

## Deformation of the Valence Electron Distributions in the Icosahedral Boron Structure of $\alpha$ -AlB<sub>12</sub>

TETSUZO ITO, IWAMI HIGASHI, AND TOSIO SAKURAI

*The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351, Japan*

Received November 2, 1977; in revised form, July 29, 1978

X-ray difference electron densities in  $\alpha$ -AlB<sub>12</sub> were examined. Broad peaks presumably characteristic of highly delocalized three-center bonds were observed at the centers of the triangular faces of the B<sub>12</sub> icosahedron. Another kind of prominent peak on the external B-B bonds of the icosahedron indicated that the inter-icosahedral B-B bonds are two-center bonds. An averaging over the icosahedral symmetry significantly reduced the random noises in the difference densities. Theoretical difference electron densities for a B<sub>12</sub>H<sub>12</sub><sup>2-</sup> molecular ion, calculated by the CNDO/2 molecular orbital method, were qualitatively in good agreement with the observed densities mentioned above. Residual peaks were observed on all the five edges of the open pentagonal face of the B<sub>19</sub> unit; they had broad tails extending toward the aluminum triplet sites. The observed difference densities around the "single" B(23) atom suggested that the atom belongs to the B<sub>19</sub> unit rather than being single.

### Introduction

Since X-ray analysis revealed that the structure of boron carbide, B<sub>4</sub>C, is principally made up of boron icosahedra (1, 2), numerous crystals of boron icosahedral structures have been investigated. Because of the unusual boron framework that is impossible to interpret in terms of the ordinary rules of covalency, these structures have been one of the centers of interests among theorists and crystal chemists (3, 4, 5). Recently, we have solved the crystal structure of  $\alpha$ -AlB<sub>12</sub> by X-ray diffraction (6). The structure has been confirmed by an independent work by Kasper, Vlasse and Naslain (7); their result is in an excellent agreement in all respects with ours. The basic framework of this structure consists of typical B<sub>12</sub> icosahedra and novel B<sub>19</sub> twinned icosahedra. The structure was refined to the final *R* value of 3.0%. The final difference Fourier map showed no maxima or minima greater than 2% (0.45 e Å<sup>-3</sup>) of a boron peak

in the Fourier map. However, after careful examination of these small residual peaks, we noticed some systematic distributions, which encouraged us to pursue details of the electron distribution.

### Determination of the Electron Density

The X-ray diffraction data and the atomic parameters used in the present investigation were the same as reported in the previous paper (6). The 1478 independent diffraction intensities within the range  $\sin \theta/\lambda < 0.78$  were collected on a diffractometer using graphite monochromatized MoK $\alpha$  radiation.<sup>1</sup> The crystal structure of  $\alpha$ -AlB<sub>12</sub>

<sup>1</sup> Absorption corrections were not applied because the crystal was a slightly distorted octahedron with the approximate radius of 0.35 mm ( $\mu r = 0.10$ ). Extinction effects were not significant in the final  $F_o - F_c$  table; the discrepancies between the observed and calculated structure factors of the three strongest lower angle reflections ( $\sin \theta/\lambda < 0.3$ ) were only 0.7%.

consists of  $B_{12}$  icosahedra,  $B_{19}$  units, single B atoms and interstitial Al atoms;  $8B_{12} \cdot 4B_{19} \cdot 4B \cdot 13.0 \text{ Al}$  are contained in the tetragonal unit cell ( $a = 10.158(2)$ ,  $c = 14.270(5) \text{ \AA}$ , space group  $P4_12_12$  or  $P4_32_12$ ). All the boron sites are fully occupied, whereas the Al atoms are distributed statistically over the five sites with varying occupancies. As shown in Fig. 1, the boron units are linked by the intericosahedral B–B bonds and also through the single B(23) atoms, making up an infinite three-dimensional boron framework. All the intericosahedral B–B bonds are formed approximately along the pseudo-fivefold axis of the icosahedron or the defect icosahedra of the  $B_{19}$  unit.

Difference electron density maps through various sections in the unit cell were calculated. The most interesting sections of the  $B_{12}$  icosahedron are the ones through the triangular faces and the ones bisecting the icosahedron through the two opposite edges (Fig. 2). Since the  $B_{12}$  icosahedron is on a general position in the unit cell, it has no crystallographic symmetry. In fact, the intraicosahedral B–B bond lengths range from 1.736 to 1.863  $\text{\AA}$  and the coordinations of the Al atoms and the adjacent boron units

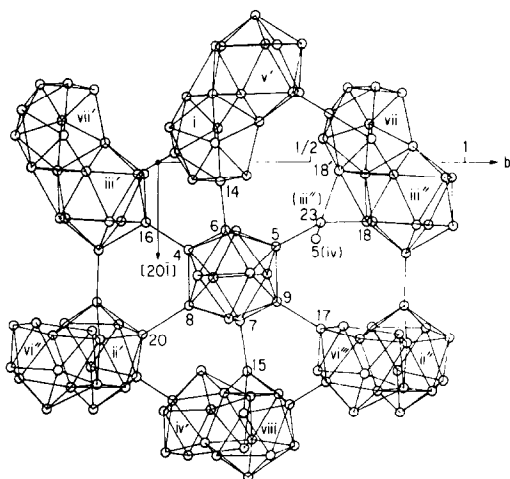


FIG. 1. Linkages between the boron units viewed along the  $[101]$ -axis. Fig. 4 of the reference (6).

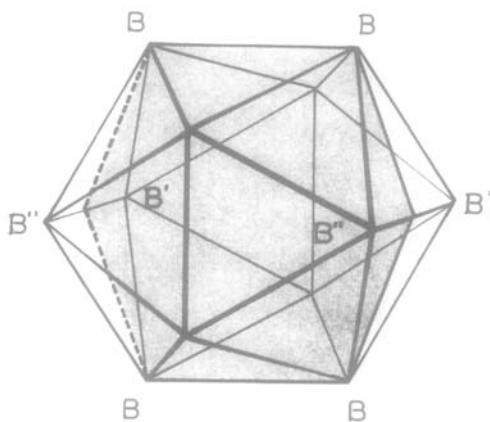


FIG. 2. Bisecting plane of the icosahedron through two opposite edges. It bisects the icosahedron through the center, and also the triangular faces  $BB'B''$  through B and the mid-points of  $B'-B''$ .

are different for every boron. However, in spite of these different environments, the observed distributions of the residual peaks around the icosahedron were systematic and approximately conformed to the regular icosahedral symmetry. Two examples are shown in Fig. 3; although the triangular face in Fig. 3a has the shortest and that in Fig. 3b the longest B–B bond lengths, the distributions of the residual peaks are similar. Therefore, the difference electron densities were averaged assuming the regular icosahedral symmetry. There are then 20 equivalent triangular faces on the icosahedron, and each face has  $3m$  symmetry. Therefore, the difference density on the face was calculated as the average of the 120 original densities.<sup>2</sup> Since the icosahedron has 30 edges, there are 15 equivalent planes bisecting the icosahedron through two opposite edges, and each plane has  $mm$

<sup>2</sup> The difference electron densities were so averaged that the centers of gravity of the three B atoms defining the triangular faces or those of the four B atoms approximately on the bisecting planes were superimposed, and that the basal B–B lines on the planes were horizontal. In this averaging process, the positions of the individual B atoms scattered only less than 0.05  $\text{\AA}$  around the mean positions.

symmetry. The difference density on the bisecting plane was, therefore, calculated as the average of the 60 original densities.<sup>2</sup> These processes reduced the random noises (0.05–0.10 e Å<sup>-3</sup>) in the original densities by an order of magnitude.

