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Fundamental Structure of Amorphous Boron

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Short-range order (SRO) structures of various grades of amorphous boron show similar undulations on their reduced radial distribution functions ($G(r)_{obs}$s). The profiles of these undulations resemble those derived from the structure models of β-rhombohedral boron, β-tetragonal boron, and a giant cluster made up of 13 B_{12} units. From this examination, the interconnected B_{48}–(Td) unit, which is a main substructure of all the structure models mentioned above, seemed to be responsible for the similar undulations. In this work, however, structure simulation of amorphous boron was made solely with the B_{12} icosahedron. Two series of boron cluster models were considered based on the difference in their bonding state through pseudo-fivefold axes, i.e., "in-phase" without rotation and "out-of-phase" differing by $\sim \pi/5$. The $G(r)_{calc}$s were calculated by means of the Fourier integral of the interference intensity functions wherein the scattering intensities were derived through a partly modified Debye's scattering intensity equation. From the comparison of the SRO structures of the cluster models to those for amorphous boron, it is indicated that the number and the bonding state of the icosahedra which constitute the boron cluster should be greater than 9–13 and should be in out-of-phase state for better correspondence.

1. INTRODUCTION

Short-range order (SRO) structures of various grades of amorphous boron exhibit similar undulations in their reduced radial distribution functions (reduced RDF: $G(r)_{obs}$s) regardless of their appearance, preparation methods, and boron sources, as shown in Fig. 1a. The profiles of these undulations resemble those derived from the structure models of β-rhombohedral boron, β-tetragonal boron, and a giant cluster made up of 13 B_{12} units (1–3) as shown in Fig. 1b. From this examination, the interconnected B_{48}–(Td) unit, which is a common substructure of all the above structure models, seemed to be responsible for the similar undulations (3). This is in striking contrast with the first description of evaporated amorphous boron films made by Katada, that the arrangement of B_{12} icosahedra is quite random except for the validity of B_{12} icosahedron (4). In the present work, therefore, structure simulation of amorphous boron was made solely with the B_{12} icosahedron because the B_{48}–(Td) unit is made up of four B_{12} icosahedra and their bonding state for the boron cluster was investigated using two sorts of linking modes.

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2. EXPERIMENTAL

2.1. Model Preparation

In the calculation of $G(r)_{calc}$s for the various structure models of amorphous boron, we used a regular B_{12} icosahedron as a basic structural unit with intra- and intericosahedral B–B bonding distances of 1.767(3) and 1.621(3) Å. Although the icosahedron has three different directions exposing the twofold, threefold, and pseudo-fivefold axes, it combines mainly through the pseudo-fivefold axes. However, there are two sorts of bonding states between icosahedra which are shown in Figs. 2a and 2b where 2a shows an "out-of-phase" bonding rotated by $\sim \pi/5$ and 2b represents an "in-phase" linkage without rotation to each other. These icosahedra combine further into a larger cluster through the pseudo-fivefold axes. Thus, the two groups of boron cluster models adopted based on the difference in their bonding states as described above are as follows:

(a) boron cluster models composed of (1), 2, 3, 4, 5, 9, and 13 B_{12} icosahedra which arrange themselves in "out-of-phase" to each other and

(b) boron cluster models in "in-phase" state which are composed of (1), 2, 3, 4, 7, and 13 icosahedra. These structure models are respectively depicted in Figs. 2 and 3.

2.2. Calculation of $G(r)_{calc}$

In this work $G(r)_{calc}$s (calculated) are obtained by means of the Fourier integral of the interference intensity functions wherein the scattering intensities are derived through a partly modified Debye's scattering intensity equation, i.e., by the same method previously described in paper (1). The numerical equations, however, will be recapitulated

