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Ground and Excited States of an Icosahedral $B_{12}H_{12}$ Cluster Simulating the B_{12} Cluster in β-Rhombohedral Boron

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From many experimental studies, a localized intrinsic acceptor level is assumed to exist at about 0.2 eV above the valence band edge in β-rhombohedral boron. The acceptor level has been tentatively originated from the unoccupied intracluster bonding level split away from the valence band due to the distortion of the electron-deficient B_{12} icosahedral cluster. We investigated numerically the ground and the excited states of the $B_{12}H_{12}$ cluster simulating the B_{12} cluster in β-rhombohedral boron. One stable and two metastable geometries for the B_{12} cluster at a vertex of the rhombohedral unit cell are found. The energy of the first excited state for only one of the metastable structures is lowered toward a valence band close to that of the acceptor level, while the energies of the other two structures have values corresponding to the band gap. The origin of localization is assumed to be the random distribution of the intrinsic acceptor levels originating from the metastable geometry of the B_{12} cluster. © 1997 **Academic Press**

INTRODUCTION

A B_{12} icosahedral cluster forms two kinds of elemental boron solid, α- and β-rhombohedral boron (α- and β-boron). Both are semiconducting materials. In β-boron acceptor levels have been experimentally detected in undoped samples. For example, optical absorption spectra near the absorption edge (1), photoluminescence spectra (2), time of flight measurements (3), and doping experiments (4) strongly imply existence of the levels. From optical experiments, these acceptor levels are located about 0.2 eV above the valence band edge. According to Werheit's evaluation of the density of states (DOS) of the acceptor levels from optical absorption experiments, the DOS is very high (10^{18}–10^{20} cm^{-3}) (1). Electrical conductivity experiments show hopping type conduction over a wide range of temperature (< 250 K) (4, 5). In this temperature range, most of the carriers contributing to current are populated in the acceptor levels, rather than in the conduction or valence band. This reveals that the acceptor levels are localized in spite of the high DOS. Werheit *et al.* proposed the origin of these acceptor levels oriented to the B_{12} clusters (6): a B_{12} cluster has 36 valence electrons and 13 intracluster and 12 intercluster bonding orbitals. If each atom in a cluster has a bond to an atom in a neighboring cluster (this is the case of β-boron), 12 electrons are spent on the intercluster bonds. Thus the 13 intracluster bonding orbitals are not fully occupied by the remaining 24 electrons. When the cluster shape has I_h symmetry, the highest occupied molecular orbitals (HOMO) of the cluster are degenerated fourfold. Since the cluster is two-electron-deficient, the HOMO are partially occupied. The Jahn–Teller distortion will occur. In β-boron, therefore, the clusters are considered to distort its shape into D_{3d} symmetry induced by the Jahn–Teller effect. Consequently, degeneracy of HOMO is partially reduced and a split empty orbital produces intrinsic acceptor levels in a solid.

According to this model, it is expected that the empty orbitals split away from HOMO make up a conduction band in β-boron, because every B_{12} cluster produces an empty orbital and the clusters are periodically located in β-boron. However, experimental results show that localized acceptor levels distinguished from conduction bands exist as low energy excited states.

In this paper, ground and excited states of the B_{12} cluster have been investigated numerically to confirm the formation of the acceptor level. The origin of localization of the intrinsic acceptor levels in β-boron is discussed. Since the B_{12} clusters in β-boron are surrounded by 12 nearest boron atoms, each of the 12 boron atoms in the cluster has an outward covalent bond. We simulated the surrounding environment by using a $B_{12}H_{12}$ cluster in the actual calculations.

METHOD

All the calculations were done by an *ab initio* SCF-MO method (7) except for calculations drawing total energy surfaces of the ground state of the clusters. These were done

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using a semiempirical method (8). We chose the 6-31G* basis set for *ab initio* calculations in the present study and performed total energy calculations of the ground states after geometry optimizations. Minimum energy of the atomic configuration was confirmed by analyzing the hessian matrix (9). To obtain the energies of the excited states of the cluster, we used a configuration interaction (CI) method (10). The CI segments of our calculations were limited within the triply excited configurations obtained by promoting one, two, or three electrons from the 6 or 7 highest occupied to the 14 or 17 lowest unoccupied MOs. The CI segments produce over 100,000 configuration state functions. The restrictions on the use of highest occupied and of lowest unoccupied MOs are due to the avoidance of MOs consisting mainly of hydrogen atomic components and to being energetically far from HOMO, respectively.