As for the B<sub>19</sub> unit and the single boron, the features of the observed difference densities through various sections were not so systematic as to justify such an averaging process as was used for the B<sub>12</sub> icosahedron. This was expected from the lower symmetry of the B<sub>19</sub> unit which has the plane of fusion and the two open pentagonal faces. Since the phases of the structure factors were estimated neglecting the contributions of the residual peaks, the peak heights which we report in the present paper may be systematically lower than the correct values (8, 9). The peak positions, however, are probably much less affected by the phase errors.<sup>3</sup>

## Results and Discussion

### a. The B<sub>12</sub> Icosahedron

The averaged difference electron density contours through the triangular face and those through the bisecting plane of the icosahedron are shown in Figs. 4 and 5, respectively. The most interesting feature of these maps is the piling up of the residual electrons with the peak heights of 0.1 e Å<sup>-3</sup> at the centers of the triangular faces. These central peaks are considered to demonstrate characteristic electron distributions of highly delocalized three-center bonds in such a

highly symmetrical boron framework as the B<sub>12</sub> icosahedron.

Another kind of prominent peaks with the peak heights of 0.2 e Å<sup>-3</sup> are seen in Fig. 5 on the external B–B bonds along the pseudo-fivefold axes of the icosahedron. Before averaging, the twelve external B–B bonds consisted of the six B<sub>12</sub>–B<sub>12</sub>, five B<sub>12</sub>–B<sub>19</sub> and one B<sub>12</sub>–single B bonds. In spite of the differences in the environments, the distributions of the residual peaks on all the external bonds were similar to each other.<sup>4</sup> These peaks resemble those on the two-center B–H bonds in decaborane (10), indicating the two-center bond nature of the intericosahedral B–B bonds. We note also a very large depression (–0.18 e Å<sup>-3</sup>) at the center of the icosahedron.

The observed two-center bond nature of the external B–B bonds suggested a close similarity in the electronic structure of the icosahedral unit in  $\alpha$ -AlB<sub>12</sub> with that of a B<sub>12</sub>H<sub>12</sub><sup>2-</sup> molecular ion (11). Therefore, theoretical “molecule-free atoms” difference electron densities,

$$\Delta\rho = \rho(\text{molecule}) - \sum_i \rho_i(\text{free atoms})$$

for an isolated B<sub>12</sub>H<sub>12</sub><sup>2-</sup> ion were calculated and compared with the observed densities of Figs. 4 and 5. The molecular densities  $\rho$  were calculated with the molecular wave functions obtained by the semi-empirical CNDO/2 molecular orbital method (12), whereas the atomic densities  $\rho_i$  of the neutral spherical atoms were calculated with the 2s(B) and 1s(H) atomic wave functions of the CNDO/2 basis set (13). In the CNDO/2 calculations, the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> ion was assumed to have the regular icosahedral symmetry and the bond lengths of B–B = 1.75 and B–H = 1.21 Å. Assumption of the B–B bond lengths of 1.80 Å, corresponding to the average B–B

<sup>3</sup> In order to assess the phase errors, the structure was refined using 719 higher angle reflections with  $\sin \theta/\lambda > 0.6$ . However, the average shift of the phases was only 0.7°, and the difference electron densities calculated with the new phases were essentially the same as those shown in the Figures. This is probably due to the facts that approximately one-third of the total reflections have discrete phase values (0,  $\pi$ ,  $\pm\pi/4$ ,  $\pm\pi/2$  and  $\pm3\pi/4$ ), and that there are no lone-pair bonding electrons in the structure.

<sup>4</sup> The residual peaks on three B<sub>12</sub>–B<sub>19</sub> bonds are seen in Fig. 9, although the bonds are not exactly on the section shown in the figure.

