-icosahedral bond lengths vary from $1.73\AA$ to $1.79\AA$. Of the twelve intericosahedral links, six lie along the five-fold axes with bond distances of $1.71\AA$ while the remaining six delta bonds are $2.02\AA$ in length. Alpha-rhombohedral boron has a density of $2.46$ g/cc.

2) **Tetragonal boron.** The unit cell, $a_o = 8.75\AA$, $c_o = 5.06\AA$, space group $P4_2/nm$, contains 50 atoms distributed among four icosahedra and two individual atoms\textsuperscript{17}; see Fig. 4. The intra-icosahedral bond length is $1.81 \pm 0.03\AA$. Ten of the twelve external bonds are to neighboring icosahedra, with length of $1.68 \pm 0.03\AA$ along the quasi-five-fold axis. The remaining two links are to tetrahedral atoms at distances of $1.601 \pm 0.005\AA$. Tetragonal boron has a density of $2.31$ g/cc.

3) **Beta-rhombohedral boron.** The unit cell, $a_o = 10.17\AA$, $\alpha = 65.2^\circ$, space group R3m, contains 105 atoms\textsuperscript{18,19}; see Fig. 5. The structure consists
Fig. 1. Icosahedral bonding in boron$^{26}$.  
Fig. 2. The preferred pentagonal co-ordination polygon$^{26}$.

Fig. 3a. $\alpha$-Rhombohedral boron$^{16}$.  
Fig. 3b. One-cell model for $\alpha$-rhombohedral boron showing all of the atoms associated with each lattice site.
Fig. 4. Tetragonal boron structure\textsuperscript{17}.

Fig. 5. Beta-rhombohedral boron structure\textsuperscript{26}.
almost entirely of slightly deformed icosahedra arranges in a rather complicated array. Beta-rhombohedral boron has a density of 2.35 g/cc.

Icosahedra do not lend themselves to the construction of an ideal three-dimensional framework, and various degrees of compromise in the pattern of icosahedral linkage give rise to the observed proliferation of polymorphs\textsuperscript{20}. The choice of framework is strongly influenced not only by the temperature during deposition, which imposes kinetic limitations on the process of crystal growth, but also by the boron source used and the choice of substrates upon which the crystals form\textsuperscript{21,22}. At temperatures below 1000\degree C, the alpha-rhombohedral polymorph is the only crystalline form of boron obtained; below 800\degree C the product is amorphous. At temperatures above 1500\degree C the beta-rhombohedral polymorph is formed. Beta-rhombohedral boron is the equilibrium phase at all temperatures between 0\degree K and the melting point, and contains the largest percentage of atoms exhibiting a co-ordination of six. Beta-rhombohedral boron does not form at lower temperatures, possibly due to kinetic limitations imposed on its formation. The tetragonal polymorph is found in the temperature range of 1000\degree C to 1500\degree C, and should more correctly be referred to as tetragonal I, since at least five other polymorphs\textsuperscript{20} lay claim to recognition in this temperature range. It is highly improbable for so many polymorphs to be thermodynamically stable in such a temperature range, and the choice of framework appears to be kinetically determined. As will be shown, the existence of such variants does not affect the present study.
C. Production Methods

The preparation of pure elemental boron by the "filament method" led to the characterization of the various crystalline polymorphs of boron. Talley, et al.\textsuperscript{3}, were the first to pursue production of rods of amorphous boron of high purity by varying the deposition conditions. The process itself was basically the same. The product was a filament that was surprisingly flexible, with high tensile strength (2.07 GN/m\textsuperscript{2} or 3.5 x 10\textsuperscript{5}psi) and Young's modulus (418 GN/m\textsuperscript{2} or 60.5 x 10\textsuperscript{6}psi).

X-ray diffraction patterns of the fiber revealed only two very diffuse "amorphous" rings. The process has since been updated to produce consistent, high quality fibers on a commercial scale for use in advanced composites.

The boron fibers used in this investigation were supplied by Avco Systems Division through NASA. The 203 \textmu m (8mil) fibers were produced in a continuous single stage reactor by the vapor phase reduction of BCl\textsubscript{3} by H\textsubscript{2} on a 12.7 \textmu m (0.5 mil) tungsten wire substrate held near 1300\textdegree C by resistive heating supplemented by VHF heating. Electrical contact was maintained by the use of mercury electrodes, which also acted as a quenching medium at the exit end of the reactor. The tungsten wire substrate reacts to produce a W\textsubscript{2}B\textsubscript{5} inner core (12.7 \textmu m or 0.5 mil) and a WB\textsubscript{4} outer core (17 \textmu m or 0.67 mil)\textsuperscript{4}. There is a well-defined interface between the tungsten boride core and the surrounding sheath which consists of essentially pure (99.9\%) boron (Fig. 6).

The factors affecting the deposition and the type of product formed have been studied by a number of workers\textsuperscript{13,14,23,24,25}, and are briefly summarized here. Varying the hydrogen flow rate has no apparent effect. A slower deposition rate, obtained by lowering the vapor-pressure of BX\textsubscript{3}.
Fig. 6. 8 mil fiber showing the tungsten boride core.

Fig. 7a. Residual stress pattern.

Fig. 7b. Longitudinal residual stress distribution in 203 μm (3 mil) diameter B/W fiber, from Behrendt."
in the reaction chamber, yields a more crystalline deposit\textsuperscript{13}. The filament temperature is the most important factor affecting the nature of the deposit. Specimens produced below 1300°C generally showed "amorphous" diffraction patterns, whereas higher temperature deposits exhibited crystalline diffraction. It has been suggested\textsuperscript{26} that each boron atom tries to diffuse along the surface to a regular lattice site before it is "frozen" into place by later deposition. Subsequently, the boron atom tries to diffuse through the bulk towards a low potential energy site. The success of its attempt hinges on its kinetic energy, and hence on the temperature during deposition. The greater mobility at higher temperatures yields a more crystalline product.
D. Properties

Boron has five electrons and is trivalent. Electrically it is a semiconductor with a room temperature conductivity of $10^{-6}$ ohms$^{-1}$ cm$^{-1}$. Boron has a melting point of 2200°C and a hardness surpassed only by that of diamond (Knoop 2210 to 2380).

Boron fibers have a high tensile strength (2.07 GPa or 3 x $10^5$ psi) and Young's modulus (418 GPa or 60.5 x $10^6$ psi)$^{4,9}$. The strength of boron fibers is due in part to the fact that primary flaws are located at the surface and in the tungsten boride core, where residual stresses are found to be compressive, thus inhibiting crack propagation. The longitudinal residual stress distribution$^4$ shows a compressive stress at the surface (-1.38 GPa or -200 ksi), changing monotonically to a region of tensile stress within the boron sheath (1.03 GPa or 150 ksi, maximum at about 25% of the fiber radius) and then decreasing to a compressive stress near the boride core. The core itself is under a residual compressive stress of -1.313 GPa (-190 ksi). Smith$^{27}$ found that, after etching the fiber surface, essentially all cases of fracture could be explained by crack initiation within the tungsten boride core. Behrendt$^4$ showed that etching increases the ultimate tensile strength of the fiber by causing a contraction which increases the residual compressive stress in the core. The residual stress distribution is shown schematically in Fig. 7.

The following factors are known to influence the residual stress distribution$^4,5$:

1) Volume expansion in the core due to boron diffusion and the formation of tungsten boride
2) Thermal expansion mismatch between the boride core and the outer boron mantle

3) "Boron elongation" during the deposition process of fiber formation

4) Quenching in the mercury electrode at the exit end of the reactor.

"Boron elongation" during fiber production was mentioned earlier to arise from the structural rearrangement of the imperfect deposit, resulting in the increased densification and expansion of the inner layers of the boron mantle. The phenomenon was first detected by Talley\textsuperscript{6} and later studied by Mehalso\textsuperscript{7} and others\textsuperscript{28,29}.

DiCarlo\textsuperscript{9} reported a slight radial density variation with a less than average density in the surface layers. Using a liquid density gradient technique\textsuperscript{30}, he measured the theoretical density of amorphous boron to be 2.3465 g/cm\textsuperscript{3}. While the observed radial density variation supports the above boron elongation theory, Wawer\textsuperscript{5} found no difference in the electron diffraction patterns obtained from the inner and surface layers of the boron fiber. Our own experiments on etched fibers showed some changes in the x-ray diffraction pattern with varying degrees of etch. There was a small increase in the width of diffuse peaks with increased etch along with a slight increase in the peak intensities relative to the first peak intensity (Fig. 12). It follows that the change in the residual stress distribution caused by etching affects the atomic structure and hence the diffraction pattern.

DiCarlo\textsuperscript{8b} observed that the complete creep strain recovery obtained with time and temperature indicates that chemically vapor-deposited vapor fibers deform flexurally as anelastic solids with no
plastic component. He also found that up to 800°C all non-elastic axial stress behavior could be explained solely by anelastic mechanisms. Both flexural stress relaxation (FSR) and flexural internal friction (FIF) techniques were employed. The relaxation processes responsible for the anelasticity were found to be controlled by a continuous distribution of thermally activated relaxation times, $\tau=\tau_0 \exp(Q/kT)$. An excellent theoretical fit with experimental data was obtained by assuming $\tau_0$ to be a constant with a broad and continuous distribution in energy $Q$. The existence of an anelastic effect with a fairly well-defined energy is an indication of some degree of crystallinity within the vapor-deposited fibers. The existence of the internal friction peaks and the magnitude of their relaxation strength was comparable to that predicted by Zener for grain boundary sliding or a mechanism of similar nature. Although no grain boundaries have been observed in amorphous fiber boron, one may still retain the sliding model by considering the relaxation to occur by the breaking of atomic bonds between smaller subunits in the boron structure. Additionally, it was found that high strains induced the activation of anelastic processes which were inhibited from operating at low strains by some unknown microstructural locking mechanism. It was hypothesized that the relaxing entities are boron icosahedra and the internal locks are unknown atomic imperfections quenched in after deposition.

Other properties of the amorphous fiber boron such as shear modulus, Poisson's ratio, damping capacity, thermal expansion and electrical conductivity have been measured by DiCarlo; see Table I.
Table I. Properties of the 203 μm (8 mil) diameter boron fiber.

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<td>Shear modulus, $G$</td>
<td>$177 \pm 4 \text{ GN/m}^2$</td>
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<td>Thermal expansion strain, $\lambda$</td>
<td>$\approx 0.05%$ (at room temperature)</td>
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<tr>
<td>Resistance per unit length, $R$, $\Omega/cm$</td>
<td>26.9 (at room temperature)</td>
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<td>Poisson ratio</td>
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E. Previous Work

The diffraction pattern obtained from fiber boron shows broadened peaks and a large amount of structure (Fig. 10). While the extremely broad peaks are amorphous in nature, the large amount of structure present indicates some degree of crystallinity. Attempts have been made by several workers to explain the experimental diffraction pattern of fiber boron.

Radial distribution functions (RDF) are obtainable from diffraction patterns and show the distribution of interatomic distances in an amorphous material. This subject will be dealt with in greater detail later; however, it is mentioned here that a radial distribution analysis by Badzian\textsuperscript{32} of bulk amorphous boron indicated icosahedral distances between boron atoms. Katada\textsuperscript{33} also obtained icosahedral distances when he calculated the RDF for thin films of vacuum deposited boron. This is not surprising since Hoard, et al.\textsuperscript{26}, and Longuet-Higgins, et al.\textsuperscript{15}, have demonstrated that boron displays a strong tendency to form icosahedra. Icosahedral units have been observed in all of the polymorphs and in most of the compounds of boron. It seemed natural, therefore, to assume some form of icosahedral distributions in the amorphous fiber boron structure. Lipsitt and Otte\textsuperscript{10} studied vapor-deposited boron using x-ray diffraction and electron microscopy. The diffraction patterns they obtained using Cu\textsubscript{K\alpha} radiation displayed four very diffuse peaks at positions similar to those obtained in the present study. The intensities of the diffuse peaks were not reported. Their electron microscope experiments showed crystalline spot patterns along with amorphous diffuse rings. On the basis of these observations, Lipsitt and Otte interpreted the structure of amorphous fiber boron to be layers of
face-centered cubic (fcc) distributions of $B_{12}$ icosahedra, with extensive faults in the stacking sequence of the layers. They postulated that upon heating amorphous boron over $1200^\circ C$, the fcc cell of $B_{12}$ groups converts into the rhombohedral structure of boron.

Lindquist, Hammond and Bragg\textsuperscript{31} criticized the model proposed by Lipsitt and Otte. Well-defined single crystal spot patterns are observed infrequently, indicating that crystalline regions comprise only a small volume fraction of the material and are not typical of their overall structure. Recently, Wawner\textsuperscript{5} has reported seeing no evidence of crystalline regions in amorphous fiber boron manufactured in conditions identical to those used in the present study. The fcc structure has not been observed in any of the boron polymorphs or compounds. In all of the known polymorphs of boron, the $B_{12}$ icosahedra do not behave like close-packed metal atoms. They exhibit definite orientation relationships and are separated by bond lengths comparable to the icosahedral radius. Additionally, Lindquist, et al., showed that the spot patterns could be interpreted in terms of known boron structures, making it unnecessary to postulate a new boron structure. Lipsitt and Otte proposed excessive faulting in the layers to account for the line broadening. However, no evidence of stacking faults, such as stacking fault fringes, was presented. The Lipsitt-Otte model was, therefore, found to be inadequate. Lipsitt and Otte had dismissed the possibility of line broadening due to small crystallites without reason. Using the Scherrer equation, Lindquist, et al.\textsuperscript{11}, interpreted the pattern as arising from a microcrystalline material with a computed crystallite size of about $30\AA$.

The structure of amorphous boron fibers, vapor-deposited in the
temperature range of 870°C to 1260°C with traverse speeds ranging from 2/3 ft/sec to 6 ft/sec, were studied by Lindquist, et al.\textsuperscript{11}, using x-ray diffraction and electron microscopy. They reported observing six or seven broad haloes. No differences in halo positions or relative intensities were observed among the various samples, even though there was considerable variation in their growth morphologies as revealed by optical microscopy. The halo positions and intensities were compared with those of crystalline alpha-rhombohedral boron, tetragonal boron or a mixture of the two. The presence of the beta-rhombohedral form as a major constituent of amorphous fiber boron was considered doubtful because of the absence of diffracted intensity for d spacings greater than 4.4\AA{} (Table II). The broadening of the haloes was accounted for by suggesting a very small average crystallite size of about 30\AA{}.

