Icosahedral boron-rich solids

The unusual three-center bonding and unique crystal structures of these refractory materials produce many exceptional properties: Some compounds are, for example, very high-temperature thermoelectrics.

David Emin

Boron-rich molecules and solids hold a special place within chemistry. They do not follow the general bonding rules we are taught in chemistry classes. For example, some boron-rich solids are composed of 12-atom clusters of boron atoms in which each boron atom resides on a vertex of an icosahedron. These solids are very stable refractory materials with melting temperatures up to 2400 °C—a thousand degrees greater than silicon's. Beyond this, they possess numerous novel structural, electronic and thermal properties that are not only interesting but useful.

The icosahedral boron-rich solids do not fall into an established category of solids; rather, they constitute a novel class, which I call "inverted molecular solids." The basic structure can accommodate a variety of other constituents. Depending on the minority constituents, these icosahedral boron-rich solids range from conductive materials (such as the boron carbides $B_{1-x}C_x$) to insulators with wide energy gaps (such as icosahedral boron phosphide, $B_{12}P_2$). The boron carbides are the best studied of these materials. They display an amazing array of "anomalies" in their electronic, magnetic and thermal properties. In fact, their unexpected features have already suggested applications of the boron carbides as very high-temperature thermoelectric materials (usable up to roughly 1800 K). In general, the distinctive features of the icosahedral boron-rich solids suggest that they will have other novel applications.

David Emin is a Distinguished Member of the Technical Staff in the solid-state theory division of Sandia National Laboratories.

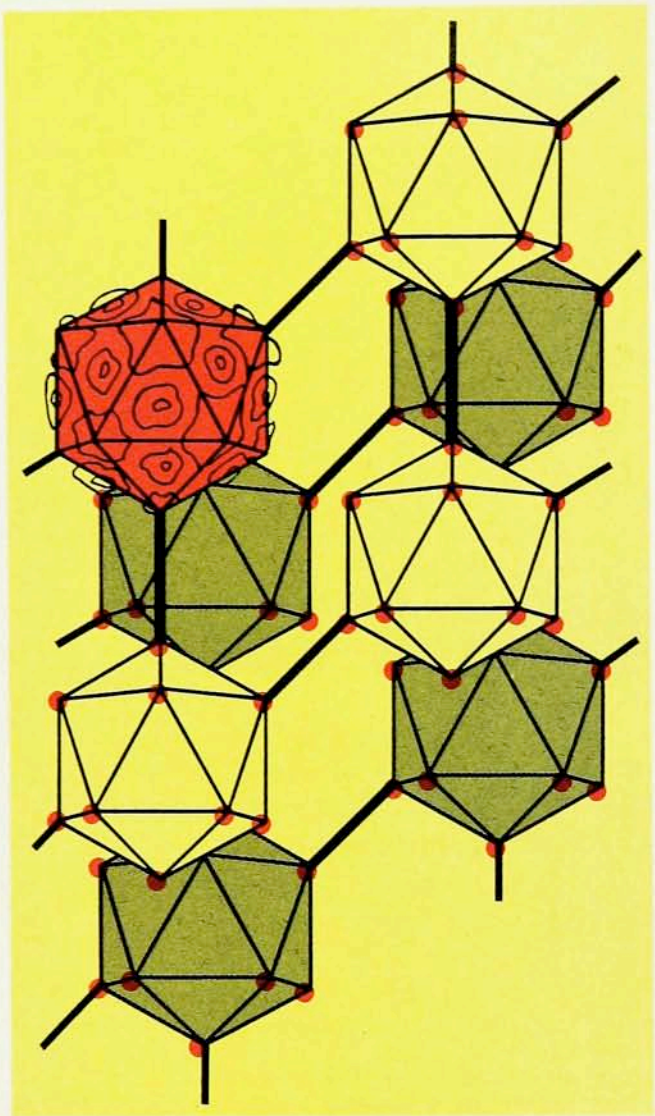
Structure and bonding

In this article I will concentrate on the icosahedral boron-rich solids that are based on the insulator α-rhombohedral boron (figure 1). The basic unit cell, as determined by x-ray crystallographic studies, is a rhombohedron; at each vertex of the rhombohedron is an icosahedral structural unit composed of 12 boron atoms, one occupying each vertex of the icosahedron. Six of these atoms (in two groups of three mutually adjacent atoms) are directly bonded to atoms of the six neighboring icosahedra.

Each boron atom has five neighboring atoms within the icosahedron. Thus, in terms of conventional (two-center) covalent bonding, each boron atom must supply five electrons toward the creation of bonds to each of the five neighboring atoms on the icosahedron. However, each boron atom has no more than the three valence electrons from the second shell available for bonding. Indeed, some electrons are required for bonding among icosahedra, so fewer than three electrons per atom are available for bonding within icosahedra. Thus, the internal bonding of the icosahedron cannot be based on the usual two-center bonding scheme.