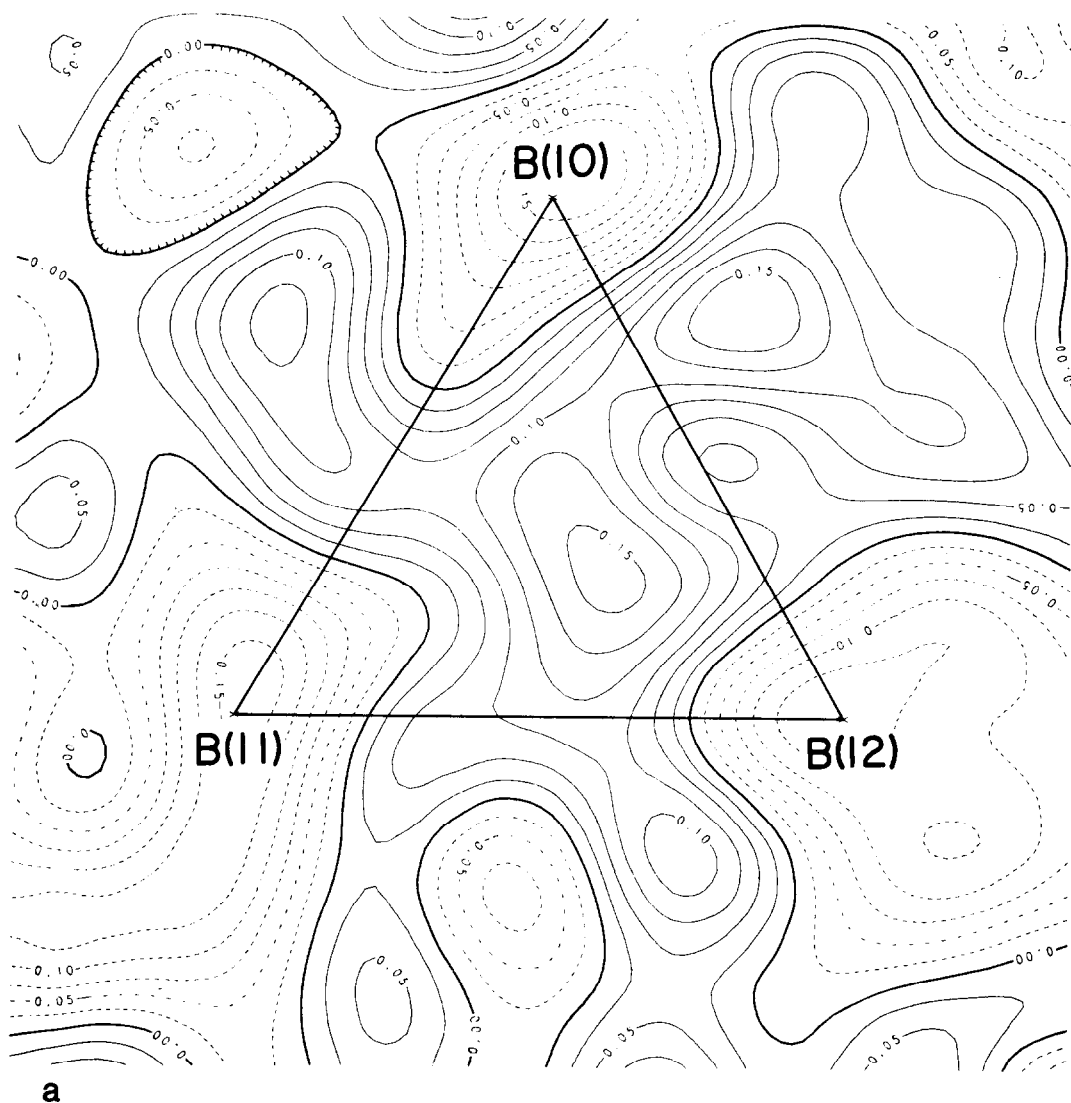
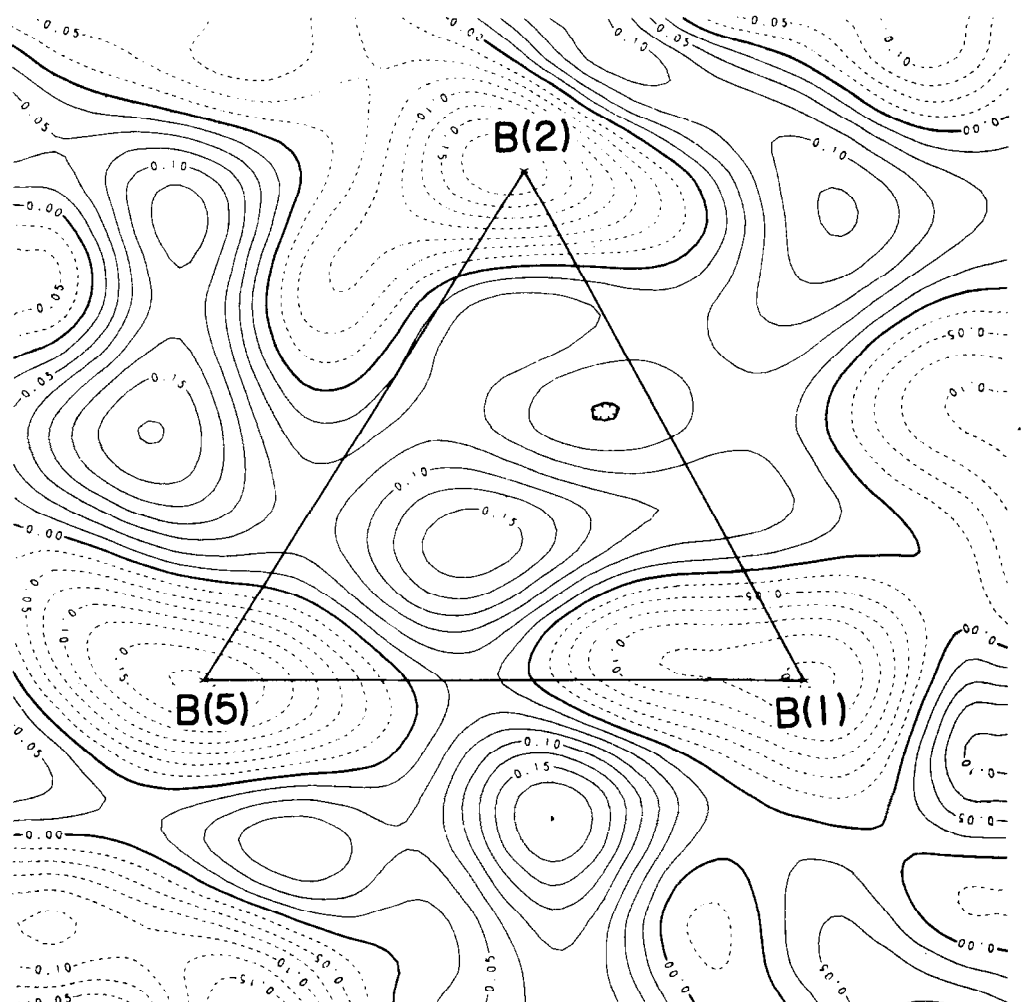


FIG. 3. Difference Fourier maps of the icosahedron. Sections through triangular faces with (a) the shortest ( $B(10)-B(12) = 1.736 \text{ \AA}$ ) and (b) the longest ( $B(2)-B(5) = 1.863 \text{ \AA}$ ) B-B bond lengths. Contours at  $0.025 e \text{ \AA}^{-3}$ . Negative contours dotted, zero contours thick.

length in the icosahedron in  $\alpha\text{-AlB}_{12}$ , gave essentially the same theoretical densities.

The "molecule-free atoms" densities for the  $B_{12}H_{12}^{-2}$  ion through the sections corresponding to Figs. 4 and 5 are shown in Figs. 6 and 7, respectively. Characteristic peaks of delocalized three-center bonds are seen

about the centers of the triangular faces, but in this case the centers of the peaks with the densities of  $0.08 e \text{ \AA}^{-3}$  are displaced approximately  $0.3 \text{ \AA}$  above the faces. The large peaks around the hydrogen atoms in Fig. 7 indicate the two-center bond character of the B-H bonds and also localization of the extra



b

-2 charges onto the hydrogen atoms.<sup>5</sup>

If allowance is made for the effect of the crystal field (the isolated B<sub>12</sub>H<sub>12</sub><sup>-2</sup> ion versus the B<sub>12</sub> unit in the three-dimensional network of  $\alpha$ -AlB<sub>12</sub>), and also for the

<sup>5</sup> Since theoretical net charges on each atom in boron hydrides are sensitive to the Coulomb integral parameters adopted for hydrogen atoms (14), those in the B<sub>12</sub>H<sub>12</sub><sup>-2</sup> ion (B<sup>+0.07</sup> and H<sup>-0.23</sup>) obtained with the standard CNDO/2 parameters may deviate from the real distributions. However, qualitative spatial distributions of electron densities are less sensitive to the parameters.

approximate nature of the CNDO/2 molecular orbital method, the theoretical difference maps of Figs. 6 and 7 are qualitatively in good agreement with the observed maps of Figs. 4 and 5, respectively; the theoretical densities confirm the physical significance of the observed densities.