Thinned samples of boron fiber were examined by transmission electron microscopy and were reported by Lindquist, et al.\textsuperscript{11}, to contain a number of dark particles 100-200\AA{} in size embedded in a finely textured matrix. No evidence of dislocations, grain boundaries or stacking faults were observed. Selected-area diffraction revealed six distinct haloes and some isolated spots. The d-spacings of the halo maxima compared favorably with those for alpha-rhombohedral and tetragonal boron. Single-crystal spot patterns from the inclusions were indexed as alpha-rhombohedral boron and a defect structure of beta-rhombohedral type. No single crystal spot patterns attributable to tetragonal boron were found.

Although the diffuse halo pattern obtained from amorphous fiber boron seems qualitatively related to the alpha-rhombohedral and simple tetragonal structures of boron, the agreement is not complete. The
Table II. Comparison of the various peak positions and the relative intensities for alpha-rhombohedral, tetragonal and amorphous fiber boron\textsuperscript{16,20}. Radiation: Cu\textsubscript{Kα}.

<table>
<thead>
<tr>
<th>HALO NUMBER</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALF-WIDTH (2\theta)</td>
<td>16.1°-22.6°</td>
<td>34.5°-37°</td>
<td>-</td>
<td>52°-56°</td>
<td>64.7°-70.3°</td>
</tr>
<tr>
<td>FIBER BORON (2\theta)</td>
<td>20.5°</td>
<td>36.0°</td>
<td>43°</td>
<td>54°</td>
<td>67°</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>77</td>
<td>-</td>
<td>21</td>
<td>46</td>
</tr>
<tr>
<td>TETRAHEDRAL (2\theta)</td>
<td>20.3°,22.7°</td>
<td>35.4°,37.1°</td>
<td>41.3°</td>
<td>55°</td>
<td>64.7°,67.8°,71.6°</td>
</tr>
<tr>
<td>BORON (I)</td>
<td>100, 75</td>
<td>24, 75</td>
<td>19</td>
<td>6</td>
<td>48, 30, 20</td>
</tr>
<tr>
<td>ALPHA-RHOMBOHEDRAL (2\theta)</td>
<td>20.9°,21.9°</td>
<td>35.3°</td>
<td>42.8°</td>
<td>-</td>
<td>64.8°,69.6°,74.9°</td>
</tr>
<tr>
<td>BORON (I)</td>
<td>45, 100</td>
<td>70</td>
<td>55</td>
<td>-</td>
<td>15, 25, 12</td>
</tr>
</tbody>
</table>
third halo near the k value \( k = \frac{4\pi \sin \theta}{\lambda} \) of 2.95 is extremely weak as recorded by electron diffraction and is not observed at all by x-ray diffraction. However, both alpha-rhombohedral and tetragonal boron have strong peaks at d-spacings of 2.13\( \AA \) (Table I). Conversely, the fourth halo with a d-spacing of 1.77\( \AA \) is much stronger than can be accounted for by either polymorph. This led Lindquist, et al.\(^{11}\), to speculate on microcrystals of a defect structure closely related to the ideal alpha-rhombohedral and tetragonal structures but involving misplaced single boron atoms.

In summary, the smearing-out of sharp Bragg diffraction peaks and the loss of long-range periodicity have been attributed to one or more of the following factors:

1) high stacking-fault densities
2) internal strains
3) small crystallite size.

No evidence of stacking faults has been found in fiber boron and the internal strains are insufficient to account for the broadening due to the high modulus. Additionally, although the experimentally observed diffraction peaks are broad, they have too much structure to suggest glassy-amorphous boron.

The positions of the broad diffuse peaks obtained from amorphous fiber boron display an excellent correlation with the positions of the Bragg peaks for crystalline alpha-rhombohedral and tetragonal boron. This correlation led Lindquist, et al.\(^{11}\), to suggest a microcrystalline structure for amorphous fiber boron. The broadening was attributed to a small average crystallite size of about 30\( \AA \). However, due to
discrepancies between the diffracted intensities from the crystalline and amorphous forms of boron, Lindquist, et al., suggested microcrystals of a possible defect structure, closely related to the ideal alpha-rhombohedral and tetragonal structures, but involving misplaced boron atoms. This defect structure was not defined, and no qualitative or quantitative work was done to substantiate the possibility of a microcrystalline structure.

The broad overlapping peaks observed in diffraction patterns obtained from noncrystalline materials have often been attributed to: (i) crystallite size, (ii) a high density of stacking faults, and (iii) internal strains. Cargill\textsuperscript{34} studied the applicability of various proposed models to the noncrystalline nickel-phosphorus alloy system. By calculating model interference functions $I(k)$, Cargill considered whether physically reasonable crystallite sizes, stacking fault densities and strain distributions could reproduce the experimentally observed $I(k)$. Additionally, all of the Bragg peaks are broadened equally by small-sized isotropic crystallites\textsuperscript{34}. Since the first peak is observed to be much sharper than the following peaks in the experimental $I(k)$, Cargill felt this to be further evidence for the failure of the crystallite model. Models combining small crystallite size with a high density of deformation-type stacking faults or small crystallite size with a Gaussian distribution of internal strains were also unable to reproduce the experimental $I(k)$. On the basis of these observations, Cargill questioned the existence of small, randomly oriented, independently scattering microcrystals in noncrystalline metallic alloys, since a number of noncrystalline metallic alloys had very similar diffraction patterns and radial distribution functions, suggesting similarities in
their atomic arrangements. Cargill felt that the high densities of the noncrystalline Ni-P alloys indicated a continuous structure rather than one in which internal boundaries separate small, well-ordered regions. Sadoc, Dixmier and Guinier$^{43}$ have since generated built-up models, using a computer, that contain up to one thousand hard spheres of two sizes. The radial distribution functions and the interference functions calculated from these models for Ni-P alloys have shown good agreement with experiment.

Several efforts have been made$^{36,37}$ to distinguish between the crystallite model and the continuous random model for the atomic arrangement in amorphous solids. Warren$^{35}$ suggested that the lack of small-angle scattering indicated a failure of the crystallite model. Bienenstock and Bagley$^{36}$ calculated that intercrystalline interference lowered the small-angle scattering, thus showing that the lack of observed intensity did not necessarily mean the failure of the crystallite model. Bagley, Chen and Turnbull$^{37}$ have suggested some physical methods to aid the characterization of the structure of amorphous solids. Girgorovici$^{38}$ notes that since order is retained over a relatively small volume in amorphous solids, a sensible approach to the determination of the structure of amorphous solids would be to describe this order. Orderly arrangements which extend over a region whose dimension is large compared to that of the basic unit of the structure, e.g., a single icosahedron, without involving crystallographic periodicity, has been termed "structural ordering" by Karle and Konnert$^{44}$.

Direct information on the structural ordering of amorphous solids may be obtained from x-ray, electron and neutron diffraction experiments. However, because the diffracting volumes are generally much larger than
the volume in which the ordering exists, the information gained from these experiments corresponds to that of an isotropic body. Anisotropic ordering information may be obtained directly only by conducting diffraction experiments from volumes of the order of $10^3 \, \rho^3$. Since the possibility of conducting such experiments is presently quite remote, methods have to be devised to obtain as much indirect information as possible about the structural ordering.

The radial distribution function is obtained from experimental data by means of a Fourier transformation, and usually takes the form of an atomic radial distribution function

$$F = 4\pi r^2 \rho(r),$$

where $\rho(r)$ is the atomic density at a distance $r$ from an arbitrarily chosen central atom. Grigorovici has noted that this erroneously implies that the atom density is uniform over a sphere of given radius. While the maxima and minima in the radial distribution function provide statistically averaged information regarding the structural ordering, these maxima are flattened and broadened and are associated with spurious maxima and minima which have no correlation with the real structure. This inherent "termination error" arises from the fact that the Fourier integral is not extended to infinity but is limited by the wavelength of the radiation used to obtain the experimental data. Grigorovici suggests that the model proposed by the radial distribution function may be checked by using the RDF to compute the diffraction pattern and then comparing it with the original diffraction pattern. Grigorovici has also suggested that additional information regarding the structural ordering may be obtained from the RDF by analyzing its
attributes, such as the area and shape of the first maxima, and the position and height of the various maxima. This method is especially effective when the RDF computed from various models is compared with the experimentally obtained RDF. For example, Richter and Breitling\textsuperscript{39} have found that the interatomic distances corresponding to faint maxima in the RDF for amorphous Ge are very sensitive to slight rotations in the neighboring tetrahedra.

The advent of large scale utilization of computers has opened up new techniques for modelling the structure of amorphous solids. Polk\textsuperscript{40} constructed a three-dimensional continuous random network (CRN) using a ball and rod model for amorphous Ge or Se by connecting slightly distorted tetrahedra; non-crystallinity was achieved by varying the tetrahedral angle and by rotating the adjoining tetrahedra into various configurations. Polk and Boudreaux\textsuperscript{41} obtained the co-ordinates of 519 atom centers from this CRN model. Using a computer, the atoms were moved in a repetitive manner until the standard deviation of the first-neighbor distance distribution was less than a predetermined value. A program was written to compute the RDF of the refined model. Additionally, statistical data such as the mean first-neighbor distance and its standard deviation; the mean tetrahedral angle and its standard deviation; the distribution of the relative rotations of adjoining tetrahedra; and density were obtained. The computed RDF compared well with the experimental one.

Steinhardt, Alben and Weaire\textsuperscript{42} relaxed the co-ordinates of the 519 atom model\textsuperscript{41} to minimize the elastic energy which depends on both bond-length and bond-angle distortions. They used the same relaxation procedure to obtain the co-ordinates of a new 201 atom model. The two
models were characterized with regard to density; elastic distortion energy; elastic constants; number of five-, six-, and seven-fold rings; distribution of dihedral angles and the radial distribution function. The models were essentially identical in their characteristics, which suggests that a unique or "ideal" CRN structure may be a reasonably well-defined concept.

Comparisons between theoretical models and experimental results in the literature have been based predominantly on the RDF, which is sensitive to errors arising from termination effects. It is of interest to compare the calculated diffracted pattern directly with the experimental pattern, thus avoiding termination effects. The structural ordering in amorphous melanin has been studied by comparing the model interference function with the experimentally obtained interference function. It was decided to use this approach in the present study to investigate the structure of fiber boron. The co-ordinates of a distribution of up to 1400 boron atoms were used to compute theoretical diffraction patterns. The atom positions were changed by a repetitive process until the calculated diffracted pattern bore a fair resemblance to the experimentally obtained diffraction pattern. The following chapters explain the methods utilized to obtain the experimental diffraction patterns and the techniques employed to model the structural ordering in amorphous fiber boron and compute the theoretical diffraction pattern.
II. EXPERIMENTAL PROCEDURES

A. Boron Fibers

The boron fibers used in this investigation were made by Avco and supplied by NASA. They were produced in a continuous single stage reactor by the vapor phase reduction of BCl$_3$ by H$_2$ on a 12.7 m (0.5 mil) tungsten wire substrate held near 1300°C by resistive heating supplemented by VHF heating. Electrical contact was maintained by the use of mercury electrodes, which also acted as a quenching medium at the exit end of the reactor. The fibers have a W$_2$B$_5$ inner core (12.7 m or 0.5 mil) and a WB$_4$ outer core (17 m or 0.67 mil). There is a well-defined interface between the tungsten boride core and the surrounding sheath which consists of essentially pure (99.9%) boron.
B. Sample Preparation

Tungsten atoms scatter x-rays some two hundred times more efficiently than boron atoms. Hence, even though the tungsten boride core occupies only a small fraction of the total fiber volume, the diffracted intensity is strongly contaminated by the intensity scattered off the tungsten boride core. This makes it difficult to separate out the component scattered purely by the amorphous fiber boron. The technique of laying parallel fibers oriented in sheets several fibers deep in a sample holder to form a corrugated "flat-faced" diffractometer sample, as used by Lindquist, Hammond and Bragg\textsuperscript{11}, was therefore discarded. It was decided to etch the boron fibers such that the tungsten boride core was preferentially etched out to yield a hollow cylinder.

Three samples were etched different amounts, enabling the study of the effect of varying the degree of etch on the diffracted pattern. The first sample, labelled E1, was etched in a solution developed by Niemski and Pracka\textsuperscript{46}. The fiber was twirled in an agitated solution of potassium hydroxide and potassium ferricyanide (20 g KOH : 20 g K\textsubscript{3}Fe(CN)\textsubscript{6} : 160 g H\textsubscript{2}O) for 20 minutes. The μm (8 mil) fiber was etched down to 159 μm (6.3 mil), i.e., though the etchant preferentially attacks the boride core, the greater flow of solution at the surface results in the loss of considerable boron. E1 was found, subsequently, to contain traces of tungsten boride and was etched for an additional 48 hours in a solution of (1:1) HF : HNO\textsubscript{3}. This second etch attacked the boron sheath only slightly and removed all traces of tungsten boride. The final dimensions of E1 were an outer diameter of 159 μm (6.3 mil) and an inner diameter of approximately 45 μm (2 mil). Samples E2 and E3 were etched in the (1:1) HF : HNO\textsubscript{3} solution for 60 and 120 hours and
had final outer diameters of 182 µm (7.2 mil) and 177.6 µm (7.0 mil), respectively, with an inner diameter of roughly 20 µm (0.8 mil). Etching the fibers caused small changes to occur in the diffracted intensity profiles. These changes will be detailed in Chapter IV.
C. X-Ray Procedure

Hollow cylinders of fiber boron, 0.2 cm long, were obtained by dipping the fibers in a (1:1) HF : HNO₃ etching solution for a period of over 60 hours. The slow etching of the core was rate-controlled by diffusion. To obtain longer hollow cylinders required prohibitively longer times, and this ruled out the practicality of constructing a corrugated "flat-faced" diffractometer sample by laying parallel, hollow fibers in a holder. The hollow fiber could be used directly as the diffracting sample in the Debye-Scherrer camera. However, in order to avail of the greater accuracy obtainable by the use of diffractometers, an attempt was made to crush the boron fibers to a powder, dissolve the tungsten boride component in acid and compact the powder into a flat-faced diffractometer sample. The high hardness of boron rendered mortar-and-pestle techniques futile. A special die was constructed wherein the fiber was crushed between two tungsten carbide bits, 1.0 cm in diameter, by impact loading. The method was unable to crush boron to sizes smaller than 80μm, which is inadequate for making accurate diffracted intensity measurements and mechanically strong compact samples without the use of adhesives. Even dilute adhesives cannot be used for compacting boron powder, since the extremely low atomic scattering factor for boron causes the diffracted intensity from boron to be strongly influenced by even very small volume fractions of contaminants. The Debye-Scherrer camera seemed to be the most promising method for experimentally obtaining the diffracted intensity profile from pure amorphous fiber boron.