Within each icosahedron there are at most 36 electrons (3 valence electrons from 12 atoms) available for bonding; on the other hand each atom provides four orbitals that may be used in bonding, so there are 48 bonding orbitals in the icosahedron. Chemists refer to such a structure as "electron deficient." A key element to understanding the electron-deficient bonding within the boron icosahedra is the "three-center bond," illustrated in figure 2, in which a pair of electrons is shared among three atoms.[1] In a conventional two-center bond, the bonding pair of electrons resides in an orbital that can

0031-9228 / 87 / 0100 55- 08 / $01.00



Structure of α-rhombohedral boron. Boron atoms are located at each vertex of the icosahedra, and icosahedra are bound to their neighbors by six two-center bonds, as shown, forming a rhombohedral lattice.[15] The contours in the icosahedron at upper left show the electron density. Figure 1

be located mostly between the pair of bonded atoms, while in the three-center bond the pair resides in the midst of the three atoms that are being bonded. The peaking of the electron density within the triangular faces of the icosahedra demonstrates the primacy of three-center bonding in intraicosahedral bonding of α-rhombohedral boron. (See the box on page 60.)

Three-center bonding occurs in molecules of light elements of the first three groups of the periodic table. The small interatomic separations in such molecules enhance the stability of three-center bonds. Indeed, the extraordinary strength and very high melting temperatures of the icosahedral borides attest to the strength of their three-center bonding. However, the three-center bonded materials that involve lighter atoms than boron, such as beryllium, do not have enough electrons available for forming intericosahedral covalent bonds. Atoms heavier than boron are also larger, and the resulting larger interatomic separations prevent their forming strong three-center bonds. Boron-rich solids are thus very distinctive, and perhaps unique, in forming strong covalent materials with structural units based on three-center bonding.

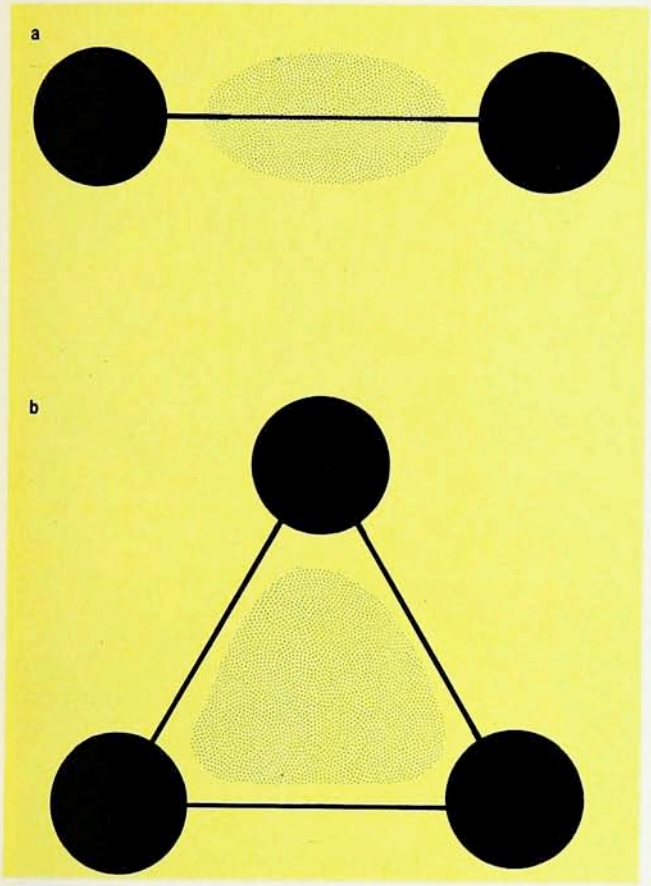
I stress that the icosahedral boron-rich solids are not molecular solids, that is, solids composed of weakly bound molecular units: The bonding between the icosahedral units is generally at least as strong as that within the icosahedra. Thus, unlike molecular solids, the properties of the icosahedral units can be strongly dependent on the intericosahedral separation and intericosahedral constituents. To emphasize this point, I term these materials "inverted molecular solids."

Electronically versatile

The electronic properties of α-rhombohedral boron can be significantly altered by the addition of other atomic constituents. The icosahedral boron pnictides, $B_{12}P_2$ and $B_{12}As_2$, and the boron carbides are examples.

In the icosahedral boron pnictides (figure 3), two pnictide atoms are placed in the middle of the rhombohedron, surrounded by the icosahedra of boron atoms, and bound to each other in a two-membered chain (P_2, for example). Each pnictide atom is bound to three adjacent icosahedra by three two-center bonds; each of these replaces a three-center bond between the icosahedra.

Replacing a pair of intericosahedral three-center bonds by a two-atom pnictide chain that is two-center bonded to the six surrounding icosahedra requires an additional ten electrons: The two-center bonding of the pnictide chain to the six icosahedra requires 14 electrons, two electrons for each of the seven bonds, whereas the two eliminated three-center intericosahedral bonds required a total of four (2×2) electrons. With each pnictide contributing its five second-shell electrons, the pnictide atoms provide the required electrons.