#### b. The B<sub>19</sub> Unit

A stereoscopic view and the atom numbering of the B<sub>19</sub> unit in  $\alpha$ -AlB<sub>12</sub> are shown in Figs. 8a and b, respectively. The single B(23) atom bonded to the B<sub>19</sub> unit is

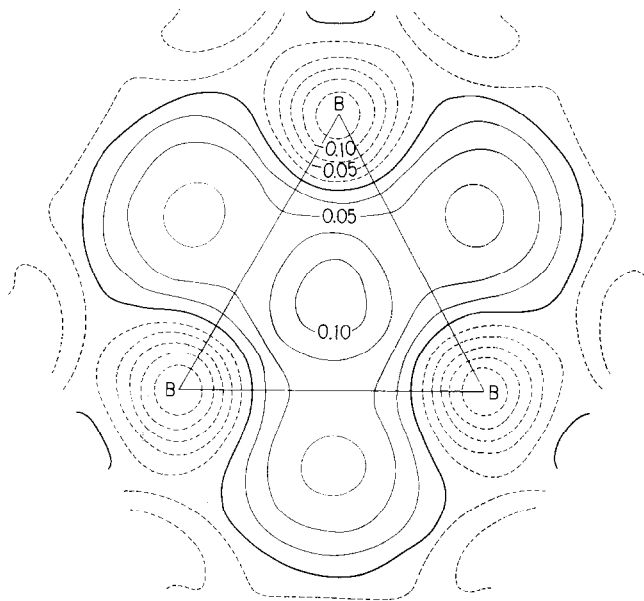


FIG. 4. Averaged difference Fourier map through the triangular face of the icosahedron. Contours as in Fig. 3.

also included in the figures. The  $B_{19}$  unit is formed by face sharing of two defect icosahedra, each lacking one apical boron; it has a twofold symmetry axis through  $B(22)$  and  $B(23)$  and one half of it is unique in the crystal.

A most interesting section of the observed difference electron distributions in the  $B_{19}$  unit is the one through the open pentagonal face (Fig. 9). Aluminum atoms occupy statistically the triplet sites  $Al(1)$ – $Al(5)$ – $Al(3)$  approximately  $1.8 \text{ \AA}$  above the face. Residual peaks with the peak heights of about  $0.2 e \text{ \AA}^{-3}$  are observed on all the five edges of the pentagon. They have broad tails above the pentagonal face; especially the two on  $B(14)$ – $B(15)$  and  $B(14)$ – $B(17)$  extend more than  $1.0 \text{ \AA}$  above the face toward the aluminum sites. These observations suggest a relatively strong interaction between the aluminum atoms and the  $B(14)$ ,  $B(15)$  and  $B(17)$  atoms on the face. The difference electron density section through the triangular face of fusion is shown in Fig. 10. As

mentioned above, the residual peak on the  $B(22)$ – $B(19)$  edge of the open face has a broad tail.

It should be noted that the structure of the  $B_{19}$  unit is closely related to that of  $B_{20}H_{16}(NCCH_3)_2$  (15); in the latter, only one apical boron is missing from the twinned icosahedra and a hydrogen atom occupies a single site above the open pentagonal face.

### c. The Single $B(23)$ Atom

One characteristic of the  $\alpha$ - $AlB_{12}$  structure is in the presence of the single  $B(23)$  atom; it joins a  $B_{19}$  unit and two  $B_{12}$  icosahedra in a distorted tetrahedral coordination in twofold symmetry. The difference electron density sections through the two  $B$ – $B(23)$ – $B'$  planes are shown in Figs. 11a and b;  $B(18)$  and  $B(18')$  belong to the same  $B_{19}$  unit, but  $B(5)$  and  $b(5')$  belong to different icosahedra. The distributions of the residual peaks in the two sections are quite different; the peak on the  $B(23)$ – $B(5)$  bond (Fig. 11a) conforms to a two-center  $B$ – $B$  bond, whereas the peaks

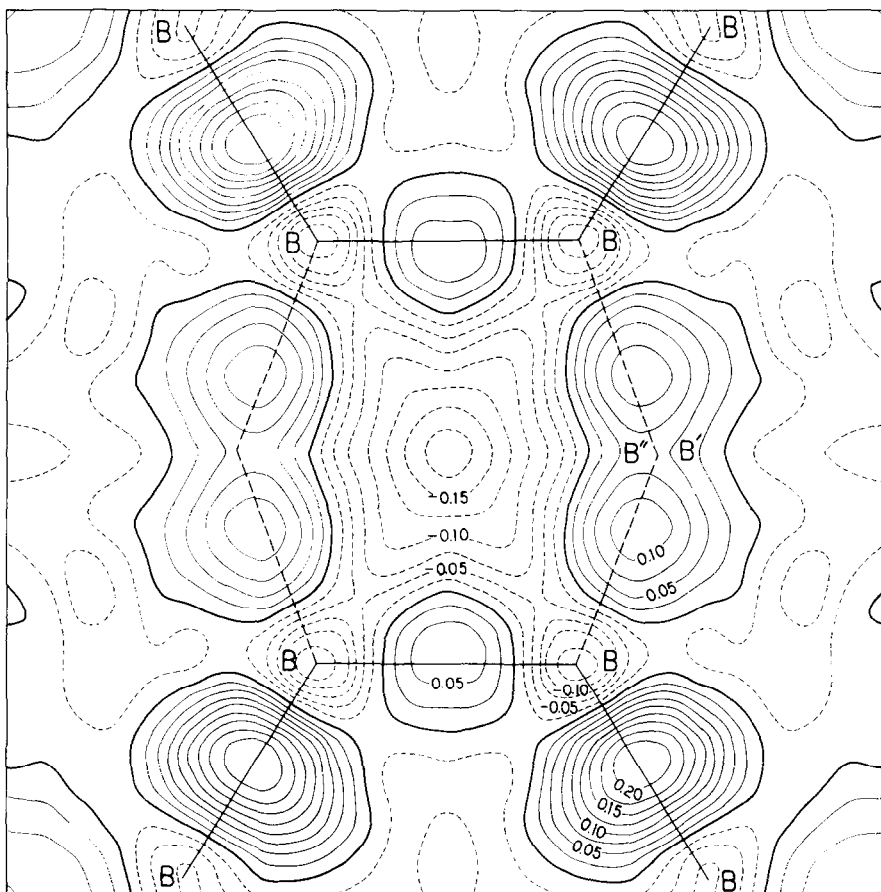
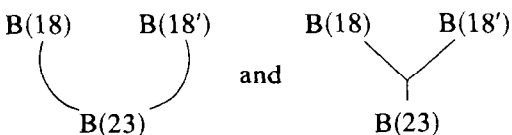


