

substance: boron compounds, general properties

property: structure and chemical bond of icosahedral boron-rich structures

B₁₂ icosahedra

The icosahedra are the structural units of many boron-rich solids – boron modifications and boron compounds as well – and determine their properties decisively. They are periodically arranged in the crystalline structures, where the outer bonds of the icosahedra are usually stronger than the intra-icosahedral bonds, and therefore these structures are qualitatively different from molecular crystals. Sometimes they are denoted as inverse molecular crystal structures. However, this description is questionable because new calculations [99K] have proved that the intericosahedral bond strengths are weaker than the intraicosahedral ones, in spite of the intericosahedral B–B distances being shorter than the intraicosahedral B–B distances.

Apparent similarities of some properties to those of amorphous semiconductors sometimes misled to the conclusion that they could be attributed to this kind of semiconductors. However, it seems proved that the icosahedral boron-rich solids form particular electronic properties, which result from the translation symmetry of the icosahedral clusters. Electronic properties of the icosahedra in [55L, 81B, 89H, 90L, 94S]. The icosahedra are distorted in consequence of the Jahn-Teller effect [90F, 90W, 91F], which leads to a separation of occupied and unoccupied orbitals and was assumed to be the reason that these materials are semiconductors. The electronic structures of these solids are narrowly related. For details of the different models, which are presently in discussion to describe the properties of the icosahedral boron-rich solids, see "Boron" in Landolt-Börnstein Volume III/41C.

All the theoretical calculations and assumptions on the electronic band structures and densities of electronic states, which were hitherto performed, were based on idealized structures, which means that all the atomic sites were assumed to be completely occupied. In reality, at least in many of the icosahedral boron-rich structures this is not the case. A quantitative estimation has shown that there is a clear correlation between the concentration of structural defects and the density of electronic states in the band gaps of these semiconductors. This leads to the following assumptions [98S, 99S]:

1. The high densities of the experimentally proved intrinsic states in the band gaps of icosahedral boron structures are essentially evoked by structural defects.
2. The semiconducting character at least of β -rhombohedral boron and boron carbide and probably of other icosahedral boron-rich solids as well originates from the generation of localized states in the band gap, which are caused by structural defects. These localized states compensate the deficiency of electrons in the valence band of the ideal crystals.
3. These intrinsic structural defects are essentially not caused by insufficient preparation methods of the crystals but originate from the energetically more favorable configuration compared with the ideal structures, when the electron deficiencies in the valence band are compensated.

Indeed, these assumptions require further verification, in particular by detailed calculations of the electronic properties of the well-known structural defects.

More or less isolated B₁₂ icosahedra have become available in B-doped Si [93M, 98Y]. The dynamical properties of these impurity clusters are investigated in [98Y].

Calculated vibrational frequencies of the icosahedral B₁₂ cluster in Si [98Y].

Irreducible representations in the T symmetry (all modes are Raman active, Only the T mode is IR active) and frequencies (in cm⁻¹)

reps.	T	E	E	T	T	T	A	T	T	E	A	T
ν/c	324	524	573	654	673	733	776	787	792	798	915	924

Comparison of the calculated and the measured IR spectrum in Fig. 1 [98Y].

References:

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Fig. 1.

B_{12} icosahedron. IR vibration spectrum and density of states vs. wavenumber. Dashed line; experimentally obtained IR absorption spectrum; solid line, calculated density of states for the B_{12} icosahedron [98Y].