Bond types. The colored regions show (roughly) the dominant parts of the electronic charge distributions of a two-center bond (**a**) and a three-center bond (**b**). Figure 2

Thus, as with α-boron, the bonding orbitals are exactly filled and the icosahedral boron pnictides are insulators.

Because these materials are inverted molecular solids, the addition of the pnictide atoms to α-boron causes a substantial deformation of the boron icosahedra. As a result, the energy gap between the valence and conduction bands rises[2] from about 2 eV in α-boron to about 3.3 eV and 3.5 eV in $B_{12}P_2$ and $B_{12}As_2$, respectively. Although the addition of the pnictide chains provides extra electronic states, it increases the energy gap of α-boron.

The boron carbides apparently exist as single-phase materials for carbon concentrations ranging from below 10% up to 20%. Like the boron pnictides, they are also based on the α-boron structure, but with a three-atom chain of smaller atoms replacing the two-atom chain of pnictides. Depending on the composition, one, two or all of the atoms in the chain may be carbon atoms—forming CBB, CBC and CCC chains (figure 4). In addition, a carbon atom may replace a boron atom within an icosahedron. It is this latitude in carbon location that accounts for the broad, continuous range of boron carbide compositions.

It is now widely believed that the ideal uppermost concentration, B_4C, corresponds to $B_{11}C$ icosahedra linked by CBC chains, that is, three-atom chains with a boron atom sandwiched between two carbon atoms. The icosahedral carbon atom is distributed among many, if not all, icosahedral positions. At this composition all of the bonding orbitals should be filled.

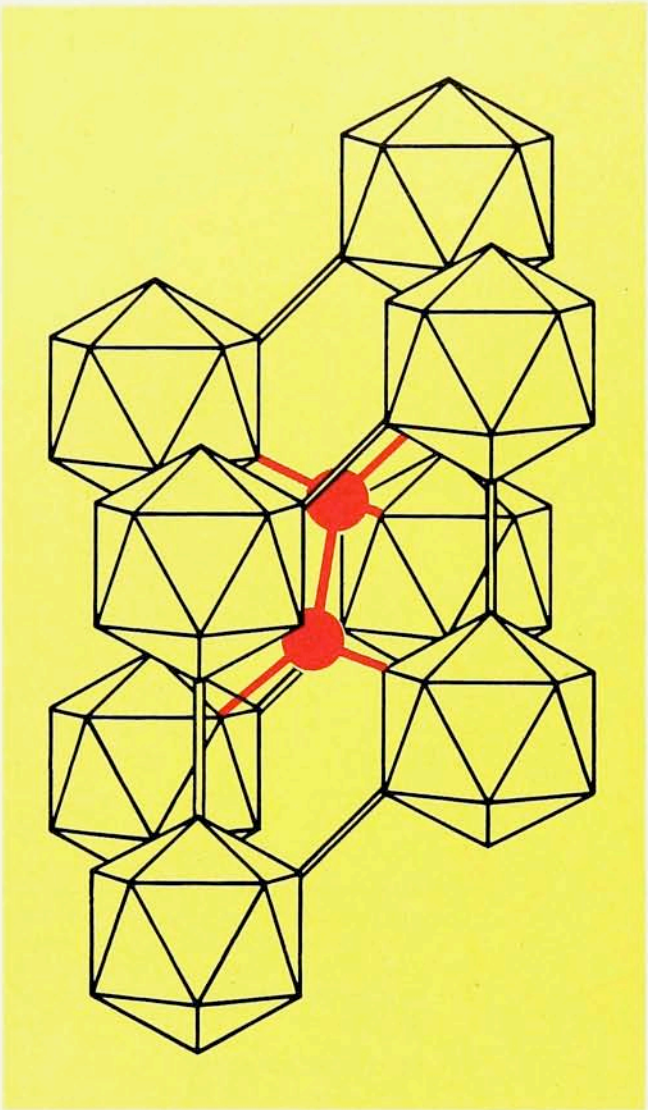
With a lower carbon concentration (or some singly ionized carbon in the middle position of the chain), the highest-energy icosahedral bonding orbitals are not completely filled, so that there are charge carriers on the icosahedra. The carrier density can be altered by varying the carbon concentration and location.

Distinctive transport

Electronic transport measurements on the boron carbides show dramatically the novelty of these materials. Indeed, the distinctive electronic transport can be understood as a direct manifestation of the atypical structure and bonding of icosahedral boron-rich solids.

I first list some of the distinctive electronic properties.