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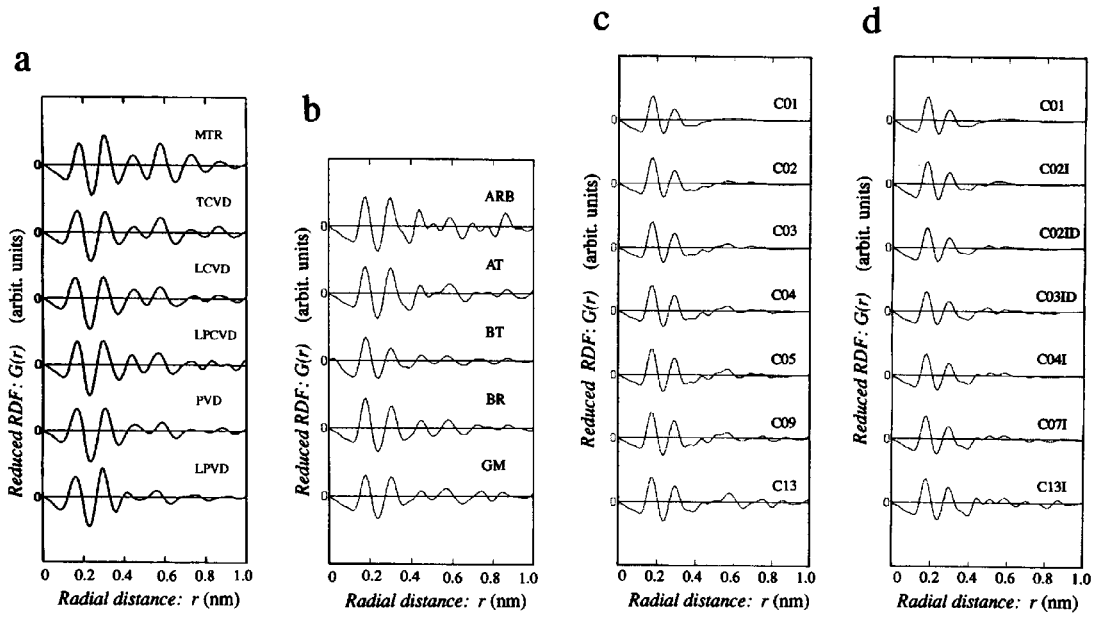

FIG. 1. Comprison of the reduced radial distribution functions [Reduced RDF(r), $G(r)s$]: (a) Various grades of amorphous boron, (b) Crystalline boron, and (c) structure models of boron clusters with "out-of-phase" bondings and (d) "in-phase" linkages between B_{12} icosahedra. Notations used are the same in the text except MTR, Moissan boron; TCVD, boron films prepared by thermal CVD; LCVD, fine boron powder deposited by laser-induced dielectric breakdown; LPCVD, thin boron films obtained by low pressure CVD; PVD, thin boron films obtained by PVD; and LPVD, boron films obtained by laser ablation. (a) and (b) are reproduced from Kobayashi *et al.* (3) for comparison.

as described as follows:

The scattering intensities of monoatomic molecules forming a noncrystalline cluster are calculated by the Debye's scattering intensity equation partly modified as

$$I'(s)_{\text{calc}} = \sum_{i}^{N} f^2(s) + f^2(s) \sum_{i}^{i \neq j} \sum_{j} \frac{\sin(sr_{ij})}{sr_{ij}} \exp(-Bs^2) \quad [1]$$

$$I(s)_{\text{calc}} = I'(s)_{\text{calc}}/N, \quad [2]$$

where r_{ij} is the interatomic distance between atoms i and j, B is a temperature factor, and N is the total number of atoms forming the cluster model concerned. s is the scattering function and defined by $4\pi \sin\theta/\lambda$, wherein 2θ is the scattering angle and λ is the X ray or electron wavelength.

The interference intensity function, $i(s)$, and the reduced RDF, $G(r)_{\text{calc}}$, are expressed as

$$i(s) = \frac{I(s)_{\text{calc}} - f_e^2(s)}{f_e^2(s)} \exp(-As^2) \quad [3]$$

$$G(r)_{\text{calc}} = \frac{2}{\pi} \int_0^{s_{\max}} si(s) \sin(rs)\, ds \quad [4]$$

$$= 4\pi rz[g(r) - g_0], \quad [5]$$

where $f_e(s)$ is the elementary scattering factor per single electron or nuclear charge and is given by $f(s)/z$ for a monoatomic specimen. $f(s)$ and z are the atomic scattering amplitude for the incident X ray or electron and the atomic number. An artificial temperature factor $\exp(-As^2)$ is introduced to minimize termination-of-series errors at the upper limit $s_{\max}$. The value of A in the exponential term was determined so that the factor becomes 0.1 at $s_{\max}$. $g(r)$ and g_0 are the electron or nuclear charge density function and its average. The SRO structures of these cluster models have been compared to those of the $G(r)_{\text{calc}}$s plots of crystalline boron and the $G(r)_{\text{obs}}$s plots for amorphous boron.