The samples used in the Debye-Scherrer camera were hollow single boron fibers, in which the cores were etched away to a depth of 2 mm
using a (1:1) HF : HNO$_3$ solution. The outer compressive layers of the fibers were also etched to varying degrees in order to study the effect of the changing residual stress distribution on the diffraction pattern. Experimental diffraction patterns were obtained both with and without rotation of the fiber sample in the camera. The use of a Gandolfi attachment$^{48}$, which simultaneously rotates the sample on one axis while precessing along an intersecting axis, generating all possible orientations in space, made possible the determination of the existence of preferred orientation (texture) in the fiber and the study of its effect. The camera chamber was evacuated to a pressure of less than 10$^{-3}$ mm of Hg by means of a mechanical pump to reduce air scattering. A Charles Supper Co. incident beam graphite-crystal monochromator was used to obtain monochromatic x-radiation. The Ilford Industrial G x-ray film was exposed for 21 hours to Cu$_{K\alpha}$ radiation and for 60 hours to Mo$_{K\alpha}$ radiation, all at 45 kV and 15 mA ratings. A densitometer was used to convert the density of the film (darkening) to relative intensity units, as described in the next section.
D. Densitometry

A Jarrel Ash microphotometer (densitometer), Model 23-050, was used to measure the photographic density of the Debye-Scherrer films by measuring $T$, the amount of light transmitted through it. In order to insure that the darkening (density) of the film was directly proportional to the logarithm of the intensity of the x-rays impinging on it, the photographic density was not allowed to exceed an experimentally determined linear response limit. This limit was established by subjecting an Ilford Industrial G x-ray film to a series of standard calibrating exposures, $I_1$, from this calibration film was measured on the densitometer and correlated to the x-ray intensity data, $I_0$, by statistically fitting all of the data points to a logarithmic curve, $I = a + b \ln(100/T)$, using a standard program (see Appendix I). The correlation coefficients were always greater than 0.96 and the results were extremely reproducible. Calibration runs were performed to establish the values of "a" and "b" both before and after each recording of the transmitted light data from the experimentally obtained Debye-Scherrer films of the boron fibers. The values for "a" and "b" were then used to convert transmission values, which ranged from 0 to 100, to intensity units. After subtracting the intensities due to the inherent background density of the film and the air scattering, the remaining intensity can be ascribed to scattering from amorphous boron. This corrected intensity, which is the total scattered intensity from amorphous boron, was converted to relative intensity units, which ranged from 100 units at the most intense peak to 0 units at the lowest point in the profile. These
values are arbitrary and were used only to compare the relative intensities and positions of the various maxima and minima in the diffracted intensity profiles. The variation utilizing this technique to obtain the final relative intensity results was experimentally established to be less than 2%.

All of the Ilford films were developed in Kodak D-11 for 7 minutes, washed in water for 1 minute, fixed in Kodak Rapid Fixer for 6 minutes and finally washed in water for 15 minutes, all solutions being held at a temperature of 68°F.

The following procedure was observed in making the corrections for the inherent background and the air scattering. A piece of unexposed film was developed and fixed, and the background intensity, I_B, was measured from it. Then a Debye-Scherrer exposure using Mo_K and Cu_K radiation with no sample in the camera was obtained, all other experimental conditions being identical to those used to obtain the Debye-Scherrer patterns from amorphous boron. The intensity of this blank shot, I_{BS}, was measured using the densitometer. The intensity of the air scattering with no sample is given by

$$I_{ABS} = I_{BS} - I_B \quad (2.1)$$

The ratio of the air-scattered intensity with and without the sample, for transmission geometries, is given approximately by

$$a_D = \exp \left( -\frac{\mu D}{\cos \theta} \right) \quad (2.2)$$

where $\mu$ is the linear mass absorption coefficient, D is the sample diameter and $\theta$ is the diffraction angle. The intensity scattered by
air is then given by

$$I_A = I_{ABS} \times a_D.$$  \hspace{1cm} (2.3)

The total scattered intensity $I_T$ from the boron sample is obtained by measuring the intensity from the Debye-Scherrer film, $I_D$, and subtracting the intensities due to the background and the air scattering, so that

$$I_T = I_D - I_A - I_B.$$  \hspace{1cm} (2.4)

$I_T$ is plotted on a scale of 100 to 0.
III. Computer Modelling

A. Calculated Patterns

The following chapter deals with methods used to compute the diffraction pattern from the various models and the techniques utilized to model the structural ordering in the amorphous fiber boron. The research was begun by investigating the possibility that the structure of the boron fibers was microcrystalline in nature and based on one or more of the three polymorphs of boron, as suggested by Lindquist, et al.\textsuperscript{11} The Debye scattering equation\textsuperscript{49} was used to calculate the diffracted intensity from a microcrystalline material. The average intensity diffracted in electron units when a rigid array of atoms is allowed to take any random orientation in space with equal probability is given by

\[
I_{\text{eu}}(k) = \sum_{m} \sum_{n} f_m(k) f_n(k) \sin\left(\frac{kr_{mn}}{k}\right) \frac{1}{kr_{mn}}
\]  

(3.1)

where \( f(k) \) is the atomic scattering factor for a boron atom, \( k \) is equal to \( 4\pi \sin \theta / \lambda \), \( \theta \) is the angle of diffraction, \( \lambda \) is the wavelength of the X-radiation and \( r_{mn} \) is the interatomic distance between the atoms "m" and "n" of the rigid array. The double summation is taken over all pairs of atoms in the array. The Debye equation computes, in effect, the intensity diffracted by a matrix consisting of randomly oriented microcrystallites of equal size, where each microcrystallite is the rigid array of atoms mentioned earlier.

The diffracted patterns form the various models were computed using the Debye equation and a computer program (see Appendix II) that

1. Generates the co-ordinates of all the atoms in the
microcrystal given the co-ordinates of all the atoms
associated with one lattice point,

2. Calculates each $r_{mn}$, the interatomic distance between atoms
"m" and "n" in the microcrystal,

3. Calculates $\sin(kr_{mn})/kr_{mn}$ for each $k = 4\pi \sin\theta/\lambda$ ,

4. Sums $\sin(kr_{mn})kr_{mn}$ over all $r_{mn}$ for each $k$.

This sum was multiplied by the square of the atomic scattering factor
to yield the coherently scattered intensity per microcrystal in electron
units. The Compton modified scattering per microcrystal was calculated
and added to the coherently scattered intensity. The net scattered
intensity was then corrected for polarization and absorption to simulate
the experimentally observed intensity. The final intensity is given by

$$I_{eu}(k)/N = \left( I_{coh}(k) \times P(k)/N + I_{incoh}(k)/N \right) \times A(k) \quad (3.2)$$

where $I_{coh}(k)/N$ is the incoherently scattered intensity per microcrystal,
$I_{incoh}(k)/N$ is the incoherently scattered intensity per microcrystal,
$A(k)$ is the absorption correction, $P(k)$ is the polarization factor and
$N$ is the number of microcrystals in the diffracting volume. The
coherent scattering per microcrystal is given by

$$I_{coh}(k)/N = f^2(k) \sum_{m} \sum_{n} \frac{\sin(kr_{mn})}{kr_{mn}} \quad (3.3)$$
as calculated from the Debye equation. $I'_{incoh}(k)/R$ values were obtained
from the International Tables for X-Ray Crystallography, Vol. III, where
R, the Breit-Dirac recoil factor, is given by

$$R = (1 + 0.0486 \frac{\sin^2 \theta}{\lambda})^2 \quad (3.4)$$
The incoherent scattering per microcrystal is equal to

\[ I_{\text{incoh}}(k)/N = \left[ I_{\text{incoh}}(k)/R \right] \times R \times N_m \]  

(3.5)

where \( N_m \) is the number of atoms in the microcrystal. The absorption correction factors, \( A(k) \), were obtained from the data compiled by Taylor and Sinclair\(^5\). For monochromatic radiation, the polarization factor \( P(k) \) is

\[ P(k) = (1 + \cos^2 \theta_m \cos^2 \theta)/(1 + \cos^2 \theta_m) \]  

(3.6)

where \( \theta_m \) is the Bragg angle for the diffracting plane of the monochromator crystal.

Finally, the total scattered intensity was scaled so that the most intense peak was equal to 100 units. This arbitrary scaling facilitated comparison between the experimental and computed patterns.
B. Distortions

Initial microcrystalline models were constructed by taking unit cells of the polymorphs of boron and stacking them together in a brick-like fashion to produce an array of atoms. For example, the alpha-rhombohedral polymorph has an icosahedron at each corner of the cell (Fig. 3). Thus, a (2x2x2) alpha-rhombohedral microcrystal contains 8 icosahedra and 96 atoms. A single tetragonal boron unit cell contains 50 atoms and a (2x2x2) tetragonal microcrystal contains 400 atoms. These atoms were arrayed in a manner exactly identical to those found in crystalline boron, the only difference being the size of the array. The model sizes were limited by the extent of the broadening of the various peaks, larger model sizes producing sharper peaks with more resolution.

The patterns computed from the microcrystalline models of the various crystalline polymorphs compared unsuccessfully with the experimentally obtained patterns because there were large discrepancies in the relative intensities of the various maxima. Since the fiber is produced in a thermodynamically metastable process, it seemed valid to consider the possibility that the atoms were not sitting on crystallographic sites. Thus, distortions were introduced.

The alpha-rhombohedral microcrystal was distorted in the following manner:

1. The rhombohedral cell parameters were changed slightly, in a random manner, so that the unit cell became essentially triclinic, with \( a \neq b \neq c \neq \neq 5.05 \text{\AA} \) and \( a \neq \beta \neq \gamma \neq 58.06^\circ \) (see I.A.1).
2. The icosahedra themselves were then distorted:
   
a) The $x$, $y$, $z$ co-ordinates of the atoms of an icosahedron with respect to its lattice point, were converted to polar co-ordinates $r$, $\theta$, and $\phi$.
   
b) These polar co-ordinates were changed to $r \pm \Delta r$, $\theta \pm \Delta \theta$ and $\phi \pm \Delta \phi$ in a random fashion, and then converted back to $x'$, $y'$, and $z'$, the new co-ordinates.
   
3. Finally, microcrystals with different shapes, such as a (2x2x4) microcrystal, were studied, in order to study the effect of the various shapes on the computed patterns.
C. Fitting Procedures

All of the modelling and the computations were performed on a PDP 11/03 microcomputer, which lacks the memory and high speeds of larger computers. Hence, an iterative approach, in which the atoms are moved continuously towards preferred positions while the computer monitors the favorableness of such atomic movements by comparing the computed and experimental patterns, was not possible. The bulk of the modelling consisted of choosing physically reasonable distortions and evaluating which ones provided favorable results in driving the computed pattern toward the experimental one.

An additional program was therefore written to find which interatomic distances were favorable, thus enabling the determination of intelligent distortions aimed at eliminating unfavorable interatomic distances. The interatomic distance analysis program calculated the various $r_{mn}$ terms, bracketed to within $0.01\AA$, and the multiplicity of their occurrence. An example of how this program was used to determine favorable distortions is detailed here.

The computed pattern from the (3x3x3) alpha-rhombohedral microcrystal model (Fig. 14) displays a very high first-to-second peak intensity ratio when compared to the experimental pattern. In order to obtain a better fit, it was necessary to increase the intensity of the second peak relative to the first. The program which computes interatomic distances $r_j$ and the multiplicity of their occurrence, $n_j$, was used to calculate which of the $r_j$ were contributing most strongly to the first and second peaks via the $(\sin kr)/kr$ term in the Debye equation.

In the (3x3x3) alpha-rhombohedral microcrystal model, the
interatomic distance \( r_j = 1.78\AA \) occurred 648 times (\( n_j = 648 \)). within the microcrystal (Fig. 8). The first peak occurred at \( k = 1.4 \) and the second peak at \( k = 2.5 \). Now, for \( r_j = 1.78\AA \) and \( k = 1.4 \), \( \sin(kr_j) \) is positive, and for \( r_j = 1.78\AA \) and \( k = 2.5 \), \( \sin(kr_j) \) is negative (Fig. 8). It was noticed that the intra-icosahedral distance of \( 1.78\AA \), which occurred with a high multiplicity, made a large positive contribution to the first peak and a large negative contribution to the second peak.

Distorting the icosahedra to change the intra-icosahedral distance from \( 1.78\AA \) to \( 1.9\AA \), for instance, would drastically reduce the disparity in contributions (Fig. 8).

An icosahedral distortion was introduced which changed the nearest-neighbor spacing from an average of \( 1.78\AA \) to an average of \( 1.88\AA \).

There are 30 such distances within an icosahedron. A distorted icosahedron has six \( 1.65\AA \), eighteen \( 1.9\AA \) and six \( 2.05\AA \) distances. With the same reasoning and intent, the cell parameters were increased from \( 5.056\AA \) to \( 5.2\AA \). This preliminary distortion resulted in an improved fit with the experimental pattern (Fig. 18).