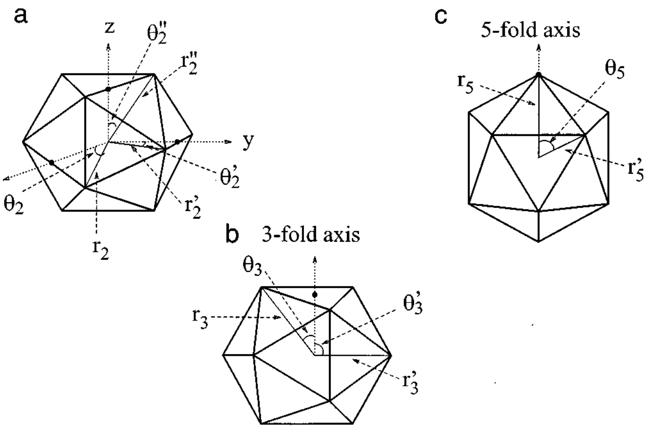

FIG. 1. Definition of optimized variables. (a) D_{2h}, (b) D_{3d}, (c) D_{5d}.

RESULTS AND DISCUSSION

The subgroups of the I_h symmetry group are included in the subject of our consideration to take into account distortion of the cluster shape from I_h symmetry. Thus the restriction on symmetry of cluster shape is more relaxed than previously reported (6). We used D_{2h} symmetry instead of T_h symmetry to construct the coordination of the clusters, whereas T_h constitutes the maximal subgroups of the I_h group as well as D_{3d} and D_{5d}. This is because the D_{2h}–B_{12} cluster, as well as the D_{3d} cluster, is actually in β-boron; the former at the edge center and the latter at the vertex, and D_{2h} is one of the subgroups of the T_h group. Concerning the D_{5d} symmetric cluster, it was calculated to obtain a simple confirmation of the validity of the calculation, while such a cluster is never present in crystals because D_{5d} symmetry possesses fivefold axes, inconsistent with translational symmetry. That is, at least we could say only that if the D_{5d}–B_{12} cluster is more stable than the other symmetric cluster, the present calculations to evaluate the solid properties using the cluster are considered to be wrong approximations.

The geometry optimizations were performed only under constraint of each symmetry. Figure 1 shows geometrically optimized variables of each symmetry. The possibility of local energy minima on the total energy surface with respect to atomic configuration suggests that the optimized atomic configuration may depend on initial atomic configuration. We therefore illustrated the total energy surface of each symmetric cluster, varying the axial angles with appropriately chosen radii using a semiempirical method. The results are illustrated in Fig. 2. It is found that there is only one energy minimum for the D_{2h}– and the D_{5d}–$B_{12}H_{12}$ cluster, but there are three energy minima for the D_{3d}–$B_{12}H_{12}$ cluster. For the D_{3d}–$B_{12}H_{12}$ cluster, we label each minimum as follows:

Stable: energetically most stable minimum

Metastable-1: the local minimum positioned at the top right in Fig. 2b

Metastable-2: the local minimum positioned on the left in Fig. 2b.

Initial atomic configurations in geometry optimization by the *ab initio* method were chosen from the total energy surface in order to converge suitable minima. The geometry optimization constraining the cluster shape to D_{2h} symmetry resulted in higher symmetry, T_h, as well as the results from the semiempirical method.