3. RESULTS AND DISCUSSION

Figure 1c shows the calculated $G(r)_{\text{calc}}$s plots for the boron clusters where B_{12} icosahedra link in out-of-phase state. The first two large coordination peaks commonly seen are due to the intra- and intericosahedral nearest neighbor atoms. The following small undulations observed at C02 are increasing in their amplitude as the number of icosahedra increased that is denoted by numerals after C, cluster. The SRO structures, i.e., undulations of C09 and C13, show almost similar profiles which also resemble the $G(r)_{\text{obs}}$s plots for amorphous boron (Fig. 1a). On the other hand, to validate these findings, the same procedures as before are employed in the calculation of $G(r)_{\text{calc}}$s for the boron

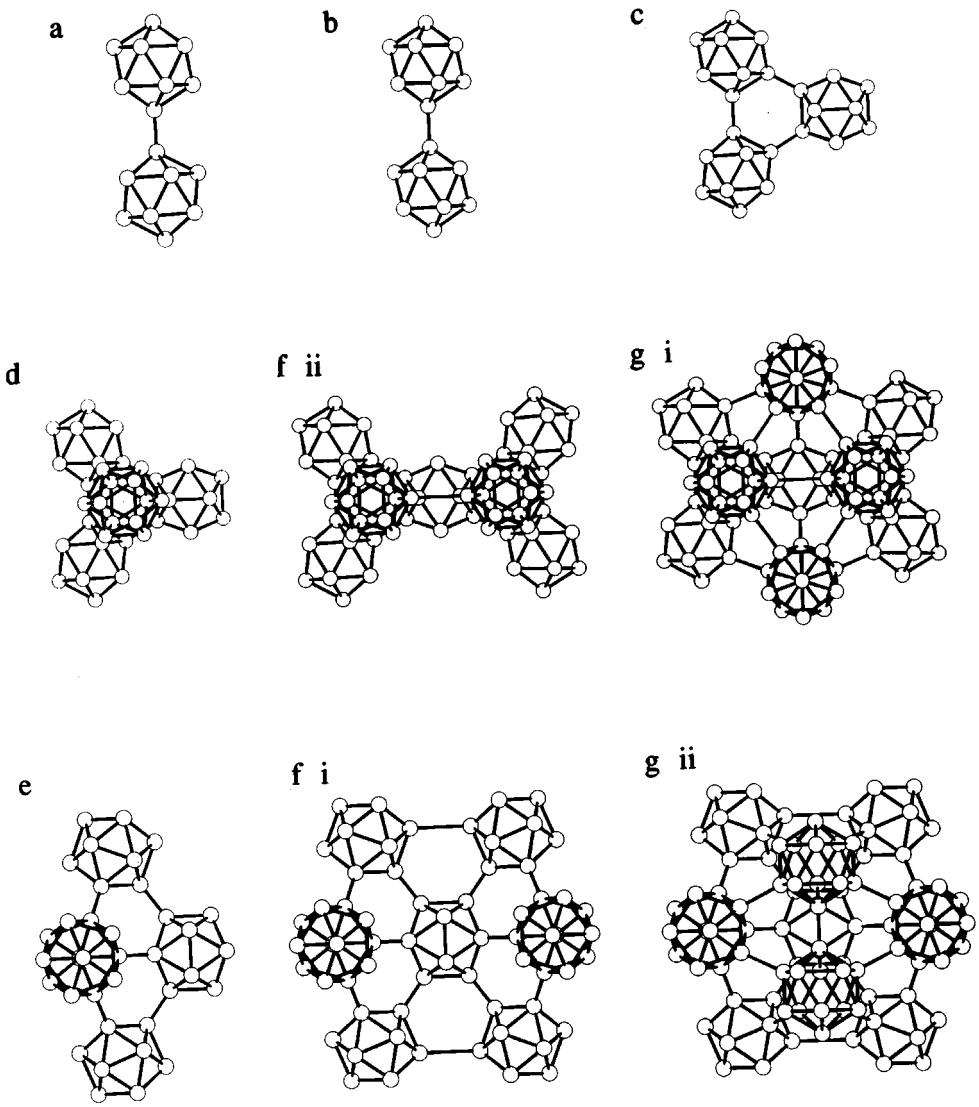

FIG. 2. Cluster models for amorphous boron (1). (a) An "out-of-phase" bonding which exists in β-rhombohedral boron (C02). (b) An "in phase" linkage which is found in α-rhombohedral boron (C02I). (c) Cluster comprising three icosahedra (C03). Each icosahedron bonds in out-of-phase state to make a ring through pseudo-fivefold axes. (d) Cluster comprising four icosahedra (C04). Each icosahedron in out-of-phase state makes a tetrahedron interconnected by pseudo-fivefold axes. (e) Sideview of a cluster comprising five icosahedra (C05). The C04 tetrahedron (d) is accompanied by another icosahedron in out-of-phase state to make a bipyramidal cluster. (f) i, Sideview of a cluster comprising nine icosahedra (C09). Four icosahedra are created by