An additional computer program, SPMDST.FOR (see Appendix III), was written to help decide which interatomic distances made significant contributions to the various peaks. This program does the following:

1. It prints the atom number \( N_i \), the \( x_i, y_i, z_i \) co-ordinates of the atom \( N_i \), the lattice point \( h_i, k_i, l_i \) of the icosahedron to which it belongs, and its intra-icosahedral number (from 1 to 12). Thus, given \( N_i \) and \( N_j \), the atom positions, vector \( r_{ij} \) can be pinpointed.

2. All of the \( r_{ij} \)'s are collated within a resolution of \( 0.01\AA \),
Fig. 8a shows the interatomic distances occurring within the microcrystal and their multiplicity of occurrence. Shifts due to the distortions have been indicated.

Fig. 8b plots $\sin(kr_{nn})$ v. $r_{nn}$. Plot 1 has $k=1.4$, which corresponds to $2\theta = 29^0$ and the first peak position. Plot 2 has $k=2.5$, which corresponds to $2\theta = 35^0$ and the second peak position. It is seen that the distorted distances make smaller positive contributions to the first peak, thus enhancing the contribution to the second peak.
and the interatomic distance \( r_k \) and the multiplicity \( m_k \) are printed with a representative \( r_{ij} \), \( N_i \) and \( N_j \).

3. All of the \( r_j \)'s are now collated within a resolution of \( 0.25^\circ \). The mean distance \( \bar{r} \) and "summed multiplicity" \( M \) are calculated and printed, where

\[
\bar{r} = \frac{\sum_{k} m_k r_k}{\sum_{k} m_k}, \\
M = \sum_{k} m_k,
\]

and the summations are over each resolution period \( \ell \).

4. Consider for the moment a hypothetical peak at \( k=0.9 \), with the base of the peak extending from \( k=0.8 \) to \( k=1.1 \) (Fig. 9). The program calculates, for each \( 0.25^\circ \) resolution period,

\[
A(k) = \sum_{\ell} \sin(k_j r_{k_j}^\ell) \times m_k \times f^2(k_j)
\]

where \( j=0.8, 0.9, 1.1 \). The following parameters are then calculated:

\[
B = A(0.9) - A(0.8) \\
C = A(0.9) - A(1.1)
\]

\( B \) and \( C \) are then plotted on the ordinate with \( \bar{r} \) on the abscissa.

It is suggested that the \( \bar{r} \) values for which both \( B \) and \( C \) are positive are interatomic distances which would increase the relative intensity of that peak if the multiplicity of these distances were to increase. This analysis may be carried out for any peak but was found to be effective only for the peaks at the lower \( k \) values.

In summary, two computer programs have been developed. One program
computes the diffraction pattern from various models by using the Debye equation. The other tabulates the various interatomic distances and their contributions to a specified peak, thus enabling intelligent distortions of the models. The following chapter presents the results of the modelling efforts.
Fig. 9. Hypothetical peak at $k=0.9$, with the base of the peak extending from $k=0.8$ to $k=1.1$. 
IV. RESULTS AND DISCUSSION

A. Experimental Patterns

1. Cu$_{K\alpha}$ Radiation

A Debye-Scherrer camera exposure using an incident beam graphite-crystal monochromator, vacuum and sample El yielded the diffracted intensity profile with four broad peaks shown in Fig. 10. This profile from amorphous fiber boron shows good qualitative agreement with the data obtained from bulk amorphous boron by Badzian$^{32}$ (Fig. 11). The third "peak" at 43° 2θ (Cu$_{K\alpha}$) is non-existent in both experimentally obtained patterns. This is the first noticeable discrepancy between the peak positions and intensities for alpha-rhombohedral, tetragonal and amorphous boron (see Table I) since both polymorphs show peaks at that position. The second discrepancy is the fourth peak at 54° 2θ (Cu$_{K\alpha}$) observed experimentally for amorphous boron. This peak is weak in tetragonal boron while alpha-rhombohedral boron has no peak at this position (Table II). These early indications suggest that simple micro-crystals of alpha-rhombohedral and tetragonal boron will be inadequate to explain the experimental results. The earlier part of the modelling and fitting was done using the Cu$_{K\alpha}$ profile. The wavelength of Cu$_{K\alpha}$ radiation is 1.54178\(\AA\), and this enables fitting the computed pattern out to a k (=4πsinθ/λ) value of 8.1 \(\AA^{-1}\). To insure that the fit was good at larger values of k, Mo$_{K\alpha}$ radiation with a wavelength of 0.71069\(\AA\) was used to provide supplemental information out to a k value of 17.6 \(\AA^{-1}\).

2. Mo$_{K\alpha}$ Radiation

Fig. 12 shows the diffracted intensity profiles obtained from
Fig. 10. Debye-Scherrer pattern from sample E1, using the Gandolfi attachment and CuKα radiation.
Fig. 11. Diffracted intensity from bulk amorphous boron, using CuKα. From Badzian 32.
samples E1, E2 and E3. These samples consist of 203 μm (8 mil) boron fibers which have been etched for varying amounts (see II.B.). Sample E1 was etched the most, having an outer diameter of 159 μm (6.3 mil) and an inner diameter of approximately 45 μm (2 mil). Sample E2 with a final outer diameter of 182 μm (7.2 mil) is the least etched, while sample E3 has an outer diameter of 177 μm (7.0 mil). Both samples have an approximate inner diameter of 20 μm (0.8 mil).

The eight peaks have almost identical positions for all three samples (Fig. 12). Sample E1 has peaks I to V shifted about 0.3° 2θ to the left relative to the others. However, peaks VI, VII and VIII for sample E1 do not display this shift. Comparing samples E2 and E3, it is observed that the peak positions are all the same. The peaks for E3 are somewhat broader than the corresponding peaks for E2, and have more intensity relative to the first peak, especially on peaks II and V. On the other hand, the relative intensities for peaks II and V are quite similar for samples E1 and E3. It therefore appears that there is a slight broadening of the peaks with a concomitant increase in relative intensities with increasing etch.

A number of Debye-Scherrer camera exposures were made of each sample, some with the sample rotating in the camera, others with a stationary sample. The diffracted intensity profiles were quite similar for each sample, regardless of whether it had been rotated or not, with variations of less than ±2% in the relative intensities. The profiles shown in Fig. 12 were averaged over the many exposures for each sample. This result is significant since it indicates that the volumes of local atomic ordering are randomly oriented over the diffracting volume and small enough to produce a smooth, uniform Debye-Scherrer powder pattern
Fig. 12. Diffracted intensity pattern for fiber samples E1, E2, and E3, using MoKα radiation.
with no sample rotation.

The Gandolfi attachment was used on the Debye-Scherrer camera to verify that the relative intensities of the various peaks were not skewed due to texture along the fiber axis. The Gandolfi attachment simultaneously rotates the sample on one axis while precessing along an intersecting axis, thus generating all possible orientations of the diffracting volume in space for a powder-type sample. Fig. 13 shows the superimposed diffracted intensity profiles for sample E3 obtained with and without the use of the Gandolfi attachment. The results indicate that any textural effects are negligibly small.
Fig. 13. Diffracted intensities obtained with and without the Gandolfi attachment to study fiber texture.

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Sample E3, Gandolfi, MoKα, Vacuum + Monochromator

---

Sample E3, MoKα, Vacuum + Monochromator
B. Microcrystalline Models

1. Microcrystals of the Boron Polymorphs

a) Alpha-Rhombohedral Microcrystals

The alpha-rhombohedral polymorph has an icosahedron at each corner of the cell (Fig. 3b), and initial alpha-rhombohedral microcrystals were fashioned by stacking the icosahedra in 3x3x3 and 4x4x4 arrays. The co-ordinates of the twelve atoms of the icosahedra associated with each lattice point were obtained from the structural data reported by Decker and Kasper\textsuperscript{16}. The lattice parameters of the alpha-rhombohedral cell for boron were used to compute the diffracted intensity profile. The results are plotted graphically as $I_{rel}$ vs. $2\theta$, Cu $K\alpha$ in Fig. 14.

The immediately arresting feature of the computed patterns is the low intensity of all the peaks relative to the first peak. The diffracted intensity of the second and third peaks is listed in the powder pattern data for alpha-rhombohedral boron\textsuperscript{16} as 70 and 55 units, respectively, whereas the computed microcrystalline intensities are not as high. The computed peak positions are in general agreement with the experimental peak positions, with the exception of peak III, which is not observed experimentally. It is interesting to note that the computed diffracted intensity profile shows a well-resolved fourth peak while no such peak is indicated in the data compiled by Decker and Kasper\textsuperscript{16} (see Table II).

Many of the characteristic features of the microcrystalline models may be observed in Fig. 14. Increasing the number of atoms in the microcrystal, in this case from 324 atoms to 768 atoms, produces the following results:

1. the resolution of all of the peaks is increased,
2. the intensity of all of the peaks relative to the first peak is increased and
3. the first peak shifts to the right.

The extent of the first peak shift decreases with increasing microcrystallite size, while the resolution of the peaks always increases with microcrystallite size. The intensities of the various peaks generally increase with microcrystalline size, stabilizing at the larger size.

b) Tetragonal Microcrystals

The diffracted intensity profile computed for a (2x2x2) microcrystalline model of tetragonal boron is shown in Fig. 15. The co-ordinates of the fifty atoms in the unit cell (Fig. 4) were obtained from data published by Hoard, Hughes and Sands. The unit cells were stacked in a brick-like fashion to produce an array of 400 atoms. The addition of peripheral atoms sitting on \((0,0,1/4)\) and \((1/4,1/4,0)\) sites produced a microcrystal containing a total of 414 atoms. The computed intensities were once again lower than the experimentally observed peak intensities. The first peak was slightly displaced while the remaining peaks had good peak positions. Another feature of the computed pattern was the absence of a resolved fourth peak at 54° 28 (Cu\(K_{\alpha 1}\)). The powder intensity data tabulated by Hoard and Newkirk indicate a low intensity peak at that position (see Table II). However, it is quite possible that a peak would be resolved at that position on increasing the size of the microcrystal.

c) Beta-Rhombohedral Microcrystals

Geist, Kloss and Follner have presented the co-ordinates of the 105 atoms in the unit cell for beta-rhombohedral boron. These co-ordinates were utilized to generate a (2x2x2) microcrystal containing
Fig. 15. Diffraction pattern from tetragonal boron microcrystals.

Tetragonal boron microcrystal, N=414, Cu Kα

---

Experimental
840 atoms. The computed diffracted intensity pattern is shown in Fig. 16. The powder pattern peak intensities and positions have been tabulated in Table III, the most intense peak position being $17.6^° \theta$ ($\text{Cu}_{K\alpha}$). The most intense computed peak is positioned at $15^° \theta$ ($\text{Cu}_{K\alpha}$), at a much lower angle than that observed experimentally. It is fairly obvious that the pattern computed for the microcrystalline model of beta-rhombohedral boron has very little in common with the experimental pattern.

To summarize the effort to model the experimentally observed diffraction pattern obtained from amorphous fiber boron using simple microcrystals of the various boron polymorphs, all of the models were found to be inadequate. Microcrystals of the beta-rhombohedral polymorph were not found to be present in the experimental sample. The alpha-rhombohedral polymorph has an extra peak at $43^° \theta$ ($\text{Cu}_{K\alpha}$), while the tetragonal polymorph lacks the presence of a resolved peak at $54^°.20$ ($\text{Cu}_{K\alpha}$). The peak positions are in reasonable experimental agreement, while all of the computed relative peak intensities are found to be much lower than the experimentally observed peak intensities. The alpha-rhombohedral polymorph was considered to be the most promising structure to work with, overall. Because the fiber is produced in a thermodynamically metastable process, it is possible to consider that the atoms and the icosahedra are displaced from their crystallographic lattice sites. To successfully model the experimental pattern, it was deemed necessary to distort the alpha-rhombohedral structure in order to simultaneously increase the intensities of all peaks relative to the first and shift the third peak into a common envelope with the second peak. The
Fig. 16. Diffraction pattern from beta-rhombohedral boron microcrystals.

Beta-rhombohedral microcrystal, N=840

Experimental
Table III. Major peak positions and their relative intensities, from the powder pattern for beta-rhombohedral boron\textsuperscript{20}.