Total energies of the clusters with the shape fixed to the obtained atomic configuration are calculated for comparison of energetic stabilities (Table 2). The difference of the total energies between the T_h- and the D_{3d}–$B_{12}H_{12}$ clusters is small, while the differences of those between the D_{5d}–$B_{12}H_{12}$ and the other clusters are large. Even though the geometry is located at the energy minimum, the D_{5d}–$B_{12}H_{12}$ cluster is energetically unstable compared with the other clusters. This is consistent with the fact that the D_{5d}–B_{12} cluster is not present in any crystal. Thus no further calculation for the D_{5d}–$B_{12}H_{12}$ cluster has been done. Since differences of total energies among the stable and metastable atomic configurations for the D_{3d}–$B_{12}H_{12}$ cluster are small and the heights of the potential barrier among the three minima appear to be low from Fig. 2, it could occur that the atomic configurations of B_{12} in β-boron are randomly distributed among the three minima. When such a distribution occurs in β-boron, the experimental values of the parameters in Table 1 can be explained as average values of the parameters for the three minima.

The energy spectra of the excited states for the most stable structures of the T_h- and D_{3d}–$B_{12}H_{12}$ clusters are shown in Fig. 3. The energies of the first excited states for both, which may be related to the acceptor level, are

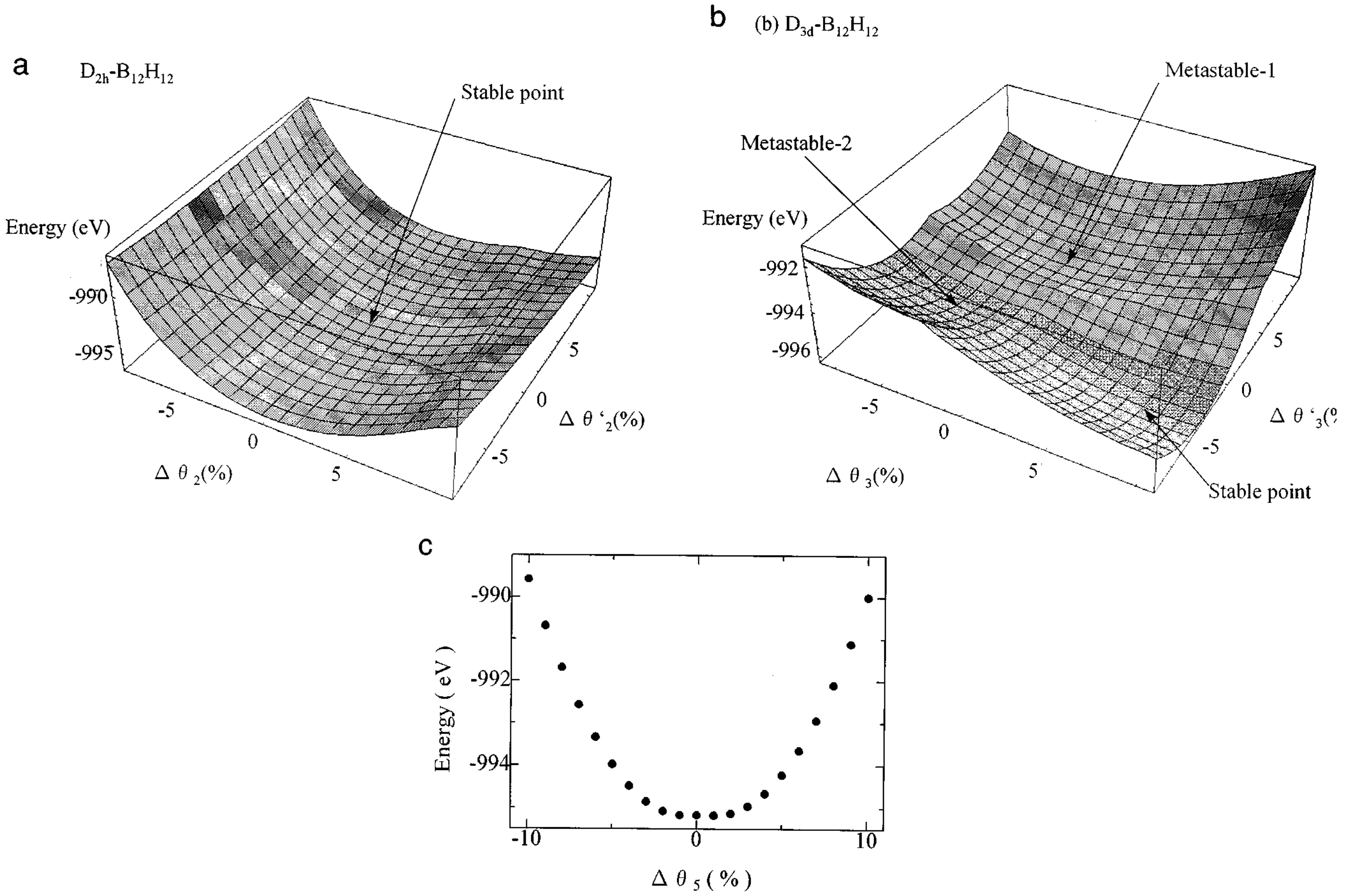

FIG. 2. Total energy surfaces calculated by the semiempirical method. Both x and y axes are graduated in deviation from ideal icosahedral values by percentage. (a) D_{2h}; only one minimum is present. θ'' is fixed at an appropriate value. (b) D_{3d}; two metastable minima, Metastable-1 and Metastable-2, are present besides global minimum (Stable). (c) D_{5d}; only one minimum is present.

roughly positioned at 1.5–2 eV. In the most stable structure, therefore, the B_{12} clusters of both symmetries have no low excited state corresponding to the intrinsic acceptor levels in β-boron.

TABLE 1
Values Optimized by the *ab Initio* SCF-MO Method for Each Symmetric $B_{12}H_{12}$ Cluster

	r(Å)	r' (Å)	θ_i (deg)	θ'_i (deg)	i
T_h	1.75	—	57.5	—	2
Ideal value	—	—	63.4	—	2
D_{3d} Stable	1.76	1.74	41.1	75.8	3