mirror-symmetry-operation to the C05. Somewhat long intericosahedral distances are seen on the symmetry plane. (f) ii, Overview of the cluster C09. Two vacant spaces are seen which have to be occupied respectively by two B_{12} icosahedra to make a cluster comprising 13 B12 icosahedra (C13). (g) i, Overview of the C13, which comprises a super icosahedron of 13 B_{12}. (g) ii, Sideview of the C13 cluster.

clusters in which the icosahedra arrange themselves in in-phase state contrary to the out-of-phase one. The results are shown in Fig. 1d, where numerals, I, and D stand for the number of icosahedra forming the cluster, in-phase, and juxtaposition of icosahedra as in Δ-bonding shown in Fig. 3a. The undulations which follow the first two coordination peaks vary in their profiles as the number of icosahedra increased. However, these profiles are quite different from those of the out-of-phase arrangement of icosahedra as seen in Fig. 1c: the characteristic peak at $r = 5.1$ Å is already seen in the profiles below C02ID. Thus, the undulations of C13I in Fig. 1d rather resemble those of ARB (α-rhombohedral boron) in Fig. 1b showing the calculated $G(r)_{\text{calc}}$s plots of the structure models of crystalline boron (AT, α-tetragonal boron; BT, β-tetragonal boron; and BR, β-rhombohedral boron) and GM, assumed giant molecules. It may be mentioned that the undulations of C13 in Fig. 1c resemble those of amorphous boron as shown in Fig. 1a rather than those of ARB in Fig. 1b. In this connection it is to be noted that the present result is different from