FIG. 5. Averaged difference Fourier map through the bisecting plane of the icosahedron. Contours as in Fig. 3. Refer to Fig. 2 for the geometry. The four external B-B bonds lie on the plane.

around the B(18)-B(23)-B(18') triangle (Fig. 11b) conform to localized three-center bonds:



Although the evidence is limited to the single set of difference maps, these maps suggest that from an electronic point of view the B(23) atom may more reasonably be thought of as a member of the B<sub>20</sub> unit as shown in Fig. 8, rather than a "single" boron

atom. The B<sub>20</sub> unit has then sixteen external B-B bonds and all of them can be regarded as two-center B-B bonds; difference maps through the four B<sub>19</sub>-B<sub>19</sub> bonds also revealed such prominent peaks on the bonds as were found on the ten B<sub>19</sub>-B<sub>12</sub> and the two B(23)-B<sub>12</sub> bonds.

In order to have an idea of the electronic structure of the B<sub>20</sub> unit, preliminary molecular orbital calculations of an extended Hückel type (initial guess calculations by the CNDO/2 method) were carried out for an isolated model molecule B<sub>20</sub>H<sub>16</sub>, which was obtained by replacing all the sixteen external B-B bonds in the B<sub>20</sub> unit by B-H bonds of

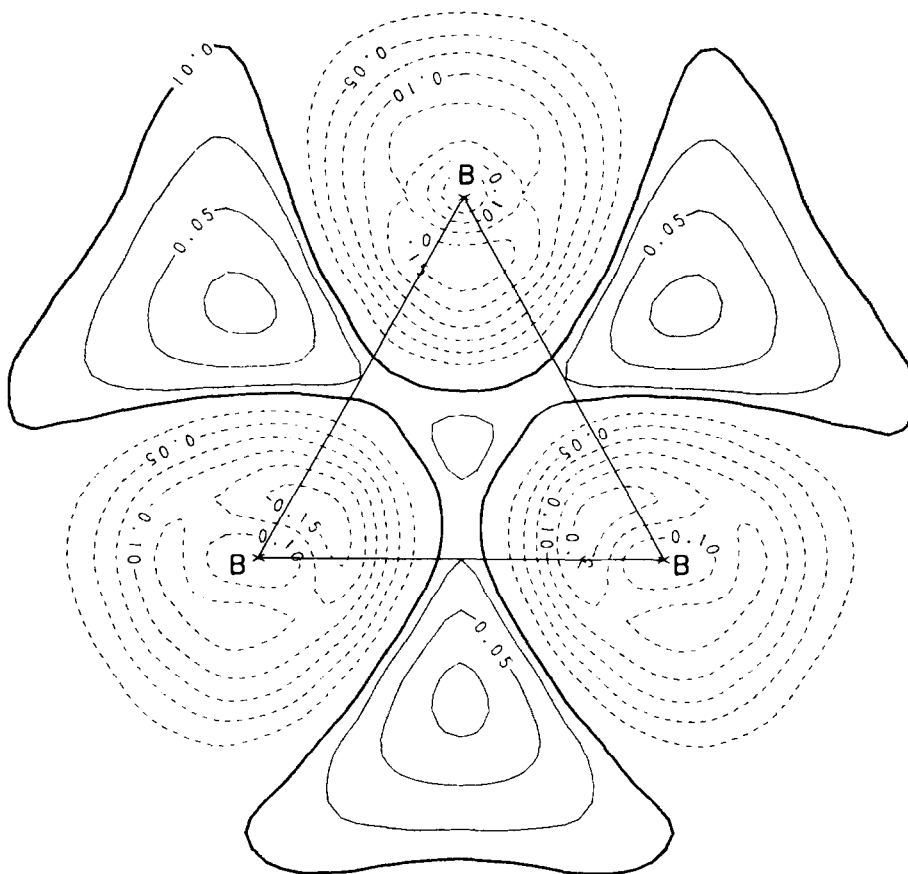


FIG. 6. Theoretical "molecule-free atoms" map through the triangular face of a  $B_{12}H_{12}^{2-}$  molecular ion. Contours as in Fig. 3, but zero contours are replaced by contours at  $0.01 e \text{ \AA}^{-3}$  because the former extend to infinity.

1.21 Å length.<sup>6</sup> The results of the calculations showed that the molecular ion  $B_{20}H_{16}^{-6}$  would give a relatively stable closed-shell electron configuration; the extra -6 charges were distributed mainly on the B(23), B(14), B(15), B(17) and the sixteen hydrogen atoms. It is interesting to note that if we assign -2 charges to the  $B_{12}$  icosahedron as in  $B_{12}H_{12}^{2-}$ , -6 charges to the  $B_{20}$  unit as in  $B_{20}H_{16}^{-6}$ , and +3 charges to the Al

<sup>6</sup> Self-consistent-field treatments of the CNDO/2 method were unsuccessful because the aluminum atoms were not taken into account.

atom, the  $\alpha\text{-AlB}_{12}$  structure with the formula unit  $2B_{12} \cdot B_{20} \cdot 3.25 \text{ Al}$  are neutral within the experimental errors ( $-2 \times 2 - 6 \times 1 + 3 \times 3.25 = -0.25$  electrons). However, the actual electron transfer from the aluminum to the boron atoms in  $\alpha\text{-AlB}_{12}$  is probably much less due to the back-transfer.

All the calculations were performed on the FACOM 230-75 computer of this Institute. The difference Fourier maps were calculated with the program MPF30 which utilizes the subroutine SPFT(16) for the Fourier summation.