D_{3d} Metastable-1	1.75	1.72	41.2	78.8	3
D_{3d} Metastable-2	1.76	1.73	35.1	76.3	3
Experiment[a]	1.69	1.67	37.6	79.1	3
Ideal value	—	—	37.4	79.2	3
D_{5d}	1.47	1.76	63.9	—	5
Ideal value	—	—	63.4	—	5

[a] Ref. (11).

Note. Corresponding values for ideal I_h symmetry and D_{3d} symmetry (experimentally, in β-boron) are also shown.

In the D_{3d}–$B_{12}H_{12}$ cluster, there are two metastable energy minima, Metastable-1 and Metastable-2, besides the most stable minimum (shown in Fig. 2b). We also performed CI calculations on the minima. Resulting energy spectra are shown in Fig. 4 for Stable, Metastable-1, and Metastable-2. The first excited state of Metastable-2 is considerably lowered, but it is higher than the experimental energy gap of 0.2 eV between the intrinsic acceptor levels and the valence band edge of β-boron. On the other hand, the first excited state of the Metastable-1 persists at nearly 2 eV. The CI

TABLE 2
Total Energy of $B_{12}H_{12}$ Clusters

	Energy (eV)
T_h	− 8247.8
D_{3d} stable	− 8247.7
D_{3d} metastable-1	− 8245.1
D_{3d} metastable-2	− 8247.1
D_{5d}	− 8244.8

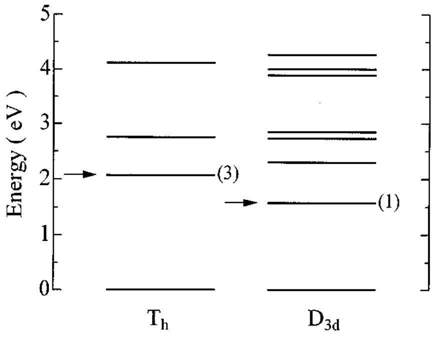

FIG. 3. Energy spectra calculated by the CI method on Stable structures for T_h– and D_{3d}–$B_{12}H_{12}$ clusters. Only nine lower excited states including degeneracy are shown in the figure. Arrows and parentheses indicate the first excited state and the degeneracy of that, respectively. Energy of the first excited state is nearly at about 1.5–2.0 eV.

method provides an exact result in principle if both numbers of the basis functions expanding a molecular orbital and of the Slater determinants making a linear combination of a wave function of a system are infinite. Actually, however, only a finite number are available in a real calculation. Estimation of the value obtained by such an ideal CI calculation by calculating the energy dependence of CI space size is possible to a certain extent. Such a calculation reveals that the energy of the lowest excited state decreases for the Metastable-2 with increasing CI size, though those of Stable and Metastable-1 remain constant. Thus the lowest excited state on the Metastable-2 is probably lowered in ideal CI calculations likely to closer to the ground state.