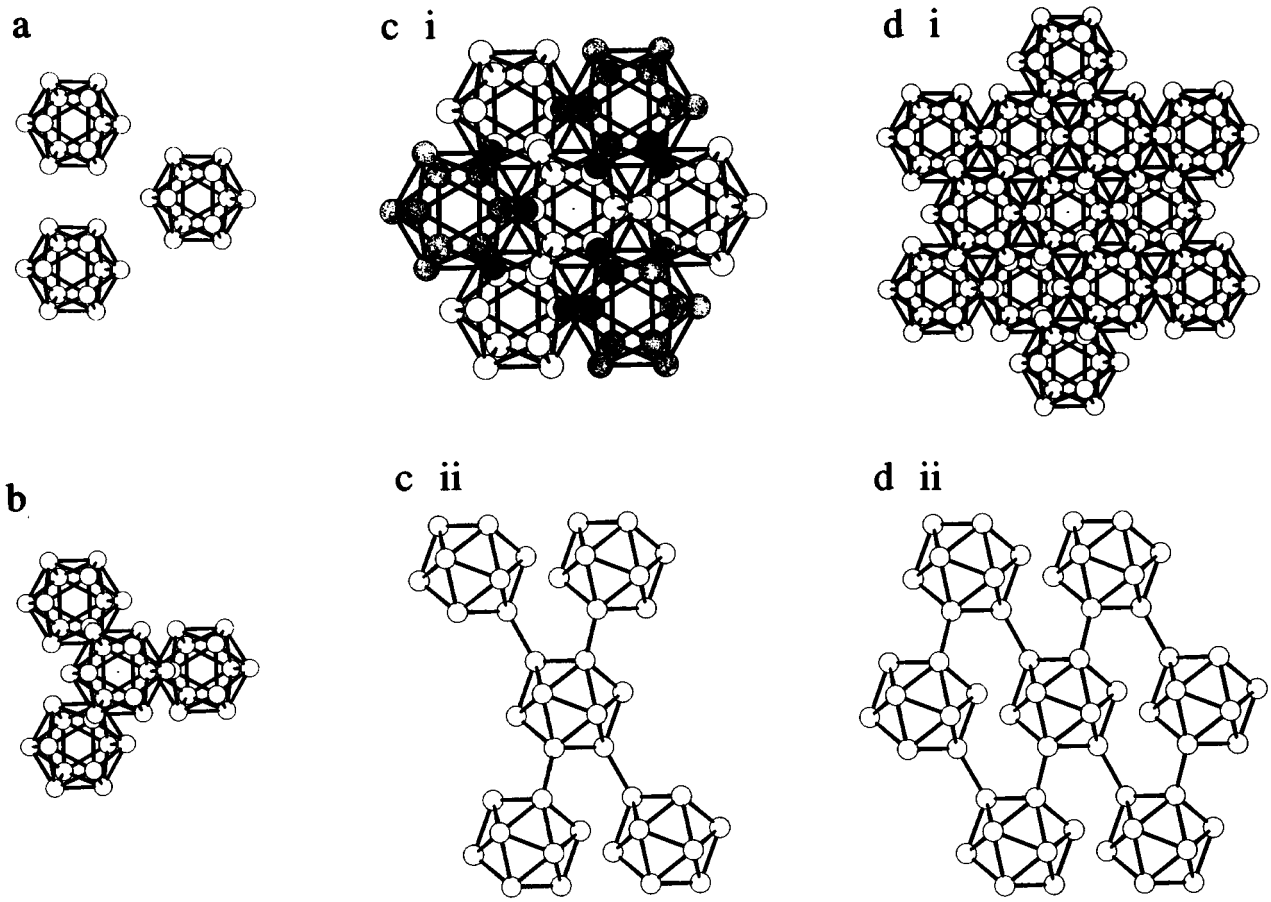

FIG. 3. Cluster models for amorphous boron (2). (a) Three B_{12} icosahedra which are respectively juxtaposed in "in-phase" state making a Δ-bonding (C03ID). I and D stand for in-phase and Δ-bonding, respectively. (b) Four B_{12} icosahedra which locate in in-phase state forming a tetrahedron (C04I). There are one Δ-bond and three in-phase bonds. (c) i, Cluster comprising seven B_{12} icosahedra which locate in in-phase state (C07I). Gray circles demonstrate three overlaid icosahedra. (c) ii, Sideview of the C07I layered cluster with in-phase bondings. (d) i, Overview of a cluster of 13 B_{12} icosahedra (C13I). (d) ii, Sideview of the C13I cluster.

the one reported by Vasiljev *et al.* (5) in that the occurrence of Δ-bonds is referred in the model of the structural "superunit."

The present results obtained are natural since both arrangements of icosahedra which exist in real boron crystals are covered in the calculation of $G(r)_{calc}$s. Although structure models of B_{12} clusters have some inevitable distortions which are seen in Figs. 2e, 2f, and 2g, the SRO structure of $G(r)_{calc}$ plots thus obtained has no appreciable difference compared with that of the real boron crystal.

4. CONCLUSION

In conclusion, it is shown that the number of B_{12} icosahedra which constitute the boron cluster should be greater than 9–13 for better correspondence to the observed undulations of $G(r)_{obs}$ plots for amorphous boron, i.e., the SRO structure. These icosahedra arrange themselves in out-of-phase, $\sim\pi/5$ rotation to each other through their pseudo-fivefold axes.

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