Measurements[3] of the electrical conductivity and Hall mobility indicate that charge transport occurs via intericosahedral hopping of low-mobility p-type charge carriers that have a nearly temperature-independent density on the order of 10^{21} cm^{-3}. As figure 5 shows, the Hall mobility and dc conductivity both tend to rise with temperature. These results suggest that the electrical transport is due to small polarons. (See my article in PHYSICS TODAY, June 1982, page 34.) In fact, the temperature variation of the Hall mobility and dc conductivity is consistent with thermal activation, and the activation energies are in accord with the theory of small-polaron hopping. In this case, unlike in cases where the



Boron phosphide, $B_{12}P_2$. The structure of icosahedral boron phosphide is much like that of α-boron (figure 1), but has two-atom chains of phosphorus atoms (red) lying within the rhombus, connected to six B_{12} icosahedra by two-center bonds. Figure 3

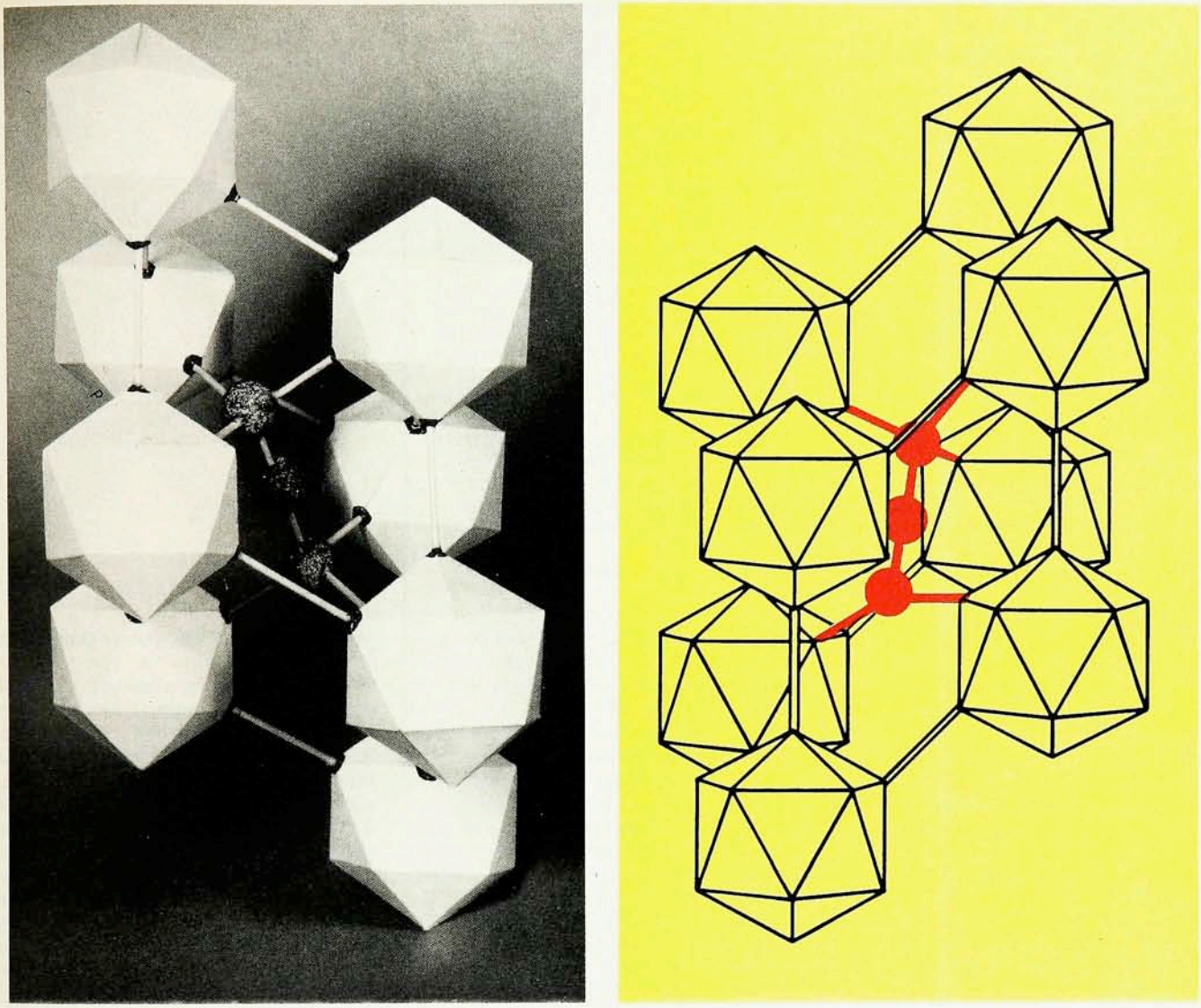
mobilities are much larger than 1 cm^2/V sec, one envisions a charge carrier to be confined at an icosahedral site and to move to another site only when the vibratory excursions of the atoms surrounding the carrier result in an appropriate atomic configuration.

Despite the high density of charge carriers, magnetic measurements detect only a relatively small density of spins: Both magnetic susceptibility and electron spin resonance measurements observe[4,5] a temperature-independent spin density of only 10^{19} cm^{-3}, two orders of magnitude smaller than the carrier density obtained from the electronic transport measurements. Apparently the charge carriers are spinless!