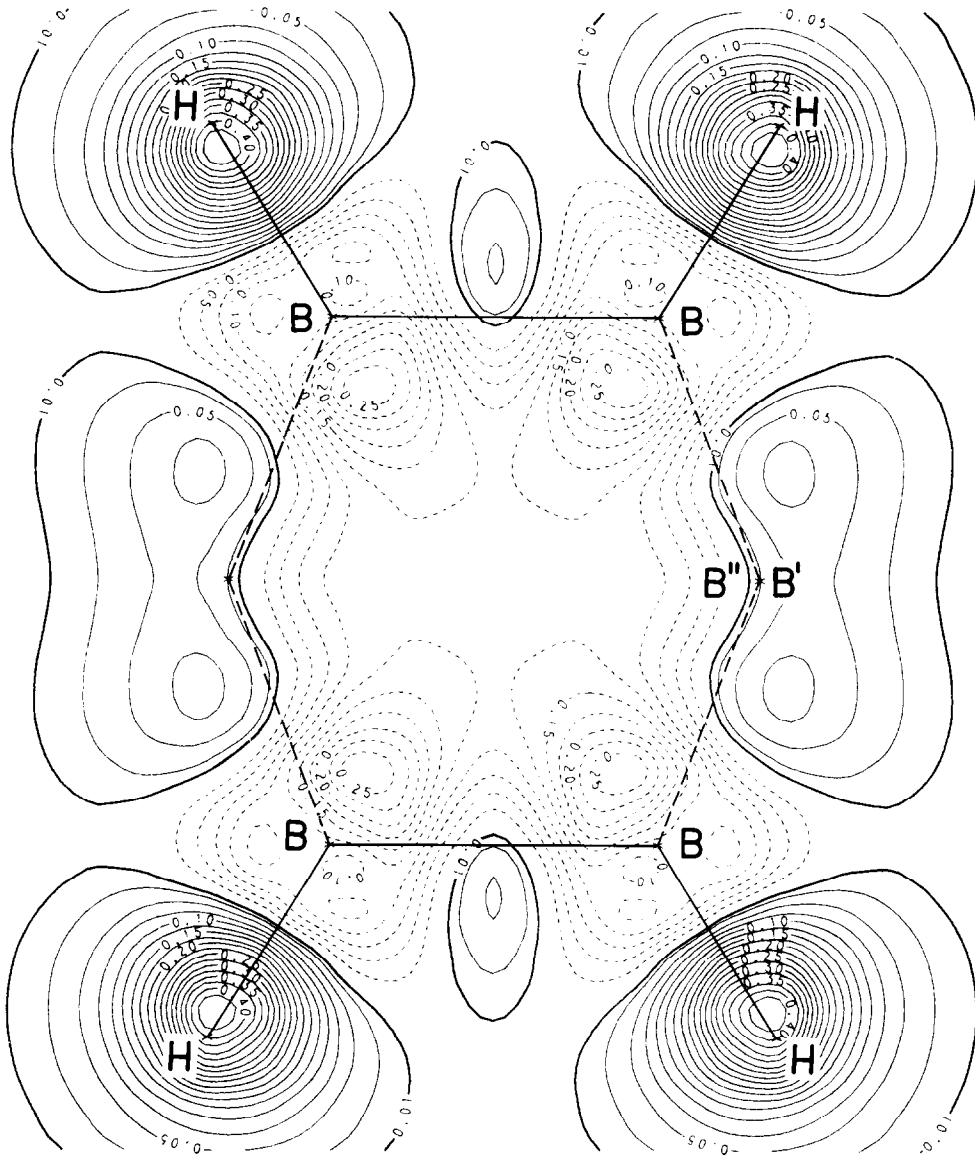


FIG. 7. Theoretical "molecule-free atoms" map through the bisecting plane of a  $B_{12}H_{12}^{2-}$  molecular ion. Contours as in Fig. 6.

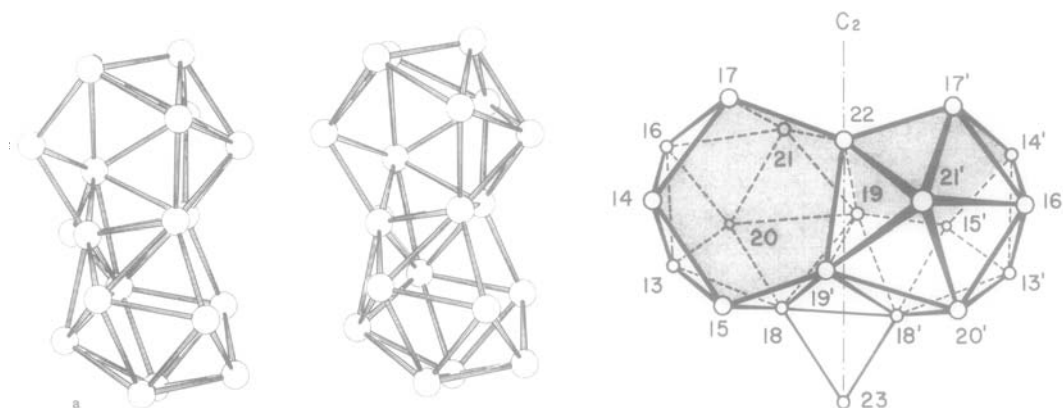


FIG. 8. B<sub>19</sub> unit with the single B(23) atom. (a) Stereoscopic view and (b) atom numbering.