If the structures of the D_{3d}–B_{12} cluster in β-boron are randomly distributed among the three minima discussed previously, the lowest excited state of the Metastable-2 must be localized due to its randomness of structure distribution and its small density of states. On the other side, there are the states at about 1.5–2.0 eV corresponding to the conduction band edge of β-boron in all the $B_{12}H_{12}$ cluster including Metastable-2. Thus the states can be expanded states even if the cluster shape is randomly distributed in the minima. We therefore suggest that the random distribution of geometry for the B_{12} cluster is the origin of localization for the intrinsic acceptor levels.

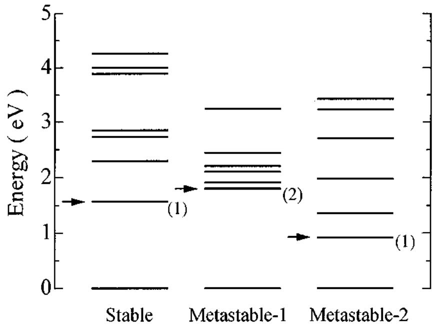

FIG. 4. Energy spectra calculating by CI method on the two metastable structures for D_{3d}–$B_{12}H_{12}$ clusters (Metastable-1 and Metastable-2). Only nine lower excited states including degeneracy are shown in the figures. Arrows and parentheses indicate the first excited state and the degeneracy of that, respectively. For Metastable-2, energy of the first excited state is considerably lowered less than 1.0 eV.

CONCLUSION

There are two kinds of symmetry for the shape of B_{12} clusters in β-boron, D_{2h} at the edge centers and D_{3d} at the vertex of the rhombohedral unit cell. The former has only one stable geometry but the latter has two metastable structures besides the most stable one. The energy of the first excited states for all the structures at the minima is nearly 2 eV except for one metastable structure of D_{3d} symmetry. Though these values correspond to the experimental energy gap, the value for the other metastable structure is considerably lowered. Since the shape of the B_{12} cluster with D_{3d} symmetry could be randomly distributed among the three atomic configurations in β-boron, the origin of localization for the intrinsic acceptor level is attributed to this random distribution of the lowest excited states on one of the metastable structures.

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REFERENCES

1. H. Werheit, *Phys. Status Solidi* **39,** 109 (1970).
2. A. Hori, K. Kimura, T. Tada, and H. Yamashita, *J. Non-Cryst. Solids* **153/154,** 308 (1993).
3. M. Takeda, K. Kimura, and K. Murayama, *J. Non-Cryst. Solids* **198–200,** 170 (1996).
4. H. Matsuda, T. Nakayama, K. Kimura, Y. Murakami, and H. Suematsu, *Phys. Rev. B* **52,** 6102 (1995).
5. H. Werheit, A. Hausen, and H. Binnenbruck, *Phys. Status Solidi B* **51,** 115 (1972).
6. R. Franz and H. Werheit, *Europhys. Lett.* **9,** 145 (1989).
7. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupus, and J. A. Montgomery, *J. Comput. Chem.* **14,** 1347 (1993).
8. J. J. P. Stewart, "MOPAC 93.00 Manual." Fujitsu, Tokyo, 1993.
9. The hessian matrix is the second derivative of energy with respect to nuclear coordinates, so that eigenvalues of the matrix are directly related to the force constant of the atomic vibrations of a system. Thus the geometry is at a minimum when all eigenvalues of the matrix are positive.
10. See, for example, A. Szabo and N. S. Ostlund, "Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory," Chap. 4. Macmillan, New York, 1982.
11. A. Slack, C. I. Hejna, M. F. Garbauskas, and J. S. Kasper, *J. Solid State Chem.* **76,** 52 (1988).