The electronic charge carriers in the boron carbides are singlet small bipolarons—pairs of electrons with oppositely aligned spins that are bound together by the atomic displacements their presence induces (see the box on page 61). These charge carriers hop between icosahedra. Uniquely, the hopping conductivity *decreases* with the application of hydrostatic pressure.[6] In addition, disorder associated with deviations of the lattice from ideal crystalline periodicity leads to an extraordinary increase in the Peltier coefficient, the heat transported with each carrier.[7–9]

Electronic charge carriers can be spinless if electrons bind together in singlet pairs. The Coulomb repulsion of electrons precludes such a circumstance in free space. However, in condensed matter the additional forces associated with the atomic displacements induced by electrons favor the pairing of electrons. (This phenomenon has a familiar macroscopic analog: Bodies on a mattress cause a depression, which favors the bodies' clustering together.) Nonetheless, the pairing of electrons is rarely seen in condensed matter. This is because the Coulomb repulsion associated with placing two electrons on a single atomic site generally overwhelms the attractive forces associated with electronically induced atomic displacements.

The situation in the boron carbides is, however, atypical. There are two factors that favor small-bipolaron formation. First, the sites between which the carrier moves are icosahedra, so that excess charges are distributed over the surface of the 12-atom icosahedron. The Coulomb repulsion between a pair of electronic charge carriers placed on a single icosahedron is considerably smaller than that associated with placing them on a single atom. Second, the attractive force associated with the carrier-induced atomic displacements is larger than in commonly studied solids such as silicon. This is because the exceptionally strong bonding and small atomic radii of boron-rich solids yield especially strong electron–lattice coupling. Thus, the strong icosahedral-based structure of boron carbides provides both the anomalously small on-site Coulomb repulsion and the large



Boron carbide. A three-atom chain replaces the two-atom chain of figure 2. Carbon atoms can occupy one end site, both end sites or all of the sites in the intericosahedral chain, as well as one of the sites within each icosahedron. The photograph shows a model of the structure. Figure 4

electron–lattice interaction required for small-bipolaron formation in solids.

Compaction of a solid generally increases two factors in the hopping mobility: the solid's vibrational frequencies and the electronic overlap between the sites involved in a hop. The application of hydrostatic pressure to a material in which the charge carriers move by phonon-assisted hopping thus generally increases the mobility of the charge carriers, which in turn increases the conductivity. The boron carbides are exceptions to this rule.[6] The conductivity of boron carbides in fact decreases with hydrostatic pressure because an increase in pressure, in addition to increasing the vibrational frequencies and electronic overlap, leads to a significant compression of the icosahedra. This compaction increases the electron–lattice interaction, so that, in turn, the polaronic hopping activation energy increases with pressure. Thus, the decrease of the hopping conductivity with hydrostatic pressure is a direct manifestation of these solids being inverted molecular solids.

Thermoelectric properties. The Peltier heat π can be thought of as the heat transported with a charge carrier as it moves through a material. (The difference in the Peltier heat as the charge carrier jumps from one material to another gives rise to the Peltier effect, a heating or cooling of the junction.) Studies of the Peltier heat in boron carbides have resulted in both important fundamental insights and an unexpected application. In particular, introducing microstructural disorder into boron carbides apparently induces an unexpectedly large increase in the Peltier heat of the charge carriers. These large Peltier heats have made the boron carbides promising materials for thermoelectric-power generation at very high temperatures.

The Peltier heat can be divided into two parts. The first is the product of the temperature T and the change in the entropy of the system associated with the presence of a charge carrier; the second is the heat transferred between sites in the jump process. The second term is potentially important for hops between sites that differ in both energy and electron–lattice coupling strength.[7] Because the energy and effective electron–lattice coupling strength at a site are related, this term rises quadratically with temperature, as an increasing fraction of inequivalent sites become thermally accessible to the charge carrier. In the more frequently measured Seebeck coefficient, or thermoelectric power, π/Tq (q is the charge of the carrier), this

Bonding in α-rhombohedral boron

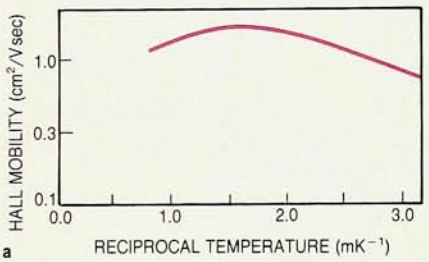
In an elemental three-center bond, the two electrons of the bond reside in the triangle formed by the three atoms that enjoy the three-center bond. With three atoms being bonded by two electrons, one regards each atom as donating two-thirds of an electron toward the three-center bond.

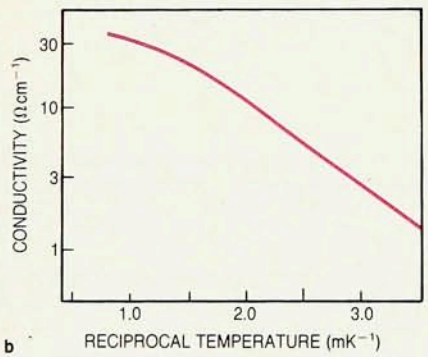
However, the internal bonding of a boron icosahedron is a more complicated matter involving resonant structures (such as occur in the bonding of benzene). It turns out that each of the 20 triangular faces of the boron icosahedron contains even fewer than the two electrons associated with a three-center bond.