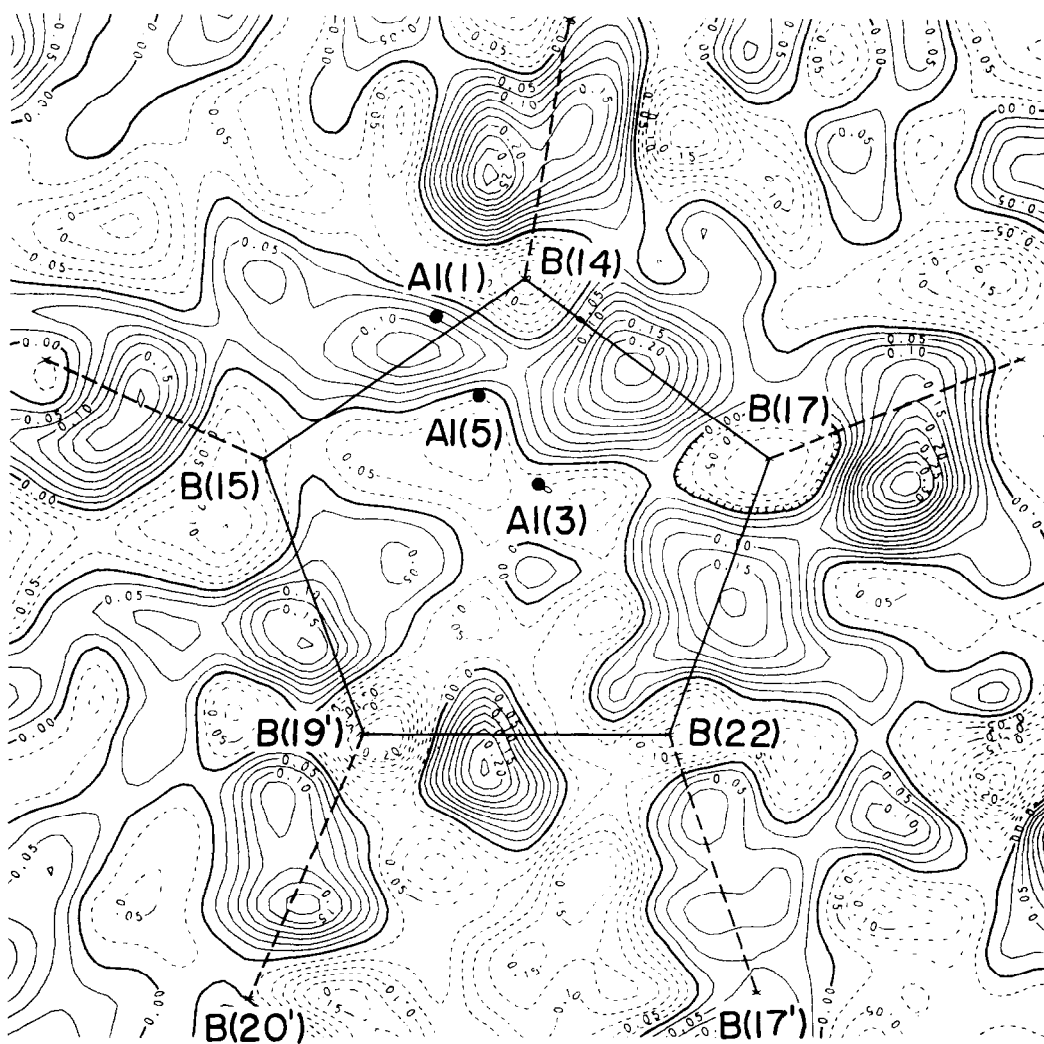


FIG. 9. Difference Fourier map through the open pentagonal face of the B<sub>19</sub> unit. Al(1)–Al(5)–Al(3) sites with the occupancies 0.717, 0.021 and 0.240 respectively are approximately 1.8 Å above the face. Contours as in Fig. 3.

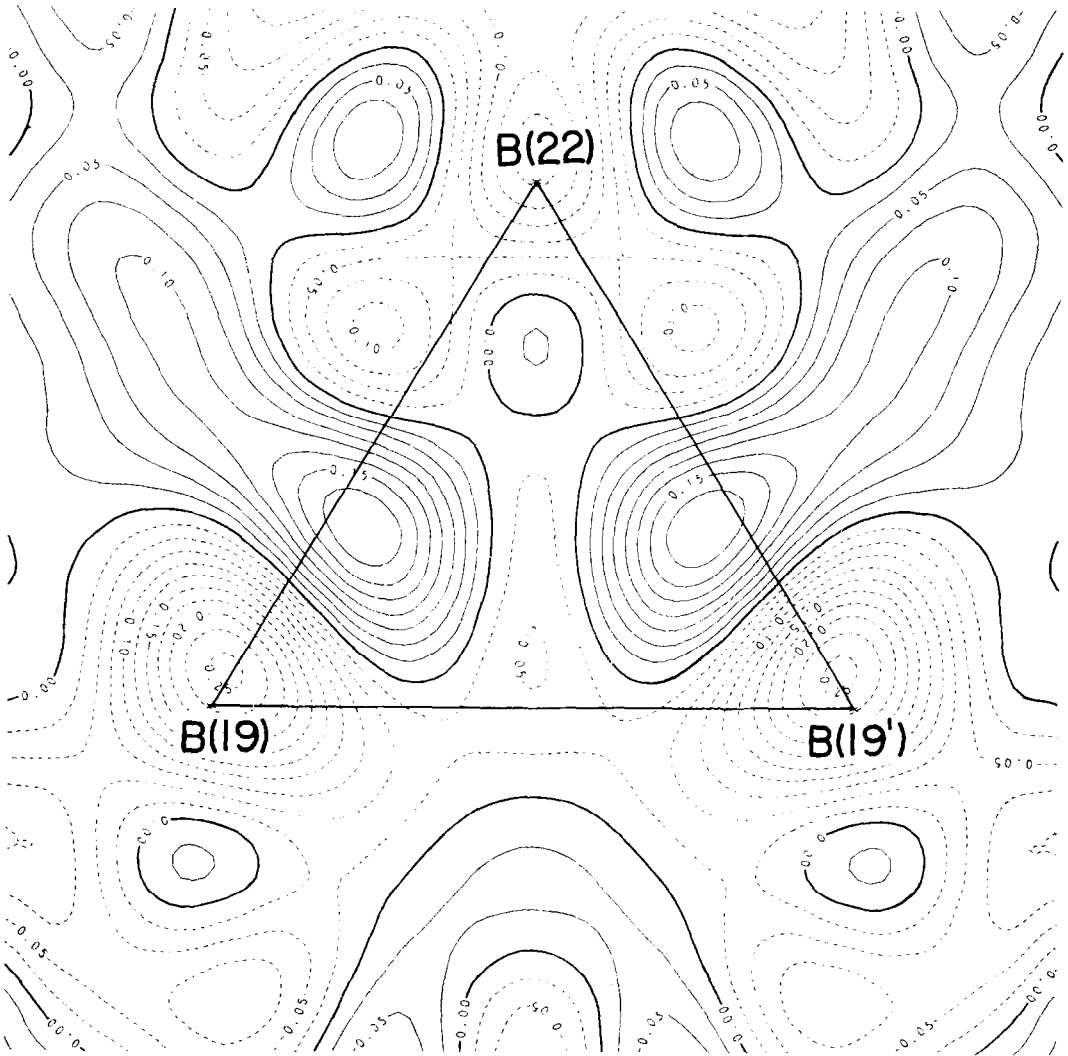


Fig. 10. Difference Fourier map through the plane of fusion of the B<sub>19</sub> unit. Contours as in Fig. 3.