<table>
<thead>
<tr>
<th>d, Å</th>
<th>2θ, Cu\textsubscript{Kα}</th>
<th>I</th>
<th>d, Å</th>
<th>2θ, Cu\textsubscript{Kα}</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.937</td>
<td>11.15°</td>
<td>40</td>
<td>2.863</td>
<td>31.24°</td>
<td>19</td>
</tr>
<tr>
<td>7.415</td>
<td>11.93°</td>
<td>24</td>
<td>2.613</td>
<td>34.32°</td>
<td>17</td>
</tr>
<tr>
<td>5.041</td>
<td>17.59°</td>
<td>100</td>
<td>2.405</td>
<td>37.39°</td>
<td>17</td>
</tr>
<tr>
<td>4.648</td>
<td>19.09°</td>
<td>56</td>
<td>1.758</td>
<td>52.02°</td>
<td>17</td>
</tr>
<tr>
<td>4.505</td>
<td>19.71°</td>
<td>28</td>
<td>1.549</td>
<td>59.69°</td>
<td>17</td>
</tr>
<tr>
<td>4.403</td>
<td>20.17°</td>
<td>18</td>
<td>1.448</td>
<td>64.33°</td>
<td>18</td>
</tr>
<tr>
<td>4.255</td>
<td>20.88°</td>
<td>25</td>
<td>1.430</td>
<td>65.24°</td>
<td>28</td>
</tr>
<tr>
<td>3.969</td>
<td>22.40°</td>
<td>17</td>
<td>1.418</td>
<td>65.86°</td>
<td>22</td>
</tr>
<tr>
<td>3.708</td>
<td>24.00°</td>
<td>23</td>
<td>1.382</td>
<td>67.81°</td>
<td>30</td>
</tr>
<tr>
<td>3.542</td>
<td>25.14°</td>
<td>28</td>
<td>1.347</td>
<td>69.82°</td>
<td>42</td>
</tr>
<tr>
<td>3.43</td>
<td>25.98°</td>
<td>17</td>
<td>1.302</td>
<td>72.61°</td>
<td>25</td>
</tr>
</tbody>
</table>
distortions applied to the alpha-rhombohedral structure will now be described.
2. Distorted Alpha-Rhombohedral Microcrystals

The alpha-rhombohedral polymorph for boron has the lattice parameters \( a = b = c = 5.057 \, \text{Å} \), \( \alpha = \beta = \gamma = 58.06^\circ \). These parameters were changed to \( a = b = c = 5.057 \pm 0.5 \, \text{Å} \), and \( \alpha = \beta = \gamma = 58.06 \pm 2.0^\circ \) in order to distort the rhombohedral lattice. Positive and negative changes were made in a random manner.\(^1\) The co-ordinates of the twelve atoms of the icosahedron at the origin of the alpha-rhombohedral lattice are given by \( x, y, z \) the fractions of the unit cell parameters. These co-ordinates were converted to polar co-ordinates \( r, \theta \) and \( \phi \), where \( \phi \) is positive going counterclockwise in the xy plane (Fig. 17). The co-ordinates of the twelve atoms in the icosahedron for alpha-rhombohedral boron are tabulated in Table IV. It is seen that atoms 1 to 6 have a lower than average \( r \) value, while atoms 7 to 12 have a higher than average \( r \) value, the average icosahedral sphere radius, \( \bar{r} = 1.687 \). Thus it is seen that even icosahedra found in crystalline boron are not regular icosahedra in the true geometrical sense, but are slightly distorted. The \( \theta \) and \( \phi \) values for the \( x, y, z \) axes in the alpha-rhombohedral lattice have the following values:

<table>
<thead>
<tr>
<th>Axis</th>
<th>( \theta )</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>x axis</td>
<td>( 0^\circ )</td>
<td>( 0^\circ )</td>
</tr>
<tr>
<td>y axis</td>
<td>( 0^\circ )</td>
<td>( 58.06^\circ )</td>
</tr>
<tr>
<td>z axis</td>
<td>( 52.77^\circ )</td>
<td>( 29.03^\circ )</td>
</tr>
</tbody>
</table>

\(^1\)Additionally, the icosahedra were flattened or elongated in the following way: 1) the rhombohedral co-ordinates of the atoms in the icosahedron were converted to orthogonal co-ordinates, and 2) the "z" co-ordinates were then multiplied by 0.8 and the "x" and the "y" co-ordinates by 1.1 to convert the icosahedral sphere into a slightly flattened disc. These distortions provided no improvement in the fit for the computed models, and the resulting patterns are not shown.
Fig. 17. Polar co-ordinates.
Table IV. Co-ordinates of the atoms of the icosahedron in the alpharhombohedral polymorph.

<table>
<thead>
<tr>
<th>ATOM NO.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>r</th>
<th>θ</th>
<th>ϕ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0104</td>
<td>.0104</td>
<td>-.3427</td>
<td>1.679</td>
<td>-55.267</td>
<td>-150.97</td>
</tr>
<tr>
<td>2</td>
<td>.0104</td>
<td>-.3427</td>
<td>.0104</td>
<td>1.679</td>
<td>1.429</td>
<td>-119.89</td>
</tr>
<tr>
<td>3</td>
<td>-.3427</td>
<td>.0104</td>
<td>.0104</td>
<td>1.679</td>
<td>1.429</td>
<td>177.95</td>
</tr>
<tr>
<td>4</td>
<td>-.0104</td>
<td>-.0104</td>
<td>.3427</td>
<td>1.679</td>
<td>55.267</td>
<td>29.03</td>
</tr>
<tr>
<td>5</td>
<td>-.0104</td>
<td>.3427</td>
<td>-.0104</td>
<td>1.679</td>
<td>-1.429</td>
<td>60.11</td>
</tr>
<tr>
<td>6</td>
<td>.3427</td>
<td>-.0104</td>
<td>-.0104</td>
<td>1.679</td>
<td>-1.429</td>
<td>-2.05</td>
</tr>
<tr>
<td>7</td>
<td>.2206</td>
<td>.2206</td>
<td>-.3677</td>
<td>1.695</td>
<td>-60.848</td>
<td>29.03</td>
</tr>
<tr>
<td>8</td>
<td>.2206</td>
<td>-.3677</td>
<td>.2206</td>
<td>1.695</td>
<td>31.597</td>
<td>-59.99</td>
</tr>
<tr>
<td>9</td>
<td>-.3677</td>
<td>.2206</td>
<td>.2206</td>
<td>1.695</td>
<td>31.539</td>
<td>118.05</td>
</tr>
<tr>
<td>10</td>
<td>-.2206</td>
<td>-.2206</td>
<td>.3677</td>
<td>1.695</td>
<td>60.848</td>
<td>-150.97</td>
</tr>
<tr>
<td>11</td>
<td>-.2206</td>
<td>.3677</td>
<td>-.2206</td>
<td>1.695</td>
<td>-31.597</td>
<td>120.0</td>
</tr>
<tr>
<td>12</td>
<td>.3677</td>
<td>-.2206</td>
<td>-.2206</td>
<td>1.695</td>
<td>-31.597</td>
<td>-61.94</td>
</tr>
</tbody>
</table>
Atoms 6 and 3 (Table IV) with $\theta = -1.43^\circ$, $\phi = -2.05^\circ$ and $\theta = 1.43^\circ$, $\phi = 177.95^\circ$, respectively, almost lie along the x-axis. Similarly, atoms 1 and 4 lie close to the z-axis, while atoms 2 and 5 lie close to the y-axis. Thus, six of the twelve atoms of the icosahedron tend to be aligned along the rhombohedral axes. This observation underscores the icosahedral propensity for alignment along the five-fold axes.

In the earlier chapter on computer modelling, it was suggested that the icosahedra could be distorted (see Chapter III.B.2) by changing the polar co-ordinates $r$, $\theta$ and $\phi$ to $r\pm r$, $\theta\pm\Delta\theta$ and $\phi\pm\Delta\phi$. It was also suggested in Chapter III.C that distorting the icosahedra to change the intra-icosahedral nearest-neighbor distances from $1.78\AA$ to $1.90\AA$ would favorably increase the intensity of the second peak relative to the first. This was achieved by changing the radii of atoms 1 to 6 (Table IV) from

$$r_{1-6} = (1.687 - .008) = 1.679\AA, \quad \Delta r = -.008$$

to

$$r'_{1-6} = (1.687 - .087) = 1.6\AA, \quad \Delta r = -.087\AA$$

while the radius of the atoms 7 to 12 were changed from

$$r_{7-12} = (1.687 + .008) = 1.695\AA, \quad \Delta r = +.008\AA$$

to

$$r'_{7-12} = (1.687 + .213) = 1.9\AA, \quad \Delta r = +.213\AA$$.

Due to the strong icosahedral tendency for alignment along the five-fold axes, the $\theta$ and $\phi$ values of the icosahedral atoms were kept initially unchanged.
There are 30 nearest-neighbor distances within the icosahedron. Incorporating the above radial changes for \( r_{1-6} \) and \( r_{7-12} \) produced six 1.65Å, eighteen 1.9Å and six 2.05Å nearest-neighbor distances, thus changing the nearest-neighbor spacing from an average of 1.79Å to an average of 1.88Å. Combining the additional suggestion in Chapter III.C. that an increase in the cell parameters from \( a_o = b_o = c_o = 5.057\text{Å} \) to \( a_o = b_o = c_o = 5.2\text{Å} \) would beneficially affect the peak intensities, the final applied distortion D2 had the following attributes:

\[
\begin{align*}
r'_{1-6} & = 1.6\text{Å}, \\
r'_{7-12} & = 1.9\text{Å} \quad \text{and} \\
a_o = b_o = c_o = 5.2\text{Å}
\end{align*}
\]

and was labelled D2(1.6, 1.9)5.2.

The computed diffracted intensity pattern from the (3x3x3)D2(1.6, 1.9)5.2 microcrystalline model is shown in Fig. 18, superimposed on the (3x3x3) alpha-rhombohedral microcrystalline (ALMIC) model. The distortion shows improved results, with an increase in the relative intensity of all of the peaks relative to the first peak with a simultaneous reduction in the diffracted intensity near the vicinity of the third peak (42O 20', CuKα). However, all of the peaks were found to have shifted to the left as a result of increasing the lattice parameter from 5.057Å to 5.2Å. This effect is shown on a magnified scale in Fig. 19, where \( a_o \) has been increased from 5.057Å to 6Å in an otherwise identical ALCMC model. Despite the increase in relative intensities of the peaks due to the applied D2(1.6, 1.9)5.2 distortion, they were still found to be much lower than the experimentally observed peak.
Fig. 18. Diffraction pattern from distorted alpha-rhombohedral boron.

- D₂ (1.6, 1.9), 5.2Å, N=324, CuKα
- (3x3x3) ALMIC, 5.057Å, N=324, CuKα
- Experimental
intensities (Fig. 18). Hence the model was unsatisfactory and other physically reasonable distortions were sought to obtain a better fit. It is necessary, while seeking a more favorable distortion, to insure that physically limiting conditions are not violated. Nearest-neighbor distances cannot be too low, for example, or the model densities cannot be too high.
Fig. 19. Diffraction pattern showing peak shifts with changing lattice parameter.

- (3x3x3) ALMIC, \(a_0=6\,\AA\), \(N=324\), Cu\(_{K\alpha}\)
- (3x3x3) ALMIC, \(a_0=5.057\,\AA\), \(N=324\), Cu\(_{K\alpha}\)
- Experimental
C. Density Considerations

Consider a matrix composed of close-packed spherical microcrystals. A simple calculation shows the density of the matrix to be approximately equal to three-fourths of the density of the spherical microcrystal. Furthermore, if the density of the spherical microcrystal of boron is considered to be 2.46 g/cm$^3$, the density of the most dense polymorph, alpha-rhombohedral boron, then the density of the matrix is calculated to be 1.82 g/cm$^3$, which is low compared to the experimentally observed density of 2.346 g/cm$^3$ reported$^9$ for amorphous fiber boron. This illustrates the difficulty of thinking in terms of randomly oriented microcrystals in a literal sense, especially since the decrease in density due to high angle "grain boundaries" is largely a function of the size and shape of the microcrystals. Using the bubble-raft model, attempts have been made by some authors$^{34}$ to calculate crystallite sizes by measuring the grain boundary density deficit $\Delta \rho / \rho$ and the energy of vacancy formation $E_F$, and assuming that the entire grain boundary surface energy $\gamma_{gb}$ is due to vacancies associated in the transition region. The density deficit $\Delta \rho / \rho$ is measured by annealing the amorphous material and measuring the increase in density. Approximate results have been obtained for materials with close-packed structures, but the method would not be useful for low density materials having loosely packed structures with highly directional covalent bonding, as found in boron, since the bubble-raft model approach would be inapplicable.

The crystalline density of alpha-rhombohedral boron is calculated to be 2.4647 g/cm$^3$, which is close to the experimental value$^{16}$ of 2.46 g/cm$^3$. Similarly, the crystalline density of 2.316 g/cm$^3$
calculated for tetragonal boron is close to the reported experimental value\textsuperscript{17} of 2.31 g/cm\textsuperscript{3}. However, a discrepancy crops up when the crystalline density of beta-rhombohedral boron (2.276 g/cm\textsuperscript{3}) is compared with its reported\textsuperscript{18,20} experimental density of 2.35 g/cm\textsuperscript{3}. Some authors have claimed that there are 108 atoms per unit cell, rather than 105 atoms, which raises the calculated crystalline density to 2.34 g/cm\textsuperscript{3}. This means that annealing amorphous fiber boron at high temperatures until it crystallizes into the stable beta-rhombohedral structure would cause virtually no change in density. One could consider the amorphous fiber boron matrix to consist of a continuous network of randomly oriented regions of density $\rho_s$, such that the density of the matrix $\rho_m$ is equal to $\rho_s$. This assumption implies that there is no "grain boundary" density deficit, therefore,

$$\rho_m = \rho_s = 2.3466 \text{ g/cm}^3 \quad . \quad (4.1)$$

If the assumption is considered valid, the microcrystal may then be defined as a randomly oriented region of local atomic ordering with a density $\rho_s$, which forms a continuous network in the bulk solid such that the bulk density $\rho_m$ is equal to $\rho_s$.

If there is a grain boundary deficit, then

$$\rho_s > \rho_m \quad . \quad (4.2)$$

This introduces a necessary boundary condition that the density of the microcrystal be equal to or greater than 2.3466 g/cm\textsuperscript{3}. Since there are 12 boron atoms per unit alpha-rhombohedral cell, this boundary condition implies that $a_0$ be equal to or less than 5.14Å in the rhombohedral cell, that is,
\( a_o = b_o = c_o < 5.14\AA \).

Applying this boundary condition, a new model was attempted with the following distortions:

\[ r_{1-6} = 1.6\AA, \]
\[ r_{7-12} = 1.9\AA \text{ and} \]
\[ a_o = b_o = c_o = 5.12\AA, \]

and was labelled D3(1.6, 1.9)5.12. The computed pattern from the (3x3x3) and (4x4x4) arrays for the D3(1.55, 1.95)5.12 model are shown in Fig. 20. The following observations are made:

1) Increasing the number of atoms in the microcrystal from 324 to 768 shifts the first Cu K\(\alpha\) peak from 19° to 20° 20, improving the agreement with the experimental peak. It also increases the resolution of all of the peaks.

2) The sharpness of all of the computed peaks for the 768 atom model suggests that the microcrystal size may be too large, since smaller-sized microcrystals cause greater broadening.

3) While the second peak position remains unaltered with increasing size, both the fourth and fifth peaks shift to the right, improving the fit for the fifth peak but producing the contrary effect for the fourth peak. It is mentioned here that the problem of having to shift the two peaks in opposite directions suggests the need for a unique distortion.
The 768 atom D3(1.6, 1.9)5.12 model was considered to be too large and the 324 atom D3(1.6, 1.9)5.12 model lacked the adequate relative peak intensities to be successful. Keeping the density consideration in mind, an attempt was made to increase the lattice parameter and introduce an extra atom in the center of each unit cell. Fig. 21 shows the two patterns computed from the (3x3x3)D4(1.55, 1.95) models, one with the lattice parameter equal to 5.12, the other with the lattice parameter equal to 5.25 but with an extra atom at \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \) position at the center of the unit cell. No significant improvement in the fit of the computed pattern with the experimental pattern was observed. The first, fourth and fifth peaks shifted to the left due to the increase in lattice parameter with no improvement in the relative intensities.
Fig. 20. Diffraction pattern from distorted microcrystals.