As mentioned in the text, each of the 12 boron atoms on the corners of each icosahedron contributes three electrons and four orbitals to the structure. There are 13 intraicosahedral (molecular) bonding orbitals.[14] These accommodate 26 electrons, with 1.3 (26/20) electrons on each triangular face of an icosahedron. The distribution of these electrons is shown in the topological electron-density map of figure 1, drawn from the x-ray diffraction study of reference 15.

The remaining ten electrons of the 12 boron atoms are used for intericosahedral bonding. Six of these are used in the two-center bonds to other icosahedra shown in figure 1. In addition, the other six atoms of the icosahedron are involved in intericosahedral three-center bonds. This requires $6 \times \frac{2}{3}$, or 4, electrons.

Thus, with 26 electrons used in intraicosahedral bonding, 6 electrons used for two-center intericosahedral bonding, and 4 electrons involved in three-center intericosahedral bonding, all 36 valence electrons of the boron atoms are engaged in bonding. As a result α-rhombohedral boron is an insulator.





Electrical properties. The graphs show the Hall mobility (**a**) and the electrical conductivity (**b**) of the boron carbide B_4C as a function of reciprocal temperature.[3] Note that as the temperature rises both quantities rise in a thermally activated manner, that is, as roughly exponential functions of $1/T$; this is consistent with a conduction mechanism of small-bipolaron hopping. Figure 5

"extra" term increases linearly with temperature.

When a current flows through a boron carbide, the bipolaronic charge carriers hop between icosahedra. If these icosahedra are in different environments they become inequivalent in energy and in electron–lattice coupling strength, so that crystallographic defects, for example, should affect the crystal's thermoelectric properties. Twin boundaries—that is, boundaries between regions of perfect crystallinity with mirror-image orientations—produce just such inhomogeneities without any other distracting effects. In addition, twin boundaries in boron carbides are directly observable with a high-resolution electron microscope.[8]

Seebeck coefficients measured for highly twinned boron carbide samples differ[3,9] markedly from that of an untwinned sample (see figure 6). The Seebeck coefficient of the twinned material manifests a large contribution that increases linearly with temperature—a contribution attributable to the twin boundaries, that is, to the disordering of the lattice of icosahedra. The boron carbides thus provide us with systems in which site disorder can be directly correlated with its effects on electronic transport.

Furthermore, the 20-fold increase of the Seebeck coefficient at 1000 °C induced by a high density of twin boundaries has a practical use. It alone raises the efficiency of boron carbides for use in thermoelectric-power generation by the square of this factor, 400. This simple microstructural modification converts boron carbides from very poor materials for thermoelectric energy conversion to exceptionally good ones. The relatively high efficiency of boron carbides as thermoelectrics, coupled with their refractory character, opens the possibility of using boron carbides within a nuclear reactor to convert the reactor's heat directly to electricity. Such a scheme has been suggested for electric-power generation in space.

In the currently available range of compositions, changing the carbon concentration in the boron carbides does not qualitatively affect the electronic transport, because the process responsible for the transport—the hopping of bipolarons between icosahedra of comparable, albeit often different, energies—is apparently not sensitive to the compositions of the chains between the icosahedra. Thermal transport, however, appears to be quite sensitive to the carbon concentration. The high-temperature thermal conductivity changes qualitatively,[10] from behavior characteristic of a crystal to the temperature-independent behavior that is characteristic of glasses, when the carbon concentration is significantly reduced below its maximal value of 20%. This effect appears to be due to a vibrational disordering of the crystal structure as the carbon concentration is reduced: The relatively stiff CBC intericosahedral chains may be randomly replaced in the crystal by much softer CBB chains.

It thus appears that electronic and thermal transport are decoupled from one another. Electronic motion is determined by the properties of the icosahedra, while thermal transport depends on the composition of the intericosahedral chains. Here again, the novel structure of the icosahedral boron-rich solids is manifesting itself.

Prospects

I have described the electronic properties of the boron carbides because they are the most thoroughly studied icosahedral boron-rich solids; this re-

view can only illustrate the distinctive bonding and structures of boron-rich solids in general. It must be emphasized that other icosahedral boron-rich solids can have quite different electronic and optical properties. For example, while the boron carbides are conductors with low carrier mobilities (far below 1 cm^2/V sec at 300 K), α-boron is an insulator with a 2-eV gap and relatively high hole mobilities (in excess of 100 cm^2/V sec at room temperature in small-grain polycrystalline samples).[11] And, as I have mentioned, the icosahedral boron pnictides, $B_{12}P_2$ and $B_{12}As_2$, are insulators with significantly larger energy gaps—3.3 eV and 3.5 eV, respectively.