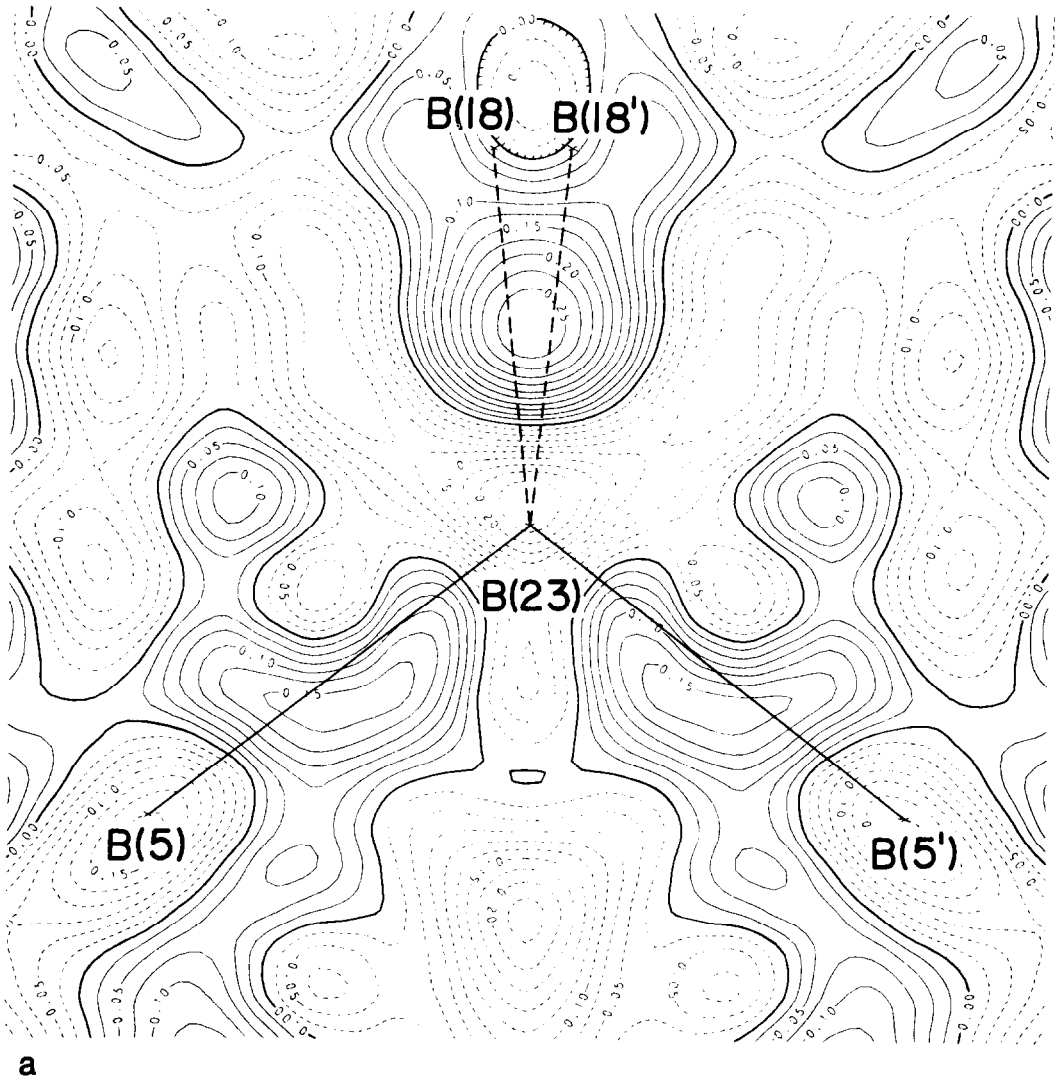
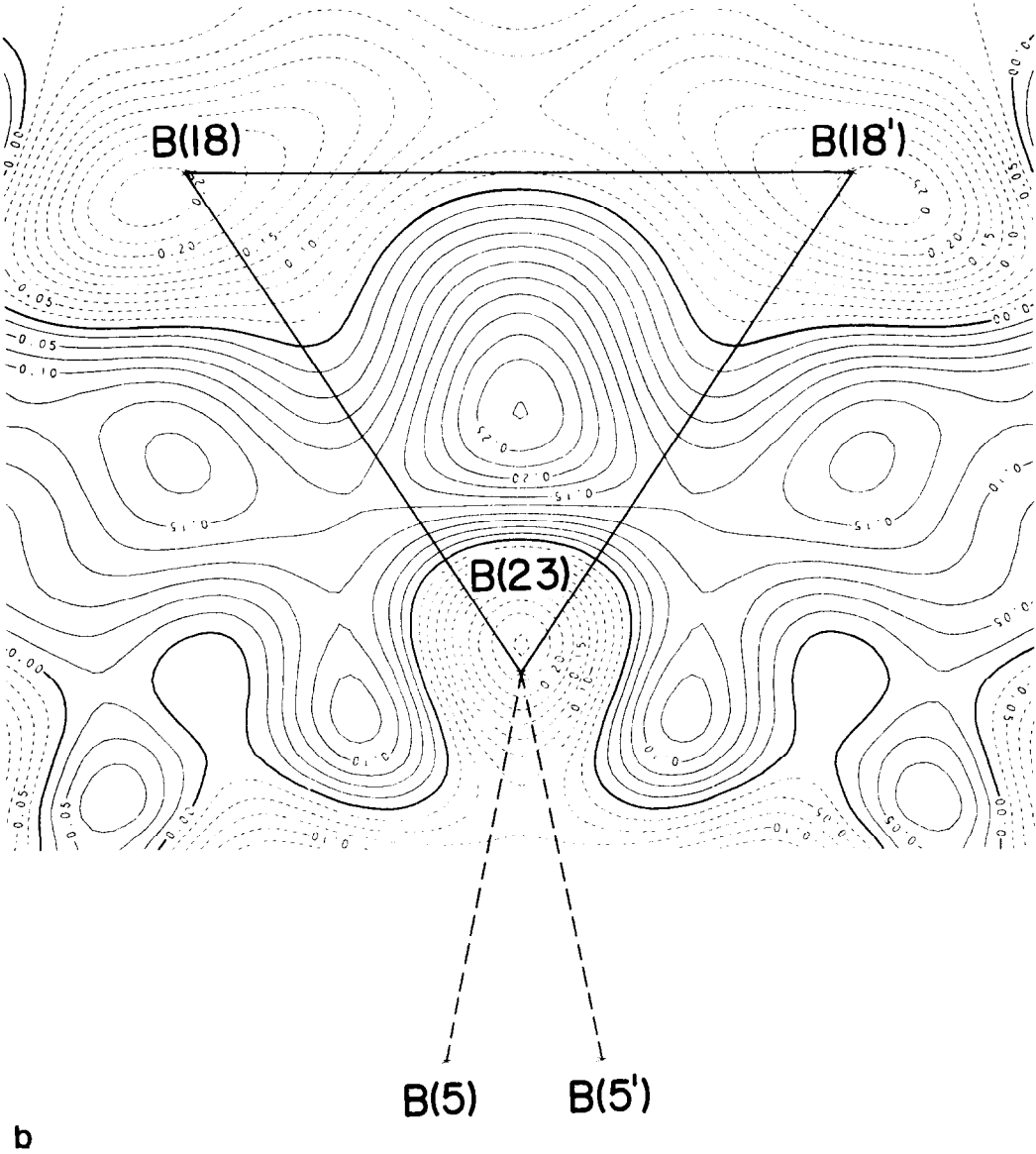


FIG. 11. Difference Fourier maps around the single B(23) atom. Sections through (a) B(5)–B(23)–B(5') and (b) B(18)–B(23)–B(18'). Contours as in Fig. 3.



b

FIG. 11 (continued).

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