(4x4x4) D₃ (1.6, 1.9) 5.12, N=768, CuKα
(3x3x3) D₃ (1.6, 1.9) 5.12, N=324, CuKα

Experimental
Fig. 21. Diffraction pattern from distorted microcrystal with extra icosahedral atoms.

- \((3 \times 3 \times 3) D_4 (1.55, 1.95) 5.2 + (0.5, 0.5, 0.5), N=351, Cu K\alpha\)
- \((3 \times 3 \times 3) D_4 (1.55, 1.95) 5.12, N=324, Cu K\alpha\)
- Experimental
D. Incomplete Icosahedra

Consider three atoms, labelled 1, 2 and 3 in space. The total number of interatomic distances \( r_{ij} \) would be given by the nine terms:

\[
\begin{align*}
    r_{1-1} & \quad r_{1-2} & \quad r_{1-3} \\
    r_{2-1} & \quad r_{2-2} & \quad r_{2-3} \\
    r_{3-1} & \quad r_{3-2} & \quad r_{3-3}
\end{align*}
\]

Of these interatomic distances, pairs such as \( r_{1-2} \) and \( r_{2-1} \) would be equal to one another, while the diagonal terms \( r_{1-1} \), \( r_{2-2} \) and \( r_{3-3} \) would be equal to zero. A computer program, DISTDT.FOR (see Appendix III) was written to calculate only those unique distances, \( r_{2-1} \), \( r_{3-1} \) and \( r_{3-2} \), occurring below the diagonal. Hence, given an array of \( N \) atoms, the total number of interatomic distances calculated would be \( (N^2 - N)/2 \). The computer also sums the total number of times an interatomic distance is repeated, differentiating between interatomic distances with a resolution of 0.01\( \AA \). In the above example, if the three atoms were placed on the corners of an equilateral triangle with 1.9\( \AA \) sides, and their co-ordinates were fed into the computer, the program output would have the following format:

\[
\begin{array}{cccccc}
    m & N_i & N_j & r_{ij} & G(k), k=1.4 & G(k), k=2.5 \\
    3 & 2 & 1 & 1.9 & .52 & -.63
\end{array}
\]

where \( m \) is the multiplicity of occurrence; \( N_i \) and \( N_j \) are representative atom numbers; \( r_{ij} \) is the interatomic distance; and \( k=1.4 \) and \( k=2.5 \) are the positions of the first and second peaks in this particular microcrystalline model. The last two columns indicate the contribution made
by this particular interatomic distance to the peak at a chosen k value, where

\[ G(k) = \frac{m \sin(kr_{ij})}{kr_{ij}} \times f^2(k) \times P(k) \quad (4.3) \]

is one of the terms in the summation of the Debye equation (see Chapter III). It may be concluded from the above example that the interatomic distance of 1.9Å makes a positive contribution to the peak at k=1.4 and a negative contribution to the peak at k=2.5.

There are twelve atoms in an icosahedron, and hence a total of \((12^2 - 12)/2 = 66\) unique intra-icosahedral distances per icosahedron. In a microcrystal containing a (3x3x3) icosahedral array, the total number of purely intra-icosahedral distances is 66x27 = 1782. This may be seen in Table V, which is a portion of the output from the DISTDT.FOR program used to analyze the microcrystalline alpha-rhombohedral model, (3x3x3) ALMIC, and the distorted D3(1.6, 1.9)5.12 model. In the (3x3x3) ALMIC model, the interatomic distance between atoms 2 and 1 is 1.733Å. This distance is repeated 162 times in the microcrystal. The summation of the multiplicities, \(m\), is equal to 1782, the total number of purely intra-icosahedral distances in the (3x3x3) array. The summations \(\Sigma G(1.4)\) and \(\Sigma G(2.5)\) reveal that the intra-icosahedral distances contribute positively to the first peak and negatively to the second peak in the (3x3x3) ALMIC model. The disparity in contributions from this source is greatly reduced by the applied intra-icosahedral distortion D3(1.6, 1.9), as may be seen by comparing the \(\Sigma G(1.4)\) and \(\Sigma G(2.5)\) values for the two models. Indeed, an improvement in the first-to-second peak ratio was observed in Fig. 18, due to the applied distortion. However,
Table V. Sample output from the DISTDT.FOR program, where, for atomic scattering factor \( F(k) \), and for polarization correction \( \text{POL}(k) \),

\[
G(k) = \frac{m \sin(kr_{ij})}{kr_{ij}} \times F^2(k) \times \text{POL}(k)
\]

<table>
<thead>
<tr>
<th>( m )</th>
<th>( N_i - N_j )</th>
<th>( r_{ij}, \AA )</th>
<th>( G(1.4) )</th>
<th>( G(2.5) )</th>
<th>( m )</th>
<th>( N_i - N_j )</th>
<th>( r_{ij}, \AA )</th>
<th>( G(1.4) )</th>
<th>( G(2.5) )</th>
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<td>2-1</td>
<td>1.733</td>
<td>1270</td>
<td>-430</td>
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<td>4-1</td>
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<td>81</td>
<td>10-7</td>
<td>3.8</td>
<td>-362</td>
<td>-8</td>
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<td>-888</td>
<td>1782</td>
<td></td>
<td></td>
<td>-783</td>
<td>-827</td>
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</table>
the improvements due to the distortions were inadequate to satisfy the experimentally observed ratio, because other inter-icosahedral distances are also being altered. Several of these are clearly acting to offset the improvement due in intra-icosahedral adjustments.

It was realized that increasing the multiplicities of favorable interatominic distances could improve the computed first-to-second peak ratio. One attempt to improve the multiplicity of favorable distances considered the possibility of adding half-icosahedra to the surface of a microcrystal, as shown in Figs. 22 and 23. An analysis of the contributions to the first and second peaks from the interatomic distances between the atoms labelled in Fig. 22 is shown in Table VI. This analysis, which was performed on the (3x3x3)D3(1.6, 1.9)5.12 microcrystal, indicated that the interatomic distances between complete icosahedra and neighboring half-icosahedra favorably affected the first-to-second peak ratio by making a positive contribution to the second peak and a negative contribution to the first peak, as shown by the $\Sigma G(k)$ values. To verify this result, the diffracted pattern from a microcrystalline model composed of a (3x3x3)D3(1.6, 1.9)5.12 array with peripheral half-icosahedra as depicted in Fig. 23, was computed. This computed profile (Fig. 24) confirmed the result that incomplete icosahedra improved the first-to-second peak ratio by increasing the relative intensity of the second peak from 40 units to 60 units.

The addition of half-icosahedra to the microcrystalline model greatly improved the first-to-second peak ratio where size and distortion variations had earlier been unsuccessful. However, the computed diffraction pattern was not satisfactory. The peaks were narrow, indicating that the microcrystal size was larger than required. The
Fig. 22. An half-icosahedron bonded to an icosahedron along the five-fold axis.
Fig. 23. (3x3x3) AIMIC + $\frac{1}{2}$ icosahedra, shown in two dimensions.
Table VI. Sample output from the DISTDT.FOR program.

<table>
<thead>
<tr>
<th>(m)</th>
<th>(N_i - N_j)</th>
<th>(r_{ij}/\overline{R})</th>
<th>(G(1.4))</th>
<th>(G(2.5))</th>
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<td>108</td>
<td>15-12</td>
<td>3.301</td>
<td>-675</td>
<td>149</td>
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<td>22-8</td>
<td>3.69</td>
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<td>29</td>
</tr>
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<td>-323</td>
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<td>115</td>
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</table>

\(-1473\) \hspace{1cm} 676
Fig. 24. Diffraction pattern from distorted microcrystal with half-icosahedra.

D₄ (1.55, 1.95) 5.12 + ½ icos, N=648, CuKα

Experimental
artificial manner in which half-icosahedra were added produced an additional peak between the first and second peak. It appeared more natural to consider partial icosahedra and microcrystalline shapes other than the rhombohedral shapes used so far.
E. Spherical Microcrystals

Consider a large array of icosahedra in space. Using the center of an icosahedron as the origin, a spherical microcrystal of radius R may be constructed such that the number of atoms N within the sphere is given by

\[ N = \frac{4}{3} \pi R^3 \rho_s \]  \hspace{1cm} (4.4)

where \( \rho_s \) is the atom density. The size of the microcrystal can be varied by changing the radius of the sphere. The surface of the sphere intersects some icosahedra, thus producing incomplete peripheral icosahedra, as shown in Fig. 25. The ratio of complete-to-incomplete icosahedra is a function of the radius of the microcrystal, the ratio increasing with the radius. The diffraction pattern computed from a D4(1.55, 1.95)5.12, SPMIC, R=9, N=390 spherical microcrystalline model of radius 9\( \text{\AA} \) containing 390 atoms is displayed in Fig. 26. The relative intensity of all of the peaks in the SPMIC model present a marked improvement compared to the (3x3x3)D4(1.55, 1.95)5.12 model. Although both models have almost similar sizes, the resolution of the third peak at 42\(^{\circ}\) 26 (Cu\( \text{K}\alpha \)) is much greater for the SPMIC model.

A Reverse D4(1.95, 1.55)5.12, R=9, N=390 SPMIC model, where (see Table IV) the sign of the \( \Delta r \) values for the atom sets 1 to 6 and 7 to 12 were reversed so that

\[ r_{1-6} = 1.95 \text{\AA} \] \hspace{1cm} \( \Delta r = +.263 \) \hspace{1cm}\n
\[ r_{7-12} = 1.55 \text{\AA} \] \hspace{1cm} \( \Delta r = -.137 \) \hspace{1cm} and \hspace{1cm}

\[ a_o = b_o = c_o = 5.12 \text{\AA} \]
Fig. 25. Spherical microcrystal with incomplete icosahedra.
Fig. 26. Diffraction pattern from spherical microcrystals.

$D_4(1.55, 1.95)$ SPMIC, $R=9$, $N=390$, $a_0=5.12\AA$, CuKα.

Experimental
displays the curious result of transposing the second and third peak intensities (Fig. 27), in addition to splitting the fifth peak into two peaks. Atoms 1 to 6 lie along the rhombohedral axes. Hence the Reverse D4 model indicates that the atoms lying on the five-fold axes prefer to lie closer to the icosahedral center than the remaining atoms.

It may be recalled from Section B.2, Chapter IV, that the alpha-rhombohedral polymorph consisted of icosahedra that were irregular, with

\[ r_{1-6} = 1.679 \AA, \quad \Delta r = -0.008, \]
\[ r_{7-12} = 1.695 \AA, \quad \Delta r = +0.008 \quad \text{and} \]
\[ a_0 = b_0 = c_0 = 5.057 \AA, \]

where \( \Delta r \) was the deviation from the average icosahedral radius \( r = 1.687 \AA \). The patterns computed from spherical alpha-rhombohedral microcrystals with no distortions, ALPHA-RH, SPMIC display intensity ratios (Fig. 28) very similar to that predicted by the crystalline powder pattern (Table II) with high intensities for both the second and third peaks. Thus the second-to-third peak intensity ratio appears to be a function of \( r_{1-6} \) and \( r_{7-12} \). This effect was confirmed by computing the pattern from the following model, \( D(1.7, 1.6, 1.4, 2.2, 2.1, 2.0) \), where the radii were arbitrarily assigned random values

\[ r_1 = r_7 = 1.7 \AA, \quad \Delta r = +.013 \]
\[ r_2 = r_8 = 1.6 \AA, \quad \Delta r = -.087 \]
\[ r_3 = r_9 = 1.4 \AA, \quad \Delta r = -.287 \]
\[ r_4 = r_{10} = 2.2 \AA, \quad \Delta r = +.513 \]
\[ r_5 = r_{11} = 2.1 \AA, \quad \Delta r = +.313 \]
Fig. 27. Diffraction pattern from distorted microcrystal with atoms 1-6 and 2-7 of radii 1.95 and \(1.55\,\text{Å}\), respectively.

- Reverse \(D_4\) (1.95, 1.55) 5.12, \(R=9\), \(N=390\), \(CuK\alpha\)
- \(D_4\) (1.55, 1.95) 5.12, \(R=9\), \(N=390\), \(CuK\alpha\)
- Experimental
Fig. 28. Diffraction pattern from undistorted spherical alpha-rhomboedral boron microcrystals.

- ALPHA-RH, SPMIC, \(a_0 = 5.057\), \(R = 10\), \(N = 606\), Cu\(K\alpha\)
- ALPHA-RH, SPMIC, \(a_0 = 5.057\), \(R = 12\), \(N = 990\), Cu\(K\alpha\)
- Experimental

\(I_{rel}\) vs. 2\(\theta\) (in degrees) for different crystallographic conditions.
\[ r_6 = r_{12} = 2.0 \bar{R}, \quad \Delta r = +.313 \]

The computed pattern for the model is plotted in Fig. 29 and shows the effect that the \( r \) values have on the second-to-third peak ratio. The above result is an argument for uniqueness, since it is an example of how only specific distortions were found suitable while others were not, thus driving the atoms toward the most suitable positions.

The above findings may be summarized by stating that the intensity of the third peak may be lowered by

1) increasing the negative \( \Delta r \) for atoms 1 to 6
2) increasing the positive \( \Delta r \) for atoms 7 to 12.

These results were incorporated into the D6(1.5, 2.0)5.12 model, which has the following parameters:

\[ r_{1-6} = 1.5 \bar{R}, \quad r_{1-6} = -1.87 \]
\[ r_{7-12} = 2.0 \bar{R}, \quad r_{7-12} = +.313 \]
\[ a_o = b_o = c_o = 5.12 \bar{R} \]

Spherical microcrystals of D6(1.5, 2.0)5.12 with radii of \( R = 9, 10 \) and 13 were used to compute the diffraction patterns shown in Fig. 30. Increasing the radius from \( 9 \bar{R} \) to \( 10 \bar{R} \) causes the first peak to shift, but further increase increase of the radius from \( 10 \bar{R} \) to \( 13 \bar{R} \) only causes a minimal shift. The second-to-third peak ratio was the highest for the \( R = 10 \) model. The \( R = 13 \) model with 1248 atoms was considered to be too large since it showed highly resolved peaks. Both the \( R = 9 \) and the \( R = 10 \) models displayed a much improved fit with the experimental pattern. However, the \( R = 10 \) model was considered to be a better fit since the
Fig. 29. Diffraction pattern from alpha-rhombohedral distorted spherical microcrystal.