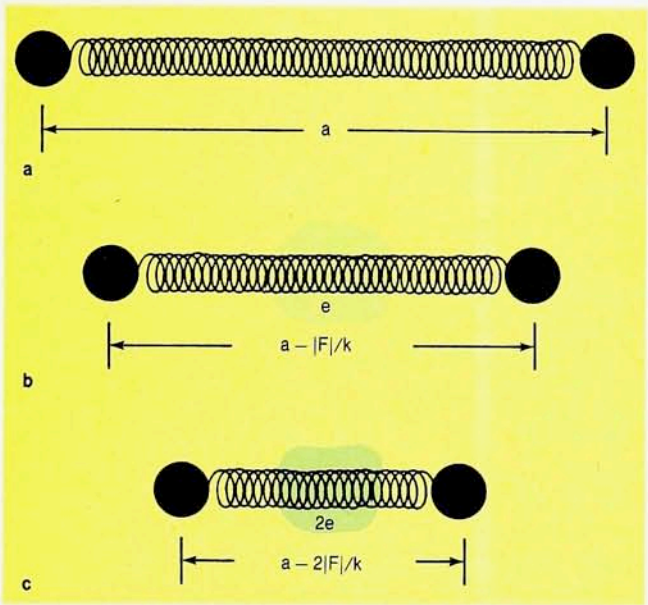
The icosahedral boron-rich solids present us with opportunities both for enhancing our basic understanding of solids and for exploring novel technologies. The following questions illustrate the wide range of fundamental issues that may be elucidated by examining these exceptional materials:

▶ What is the effect of disorder on the nature of the charge carriers? Is it the disorder inherent in their crystal structure that causes boron carbides to have charge carriers that form bipolarons, which move via low-mobility hopping, rather than having the high-mobility carriers one sees in α-boron?

▶ What is the effect of a disordered bonding arrangement on thermal conductivity? Perhaps the range of structures of the icosahedral boron-rich solids will permit a systematic and controlled approach to this question.

▶ Can bipolarons form a superconducting state? The boron carbides may provide us with a system in which to confirm the longstanding prediction of

Small-bipolaron formation



Consider a single diatomic molecule that is one unit of a molecular solid. The potential energy of the molecule obeys Hooke's law:

$$V = k(x - a)^2/2$$

where x and a are the instantaneous and equilibrium values of the interatomic separation and k is the spring constant (**a**).

The energy of a bonding electron added to the diatomic molecule depends on the interatomic separation of the molecule. This represents the electron–lattice interaction. In the simplest case the energy of the added electron depends linearly on the interatomic separation:

$$\mathscr{E} = -Fx$$

where F is the force the electron exerts on the molecular spring. In our example F is negative.

The presence of the electron shifts the equilibrium separation of the molecule from a to $a - |F|/k$ (**b**). In general, the unit comprising a bound carrier (here, an electron) and the atomic distortion it induces is termed a "polaron." If, as in our example, the distortion is confined to a single structural entity (here, one molecule of a molecular solid), the polaron is considered small.

With the shift of the equilibrium interatomic separation, the electron's energy is lowered by F^2/k while the molecule's strain energy is increased by $F^2/2k$. The net reduction of the coupled system's ground-state energy, $F^2/2k$, is the small-polaron binding energy.

Now consider a pair of electrons added to the molecule. Each of the electrons separately senses the diatomic separation, while the electrons experience their mutual Coulomb repulsion. The electronic energy for the pair of electrons is

$$\mathscr{E} = -2Fx + U$$

where U is the electron–electron repulsion energy. If U is independent of x, the addition of a pair of electrons to the molecule results in a shift of the interatomic separation from a to $a - 2|F|/k$ (**c**). Concomitantly, the ground-state energy of the molecule becomes $-2F^2/k + U$.

Finally, consider a molecular solid composed of an array of deformable diatomic molecules. The difference between the ground-state energy of a pair of electrons on a single site and the energy of two electrons on well-separated molecules is the binding energy of a small bipolaron:

$$(-2F^2/k + U) - 2(-F^2/2k) = U - F^2/k$$

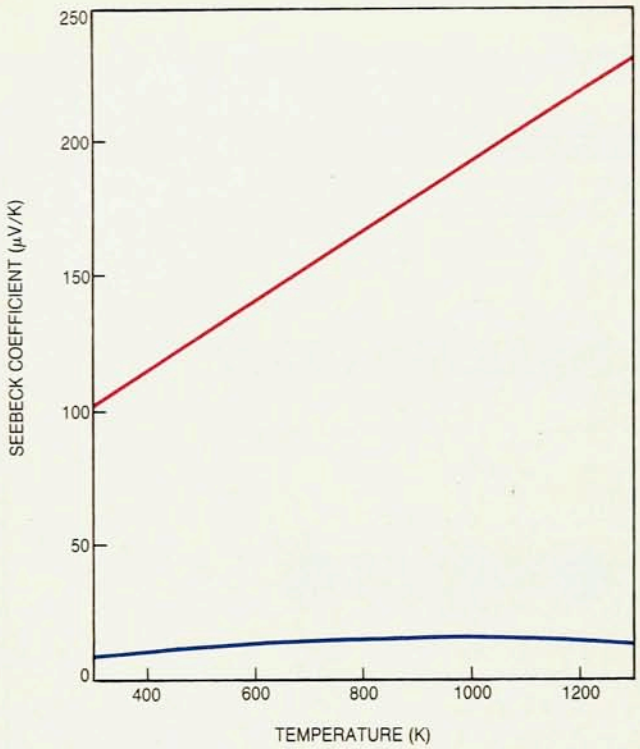
If this energy is negative, the two electrons will find it energetically favorable to pair on a single molecule rather than sit separately on two molecules. Thus, bipolaron formation requires that the attraction produced by the electron–lattice coupling strength overcome the Coulomb repulsion.

In the boron carbides, small-bipolaron formation occurs[16] on icosahedra containing 11 boron atoms and a single carbon atom, $B_{11}C$. The carbon atom contributes a background charge of one proton charge to each icosahedron. In addition, each carbon atom donates an electron to the system. As explained in the text, electron–lattice interactions make it energetically favorable for the two electrons donated by carbon atoms to a pair of $B_{11}C$ icosahedra to sit on a single icosahedron rather than occupy separate icosahedra. That is, bipolaron formation may be represented by

$$2B_{11}C \rightarrow B_{11}C^- + B_{11}C^+$$

Small-bipolaron hopping between icosahedra is then represented by

$$B_{11}C^- + B_{11}C^+ \rightarrow B_{11}C^+ + B_{11}C^-$$



Seebeck coefficient as a function of temperature. The graphs show results measured for samples of a boron carbide with (red) and without (blue) extensive twinning boundaries.[3,9] Figure 6

bipolaronic superconductivity.[12,13]

At present, the boron carbides have found application in armor and as neutron absorbers. These uses exploit only their refractory character, their robustness and the neutron-absorbing capability of B^{10}.

One immediate example of the exceptional technological potential of the boron-rich materials is the promise of the boron carbides as very high-temperature thermoelectrics. This application would exploit some of their distinctive electronic and thermal properties.

Beyond this, the large energy gaps and refractory character of the icosahedral boron-rich pnictides suggest a potential for use as very high-temperature semiconductors. These may be obtained by introducing localized states within the wide gap of the icosahedral boron pnictides. Such states could be introduced by replacing an intericosahedral pnictide atom with an element from another column of the periodic table: Elements from group VI, such as sulfur, would become donors, while group IV elements, such as silicon, would be acceptors. The dopants will be in states with low symmetry. Will they produce spatial and energetic distributions of gap states useful for electronic and optical applications?

If it indeed turns out to be possible to make doped boron pnictides with suitable properties, one can envision placing electronic or optical devices in such hostile environments as engines, turbines and nuclear reactors. But such applications will require producing materials of highest quality with controlled doping.

The message of this article is clear. The distinctive bonding of the icosahedral boron-rich materials leads to the formation of exceptional structures—refractory solids with a wide range of exceptional thermal, electronic and transport properties. We are only beginning to understand and exploit them.

* * *

This work has been supported by the US Department of Energy under contract number DE-AC04-76DP00789.

References

1. W. N. Lipscomb, *Boron Hydrides*, Benjamin, New York (1963).
2. G. A. Slack, T. F. McNelly, E. A. Taft, J. Chem. Phys. Solids **44**, 1009 (1983).
3. C. Wood, D. Emin, Phys. Rev. B **29**, 4582 (1985).
4. L. J. Azevedo, E. L. Venturini, D. Emin, C. Wood, Phys. Rev. B **32**, 7970 (1985).
5. E. L. Venturini, L. J. Azevedo, D. Emin, C. Wood, in *Boron-Rich Solids* (AIP Conf. Proc. 140), D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, C. Wood, eds., AIP, New York (1986), p. 292.
6. G. A. Samara, D. Emin, C. Wood, Phys. Rev. B **32**, 2315 (1985).
7. D. Emin, Phys. Rev. Lett. **35**, 882 (1975).
8. I. D. R. Mackinnon, T. Aselage, S. B. Van Deusen, in *Boron-Rich Solids* (AIP Conf. Proc. 140), D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, C. Wood, eds., AIP, New York (1986), p. 114.
9. C. Wood, in *Boron-Rich Solids* (AIP Conf. Proc. 140), D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, C. Wood, eds., AIP, New York (1986), p. 206.
10. C. Wood, D. Emin, P. E. Gray, Phys. Rev. B **31**, 6811 (1985).
11. O. A. Golikova, Phys. Status Solidi A **86**, K51 (1984).
12. M. R. Schafroth, J. M. Blatt, S. T. Butler, Helv. Phys. Acta **30**, 93 (1957).
13. A. Alexandrov, J. Ranninger, Phys. Rev. B **24**, 1164 (1981).
14. H. C. Longuet-Higgens, M. de V. Roberts, Proc. R. Soc. London, Ser. A **230**, 110 (1955).
15. B. Morosin, A. W. Mullendore, D. Emin, G. A. Slack, in *Boron-Rich Solids* (AIP Conf. Proc. 140), D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, C. Wood, eds., AIP, New York (1986), p. 70.
16. D. Emin, in *Boron-Rich Solids* (AIP Conf. Proc. 140), D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, C. Wood, eds., AIP, New York (1986), p. 189. □