$D (1.7, 1.6, 1.4, 2.2, 2.1, 2.0) 5.12, R=10, N=550, CuK_{α}$

---

- Solid line: Theoretical
- Dashed line: Experimental
Fig. 30. Diffraction pattern from distorted spherical microcrystal showing the effect of increasing microcrystal size.

- **SPMIC, D$_6$ (1.5, 2.0) 5.12, R=10, N=540, Cu$_{K\alpha}$**
- **SPMIC, D$_6$ (1.5, 2.0) 5.12, R=13, N=1248, Cu$_{K\alpha}$**
- **SPMIC, D$_6$ (1.5, 2.0) 5.12, R=9, N=390, Cu$_{K\alpha}$**
- **Experimental**
position of the first peak more correctly matched the experimental one. In order to insure that the fit was good to larger k values, the computed profiles for the D6 and D4 models were compared with the experimental profile obtained using Mo Kα radiation (see Figs. 31 and 32).

The D4(1.55, 1.95)5.12, R=10, N=540, Mo Kα model displays a qualitative agreement with experiment. The positions of the first, second, fourth, fifth and seventh peaks are good. However, the positions of the third, sixth and eighth peaks need improvement. While the third peak is not observed experimentally, the computed intensities of the fourth, sixth and seventh peaks are much higher and display greater resolution than their experimental counterparts. The D6(1.5, 2.0)5.12, R=10, N=540, Mo Kα model displays almost identical characteristics, the major difference being improvements in the fit for the third, seventh and eighth peaks. While it is not possible to carry this distortion technique any further since some atoms develop nearest-neighbor distances which are smaller than 1.65Å, the smallest nearest-neighbor distances found in a naturally occurring polymorph of boron, significant improvements still need to be made to fit all of the minor peaks.

Fig. 33 shows the pattern computed from a spherical microcrystal of tetragonal boron. The first peak is broad, reflecting the crystalline powder pattern information in Table II which indicates that tetragonal boron has two major peaks in the vicinity of the first experimental peak. A shoulder appears at the third peak position. There is also a shoulder at the position of the fourth peak. While the first, second, fifth and seventh peaks display good positions, the sixth and eighth peaks need to shift in opposite directions. Attempts to shift the sixth
Fig. 31. Diffraction pattern from D4 spherical microcrystal using MoKα radiation.

---

\[ D_4(1.55, 1.95) \text{ 5.12, } R=10, \text{  } N=540, \text{  } \text{MoKα} \]

---

Experimental
Fig. 32. Diffraction pattern from D6 spherical microcrystal using Mo$_{K\alpha}$ radiation.

- $D_6(1.5, 2.0)$, $R=10$, $N=540$, Mo$_{K\alpha}$
- Dashed line: Experimental
Fig. 33. Diffraction pattern from tetrahedral spherical microcrystal using Mo$_{K\alpha}$ radiation.

- Tetragonal boron, $R=10$, $N=528$, Mo$_{K\alpha}$
- Experimental
and eighth peaks with the use of icosahedral distortions were unsuccessful.

Comparing the tetragonal (TET) and the distorted D4 and D6 alpha-
rhombohedral spherical microcrystals, one sees that the D4 and D6 models
have an unwanted third peak, while the TET model has a shoulder. On the
other hand, the D4 and D6 models fit the fourth peak well, while the TET
model has only a shoulder. This suggests the possibility that while the
sample may be composed of randomly oriented small regions of local atomic
ordering, some regions may have rhombohedral order, and others tetragonal
order. Since the boron fibers are produced in a temperature range
intermediate to those required for the production of crystalline alpha-
rhombohedral and tetragonal boron, it seems feasible to consider that
some boron atoms in the fiber display alpha-rhombohedral orientation
while others display tetragonal behavior. The diffraction pattern from
a model containing 50 volume percent tetragonal microcrystals and 50
volume percent D4 is shown in Fig. 34, both spherical microcrystals
having a radius of 10 Å. The fit is good because the peak positions all
agree with the experimental pattern, with the exception of the sixth and
eighth peak, which need to shift in the opposite direction. The peak
intensities also display good agreement, the shoulder at the third peak
position being the unwanted feature. The (50-50) volume percent, D6 +
TET, SPMCIC, R-10 model shown in Fig. 35 displays similar attributes;
while the third peak shoulder is smaller, the fit for the sixth peak is
not as good. Overall, the (50-50) volume percent, D6 + TET, SPMCIC, R-10
model displays all of the essential features of the experimentally
obtained pattern. The calculated density for this model is 2.3455 g/cm³,
which is in excellent agreement with the experimentally determined value.
Fig. 34. Diffraction pattern from a sample of alpha-rhombohedral and tetragonal microcrystals.

- $D_4 + \text{Tet.}; (50-50)$ volume percent; $R=10$, $N=540,528; \text{Mo}_K\alpha$

- Dashed line: Experimental
Fig. 35. Diffraction pattern from a sample containing alpha-rhombohedral and tetragonal microcrystals.

- $D_6 + \text{Tet., (50-50) volume percent; } R=10, N=540, 528; \text{ Mo}_K\alpha$
- Experimental

![Diffraction pattern graph](image_url)
of 2.3466 g/cm$^3$. The $I_{eu}$ vs. $k$ plot for the D6 + TET model is shown in Fig. 36, again displaying a good fit with the experimental pattern.

It is possible to consider a hybrid structure which incorporates the qualities of both the alpha-rhombohedral structure and the tetragonal structure. Attempts to model this hybrid AL-TET structure were unsuccessful due to the insufficient computing facility available. While such modelling attempts lie in the realm of future work, the present model displays all of the essential features of the experimental pattern, with the exception of the shoulder at the third peak position.
Fig. 36. Diffraction pattern from sample of alpha-rhombohedral and tetragonal microcrystals.

$D_6 + \text{Tet.} \ (50-50)$ Volume percent; $R=10; \ N=540, 528; \ Mo_{K\alpha}$

Experimental, E3
V. CONCLUSION

An attempt was made to elucidate the structure of fiber boron by fitting computed diffraction patterns from various models to its experimental diffraction pattern. The conclusions that are made from this study are tabulated below:

1. The diffraction pattern from amorphous fiber boron shows eight broad peaks. There is a slight increase in the breadth and the relative intensities of the peaks with increasing amounts of etch initially. Further etching produces no changes in the pattern. The initial changes in the pattern are possibly due to shifts in the residual stress distribution caused by etching.

2. Computer modelling of the experimentally obtained diffraction patterns suggests that the sample consists of a continuous network of small, randomly oriented regions, about 20° in diameter. Approximately half of the volume of the sample has a distorted alpha-rhombohedral structure, and the other half, a tetragonal structure. The fiber contains many incomplete icosahedra and loose atoms. Some of these loose atoms are the bonding atoms between icosahedra in the tetragonal structure. These partial icosahedra and loose atoms may be the relaxing entities suggested by DiCarlo to explain the anelastic behavior of fiber boron.

3. The distorted alpha-rhombohedral microcrystals contained twenty-three complete icosahedra; that is, about half of the 540 atoms in the microcrystal were present in complete icosahedral groups. The incomplete icosahedra, which contained two groups of 11 atoms, eighteen groups of 9 atoms, six groups of 6 atoms, four groups of
4 atoms, two groups of 2 atoms and 24 individual atoms, were present on the periphery of the microcrystal. The modelling attempts indicated that alpha-rhombohedral icosahedra prefer to align themselves along the five-fold axes. The icosahedral atoms lying along the rhombohedral axes tend to position themselves closer to the center of the icosahedron, compared to the remaining icosahedral atoms.

4. The computed pattern, when compared to experiment (Fig. 36), shows an unwanted shoulder at the base of the second peak and a well-delineated sixth peak. This suggests that atom arrays in the sample are a little more disordered than the arrays used in the model; that is, the model is slightly more structured. The model, however, displays all of the essential features of the structure of amorphous fiber boron.
VI. FUTURE WORK

It is possible, ignoring the extra atoms in the tetragonal cell, to generate a primitive cell with icosahedra at its corners. The atoms in these icosahedra are not aligned along primitive cell axes. The primitive tetragonal cell parameters are

\[ a'_o = 6.1801 \AA \quad , \quad \alpha' = 52.28^\circ \]
\[ b'_o = 6.1801 \AA \quad , \quad \beta' = 52.28^\circ \]
\[ c'_o = 5.0515 \AA \quad , \quad \gamma' = 90.0^\circ \]

which has similarities with the alpha-rhombohedral cell parameters below:

\[ a_o = 5.057 \AA \quad , \quad \alpha = 58.06^\circ \]
\[ b_o = 5.057 \AA \quad , \quad \beta = 58.06^\circ \]
\[ c_o = 5.057 \AA \quad , \quad \gamma = 58.06^\circ . \]

It may be enlightening to compute the diffraction patterns from a model where the atoms are gradually forced from one orientation to the other. This approach should indicate whether a hybrid model is feasible or not. Initial attempts to obtain a hybrid model have so far been unsuccessful due to the lack of computing facilities presently available.
REFERENCES


49. Reference 47, p114.

50. Reference 47, p473.

51. Reference 47, p483.

52. Reference 47, p801.


54. Reference 47, p804.


APPENDIX I
LOGARITHMIC CURVE FIT

The set of data points \( \{(x_i, y_i), i=1,2,...,n\} \), where \( x_i > 0 \), was fit to a logarithmic curve

\[
y = a + b \ln x,
\]

using a Texas Instruments Programmable Calculator and Statistics Library (ST1).

The statistical outputs were as follows:

1. Regression coefficients

\[
a = \frac{\Sigma y_i - b \Sigma \ln x_i}{n}
\]

\[
b = \frac{\Sigma y_i \ln x_i - \frac{\Sigma \ln x_i \Sigma y_i}{n}}{\Sigma (\ln x_i)^2 - \frac{(\Sigma \ln x_i)^2}{n}}
\]

2. Correlation coefficient

\[
x^2 = \frac{\left| \Sigma y_i \ln x_i - \frac{\Sigma \ln x_i \Sigma y_i}{n} \right|}{\left| \Sigma (\ln x_i)^2 - \frac{(\Sigma \ln x_i)^2}{n} \right| \left| \Sigma y_i^2 - \frac{(\Sigma y_i)^2}{n} \right|}
\]
APPENDIX II

A. DISTDT.FOR

The computer program DISTDT.FOR was written in Fortran to calculate all of the interatomic distances \( r_{ij} \) in the microcrystal and collate these distances into sets, with a resolution of 0.01Å. The program also calculates the contribution of the sets to a specified \( k \) value. The program printed the multiplicity \( m \), the interatomic distance \( r_{ij} \), the atom numbers \( N_i \) and \( N_j \) and the contributions to two \( k \) values. The following pages list the program. The salient points of the program are mentioned below:

1. The input data was stored in the PROGDT.DAT file.

2. The "READ 12" statement requires one to input values

\[
N = \text{number of atoms per unit cell}
\]

\[
\text{NUC} = \text{number of unit cells}
\]

\[
G_{11} = a_0^2
\]

\[
G_{12} = a_0^2 \times \cos(\nu)
\]

\[
A = a_0
\]

\[
WVL = \text{wavelength of the radiation used.}
\]

The "READ 10,..." statement reads the \( x,y,z \) co-ordinates of the atoms of the unit cell. A sample input is shown at the end of the program listing.

3. The four nested "DO 100..." loops generate the co-ordinates of the microcrystal.

4. The two nested "DO 140..." loops calculate the interatomic distances \( B(K) \), while the nested loop "DO 107..." counts their multiplicity \( LA(K) \). The atom numbers are
stored in II(K) and JJ(K). The equation "RR=..." shown is used for the rhombohedral cell, where S=G11 and T=G12.
This equation is changed for the tetragonal cell.
5. CC1 and CC2 sum the contributions to the intensity at k values of 1.4 and 2.5 respectively in the "DO 160..." and "DO 170..." loops.
DISTDT.FOR

DIMENSION X(324), Y(324), Z(324)
DIMENSION LA(800), R(1000), II(1000), JJ(1000)
DIMENSION FF(75), PO(75)
CALL ASSGN (1,'DX1:PROGDT.DAT')
READ 12,N,NUC,G11, G12,A,WVL

12 FORMAT (215,4F15.10)
READ 10,(X(I),Y(I),Z(I),I=1,N)

10 FORMAT (3F15.10)
CALL CLOSE(1)
CALL ASSGN (1,'DX1:FFPO.DAT')
READ 13,(FF(I),PO(I),I=1,75)

13 FORMAT (2F15.8)
CALL CLOSE(1)
KK=1
DO 15 K=1,400
LA(K)=0

15 B(K)=0,0
PRINT 16,FF(14),FF(25),PO(14),PO(25)

16 FORMAT (4F15.6)
CC1=0,0
CC2=0,0
S=G11
T=G12
PI=3,1415926
PII=1.0/PI
CONST=180.0*PII
NATOM=N*NUC**3
RN=NATOM
DO 100 J=1,NUC
DO 100 K=1,NUC
DO 100 L=1,NUC
M=(J-1)*NUC**2+(K-1)*NUC+L
RL=L-1
RK=K-1
RJ=J-1
DO 100 I=1,N
MU=(M-1)*N+I
X(MU)=X(I)+RL
Y(MU)=Y(I)+RK

100 Z(MU)=Z(I)+RJ
PRINT 101

101 FORMAT (10X,'CO-ORDINATES CALCULATED')
DO 140 I=2,NATOM
MM=I-1
DO 140 J=1,MM
IF(J.EQ.MM) PRINT 106,I, KK

106 FORMAT (10X,'I=',I5,5X,I5)
XA=X(I)-X(J)
YA=Y(I)-Y(J)
ZA=Z(I)-Z(J)
RR=5*(XA**2+YA**2+ZA**2)+2.0*TA*X*YA+X*ZA+YA*ZA
R=SORT(RR)
DO 107 K=1, KK
P=ABS(R-B(K))
107 IF(P.LE.0.01) GO TO 108
   KK=K
   K=K-1
   B(K)=R
   LA(K)=I
   II(K)=I
   JJ(K)=J
   GO TO 140
108 LA(K)=LA(K)+1
140 CONTINUE
   DO 160 J=1,KK
   DO 170 I=1,KK
   IF(B(I).LE.0.01) GO TO 170
      E=J*0.1
   IF(B(I).LT.E) GO TO 110
   IF(I.EQ.KK) GO TO 160
   GO TO 170
110 CI1=SIN(1.4*B(I))*LA(I)*FF(14)*PO(14)*2./(1.4*B(I))
   CI2=0.5*B(I)*LA(I)*FF(25)*PO(25)*2./(2.5*B(I))
   CC1=CC1+CI1
   CC2=CC2+CI2
   PRINT 120,LA(I),B(I),II(I),JJ(I),CI1,CI2
120 FORMAT(1I7,5X,1F12.7,5X,1S5X,1S5X,1F15.6)
   C' K=1.4',5X,1F15.6,5X,' K=2.5',5X,1F15.6
   B(I)=0.0
   IF(I.EQ.KK) GO TO 160
170 CONTINUE
160 CONTINUE
   CC1=CC1+RN*FF(14)*PO(14)
   CC2=CC2+RN*FF(25)*PO(25)
   NN=0
   DO 70 I=1,KK
   NN=NN+LA(I)
   PRINT 80,NN,LA(I),CC1,CC2
80 FORMAT(5X,1S8,5X,1S5X,1S5X,1S5X,1S10X,1S15.5)
STOP
END
APPENDIX III

The SPMIC2.FOR program used the Debye equation to compute the diffracted intensity from a spherical microcrystal. The input data was stored in the PROGDT.DAT file. The program is similar to the earlier program except that it does not store $r_{ij}$ values, but uses them instead to calculate $\frac{\sin k_{rij}}{k_{rij}}$ for $k$ values 1 to 15, with 0.1 $k$ intervals, in the "DO 140..." loops. The program calculates the diffracted profile for both Cu $K_{\alpha}$ and Mo $K_{\alpha}$ radiations. The scattering factors with dispersion corrections and the polarization corrections were stored in the files FFPO.DAT and FFPOMO.DAT.
SPMIC2.FOR
DIMENSION XP(50),YP(50),ZP(50)
DIMENSION FFMO(150),POMO(150),CORIMO(150)
DIMENSION X(1500),Y(1500),Z(1500)
DIMENSION FF(150),PO(150),CORICU(150)
DIMENSION SUM(150),TH(150),TH2(150)
CALL ASSIGN(1,'DX1:PROB105.DAT')
READ 11,A,B,C,S1,S2,S3
11 FORMAT(6F15.7)
READ 12,N,NUC,LA,LB,G11,G12,WUL
12 FORMAT(4I5,3F15.10)
READ 10,(XP(I),YP(I),ZP(I),I=1,N)
10 FORMAT(3F15.10)
CALL CLOSE(1)
CALL ASSIGN(1,'DX1:FPPO,DAT')
READ 13,(FF(I),PO(I),I=1,75)
13 FORMAT(2F15.8)
CALL CLOSE(1)
CALL ASSIGN(1,'DX1:FFPOMO,DAT')
READ 15,(FFMO(I),POMO(I),I=1,150)
15 FORMAT(2F15.8)
CALL CLOSE(1)
DO 14,I=76,150
  FF(I)=1.0
14  PO(I)=1.0
S=G11
T=G12
PI=3.1415926
PII=1.0/PI
CONST=180.0*PII
LIP=0
DO 100 J=1,7
  DO 100 K=1,7
    DO 100 L=1,7
100  RL=L-1
    RK=K-1
    RJ=J-1
    IF(L.GT.4)RL=(L-4)*-1
    IF(K.GT.4)RK=(K-4)*-1
    IF(J.GT.4)RJ=(J-4)*-1
    DO 100 I=1,N
      XA=XP(I)+RL
      YA=YP(I)+RK
      ZA=ZP(I)+RJ
      RR=(A*XAX)**2+(B*YAY)**2+(C*ZAZ)**2
      RR=RR+2*(A*B*XAY*ACOS(S3)+A*C*XAZ*ACOS(S2))
      RR=RR+2*B*C*YAZ*ACOS(S1)
      RR=ABS(RR)
      R=SQRT(RR)
      IF(R.LE.10.00)LIP=LIP+1
      IF(R.GT.10.00)GO TO 100
    X(LIP)=XA
Y(LIP)=YA
Z(LIP)=ZA

100 CONTINUE
PRINT 101,LIP
101 FORMAT (10X,'CO-ORDINATES CALCULATED',5X,'LIP=',I5)
DO 105 I=1,150
105 SUM(I)=0.0
IF(LA.GT.0) GO TO 107
LAA=2
LBB=LIP
GO TO 108
107 CONTINUE
LAA=LA
LBB=LB

108 CONTINUE
DO 140 I=LAA,LBB
II=I-1
DO 140 J=1,II
IF (J.EQ.II) PRINT 106,I
106 FORMAT (10X,'I=',I5)
XA=X(I)-X(J)
YA=Y(I)-Y(J)
ZA=Z(I)-Z(J)
RR=(A*X*A)**2+(B*Y*A)**2+(C*Z*A)**2
RR=RR+2*(A*B*X*A*Y*A*COS(S3)+A*C*X*A*Z*A*COS(S2))
RR=RR+2*B*C*X*A*Z*A*COS(S1)
RR=ABS(RR)
R=SQRT(RR)
DO 140 K=1,150
CC=K
CR=0.1*CC*R
140 SUM(K)=SUM(K)+SIN(CR)/CR
DO 160 I=1,150
160 CORICU(I)=SUM(I)*FF(I)*PO(I)*0.001
CALL ASSIGN (1,'DX1:ICOCU,IEC')
WRITE (1,191) (CORICU(I),I=1,150)
191 FORMAT('IF15.7')
CALL CLOSE(1)
DO 170 I=1,150
170 CORIMO(I)=SUM(I)*FFMO(I)*POMO(I)*0.001
CALL ASSIGN (1,'DX1:ICOMO,IEC')
WRITE (1,171) (CORIMO(I),I=1,150)
171 FORMAT('IF15.8')
CALL CLOSE(1)
PRINT 190
190 FORMAT(12X,'THETA',9X,'2THETA',12X,'K',14X,'IEU',17X,'C',IEUCR')
DO 300 I=1,150
CI=I
CC=CI*0.1
F=CC*WVL*0.25*PII
IF(P.GT.1.0) GO TO 200
TH(I)=ATAN(P/SQRT(1.0-P**2))*CONST
IC012

12, 3, 2, 440, 25.57325, 13.52904, 1.54178
0.0104, 0.0104, -0.3427
0.0104, -0.3427, 0.0104
-0.3427, 0.0104, 0.0104
-0.0104, -0.0104, 0.3427
-0.0104, 0.3427, -0.0104
0.3427, -0.0104, -0.0104
0.2206, 0.2206, -0.3677
0.2206, -0.3677, 0.2206
-0.3677, 0.2206, 0.2206
-0.2206, -0.2206, 0.3677
-0.2206, 0.3677, -0.2206
0.3677, -0.2206, -0.2206

*
B. SPHMIC.DST.

The following program is identical to the DISTDT.FOR program listed earlier, except for the following:

1) The program is used for spherical microcrystals. The radius of the microcrystal in the listed program in 10Å, as shown in the IF statement:

   IF (R.LE.10.00)LIP = LIP + 1 .

   The value 10.00 is changed for a different radius in the two consecutive IF statements.

2) The intensity contributions to five k values is now measured and printed. The sample program calculates the contributions at k values of 0.9, 2.8, 1.5, 2.4 and 2.9 in the "DO 160..." loop.
SPHMIC,DST

DIMENSION X(1500),Y(1500),Z(1500)
DIMENSION FF(75),PO(75)

CALL ASSIGN (1,'DX1:PROGDT,DAT')
READ 12,N,NUC,G11,G12,A,WVL

12 FORMAT (2I5,4F15.10)
READ 10,(X(I),Y(I),Z(I),I=1,N)
10 FORMAT (3F15.10)

CALL CLOSE(1)

CALL ASSIGN (1,'DX1:FFPO,DAT')
READ 13,(FF(I),PO(I),I=1,75)

13 FORMAT (2F15.8)

CALL CLOSE(1)
KK=1
DO 15 K=1,1500
15 B(K)=.0
DO 17 K=1,1000
17 LA(K)=0

PRINT 16,FF(14),FF(25),PO(14),PO(25)

16 FORMAT(4F15.6)

CC1=0.0
CC2=0.0
CC3=0.0
CC4=0.0
CC5=0.0
S=G11
T=G12
PI=3.1415926
PII=1.0/PI
CONST=180.0*PII
NATOM=N**NUC**3
RN=NATOM
LIP=0

DO 100 J=1,7
DO 100 K=1,7
DO 100 L=1,7

RL=L-1
RK=K-1
RJ=J-1
IF(L.GT.4)RL=(L-4)**-1
IF(K.GT.4)RK=(K-4)**-1
IF(J.GT.4)RJ=(J-4)**-1

DO 100 I=1,N
XA=X(I)+RL
YA=Y(I)+RK
ZA=Z(I)+RJ
RR=S*(XA*2+YA*2+ZA*2)+2*T*(XA*YA+XA*ZA+YA*ZA)

RR=ABS(RR)
R=SQRT(RR)

IF(R.LE.10.00)LIP=LIP+1
IF(R.GT.10.00)GO TO 100

X(LIP)=XA
Y(LIP)=YA
Z(LIP) = ZA

100 CONTINUE
PRINT 401, (I, X(I), Y(I), Z(I), I=1, LIP)

401 FORMAT (I15, 3F15.10)
PRINT 101

101 FORMAT (10X, 'COORDINATES CALCULATED')
DO 140 I = 2, LIP
MM = I - 1
DO 140 J = 1, MM
IF (J .EQ. MM) PRINT 106, I, KK

106 FORMAT (10X, 'I=', I5, 5X, I8)
XA = X(I) - X(J)
YA = Y(I) - Y(J)
ZA = Z(I) - Z(J)
RR = S*(X*A**2 + Y*A**2 + Z*A**2) + 2.0*T*(X*A*Y*A + X*A*Z*A + Y*A*Z*A)
RR = ABS(RR)
R = SQRT(RR)
DO 107 K = 1, KK
P = ABS(R - B(K))

107 IF (P .LE. 0.01) GO TO 108
KK = K
K = K - 1
B(K) = R
LA(K) = I
II(K) = I
JJ(K) = J
GO TO 140

108 LA(K) = LA(K) + 1

140 CONTINUE
PRINT 111

111 FORMAT (10X, 5X, R', 5X, ATM', 5X, 'ATN', 5X, C', K=0.9', 15X, '2.8', 15X, '1.5', 15X, '2.4', 15X, '2.9')
DO 160 J = 1, 500
DO 170 I = 1, KK
IF (B(I) .LE. 0.01) GO TO 170
E = J*0.1
IF (B(I) .LT. E) GO TO 110
IF (I .EQ. KK) GO TO 160
GO TO 170

110 CI1 = SIN(0.9*B(I)) * LA(I) * FF(9) * PO(9)*2./(0.9*B(I))
CI2 = SIN(2.8*B(I)) * LA(I) * FF(28) * PO(28)*2./(2.8*B(I))
CI3 = SIN(1.5*B(I)) * LA(I) * FF(15) * PO(15)*2./(1.5*B(I))
CI4 = SIN(2.4*B(I)) * LA(I) * FF(24) * PO(24)*2./(2.4*B(I))
CI5 = SIN(2.9*B(I)) * LA(I) * FF(29) * PO(29)*2./(2.9*B(I))
CC1 = CC1+CI1
CC2 = CC2+CI2
CC3 = CC3+CI3
CC4 = CC4+CI4
CC5 = CC5+CI5
PRINT 120, LA(I), B(I), II(I), JJ(I), CI1, CI2, CI3, CI4, CI5

120 FORMAT (I15, 1F12.7, I5, I5, 5X, 1F15.6, 5X, 1F15.6, 5X, 1F15.6, 5X)
B(I) = 0.0
IF (I .EQ. KK) GO TO 160
170 CONTINUE
160 CONTINUE
   CCI=CCI+LIP*FF(9)*P0(9)
   CCI2=CCI2+LIP*FF(28)*P0(28)
   CCI3=CCI3+LIP*FF(15)*P0(15)
   CCI4=CCI4+LIP*FF(24)*P0(24)
   CCI5=CCI5+LIP*FF(29)*P0(29)
   QN=0
   DO 70 I=1,KK
70  QN=QN+LA(I)*.01
   PRINT 80,QN,KK,CCI,CCI2,CCI3,CCI4,CCI5
STOP
END
GO TO 210
200 TH(I)=0.0
210 TH2(I)=2.0*TH(I)
   PRINT 250,TH(I),TH2(I),CC,SUM(I),CORICU(I)
250 FORMAT(//,5X,5F15.5)
300 CONTINUE
   PRINT 390
390 FORMAT(//,12X,'THETA',9X,'2THETA',12X,'K',14X,'IEU',17X,'C','IEUCOR')
   DO 400 I=1,150
      CI=I
      CC=CI*0.1
      P=CC*0.71069*0.25*PI
      IF(P.GT.1.0)GO TO 500
      TH(I)=ATAN(P/SQRT(1.-P**2))*CONST
   GO TO 410
500 TH(I)=0.0
410 TH2(I)=2.0*TH(I)
   PRINT 450,TH(I),TH2(I),CC,SUM(I),CORMO(I)
450 FORMAT(//,5X,5F15.5)
400 CONTINUE
STOP
END