

Available online at www.sciencedirect.com



JOURNAL OF SOLID STATE CHEMISTRY

Journal of Solid State Chemistry 179 (2006) 2791-2798

www.elsevier.com/locate/jssc

Unusual properties of icosahedral boron-rich solids

David Emin*

Department of Physics and Astronomy, 800 Yale Boulevard NE (MSC 07 4220), University of New Mexico, Albuquerque, NM 87131, USA

Received 20 August 2005; received in revised form 18 November 2005; accepted 10 January 2006 Available online 8 February 2006

Abstract

Icosahedral boron-rich solids are materials containing boron-rich units in which atoms reside at an icosahedron's 12 vertices. These materials are known for their exceptional bonding and the unusual structures that result. This article describes how the unusual bonding generates other distinctive and useful effects. In particular, radiation-induced atomic vacancies and interstitials spontaneously recombine to produce the "self-healing" that underlies these materials' extraordinary radiation tolerance. Furthermore, boron carbides, a group of icosahedral boron-rich solids, possess unusual electronic, magnetic and thermal properties. For example, the charge carriers, holes, localize as singlet pairs on icosahedra. The unusual origin of this localization is indicated by the absence of a concomitant photo-ionization. The thermally assisted hopping of singlet pairs between icosahedra produces Seebeck coefficients that are unexpectedly large and only weakly dependent on carrier concentration. These properties are exploited in devices: (1) long-lived high-power high-capacity beta-voltaic cells, (2) very high temperature thermoelectrics and (3) solid-state neutron detectors. (1) long-lived high-power high-capacity beta-voltaic cells, (2) respectively.

Keywords: Icosahedral boron-rich solids; Boron carbides; Self-healing; Radiation damage; Beta-voltaic; Seebeck; Thermoelectric; Softening; Singlet bipolaron; Phonon-assisted hopping

1. Introduction

Icosahedral boron-rich solids are known for their unusual structure and bonding. However, these features also underlie other distinctive properties of icosahedral boron-rich solids. Here several unexpected properties of these solids are described. The manner in which these unusual properties emerge from distinctive features of the structure and bonding of icosahedral boron-rich solids is emphasized. Finally, several practical applications that exploit these exceptional properties are described.

2. Structures and bonding

Boron-rich solids are materials with boron as their primary atomic constituent. Icosahedral boron-rich solids are boron-rich solids based on 12-atom clusters in which atoms occupy the 12 vertices of an icosahedron.

E-mail address: emin@unm.edu.

Some of the distinctive features of the bonding of icosahedral boron-rich solids are evident even in the bonding of the icosahedral borane molecule, $B_{12}H_{12}$. This molecule has each atom of its boron icosahedron covalently bonded to an "external" hydrogen atom. As is evident from Fig. 1, each boron atom of the borane molecule is in six-fold coordination. That is, each boron atom has five neighboring boron atoms plus the hydrogen atom to which it is bonded. This coordination is unusual as a boron atom is a group IIIA element with a valence of 3. The unusual bonding is evident from X-ray diffraction studies which indicate charge accumulation about the center of the icosahedron's 20 triangular faces rather than along the lines that link adjacent boron atoms [1]. Borane molecules are known to have a strong tendency to garner two additional electrons thereby forming dianions.

These features are not unique to icosahedral borane. The octahedral borane molecule, B_6H_6 , manifests similar features. In particular, a boron atom of octahedral borane is in five-fold coordination. The boron atom has four boron neighbors plus the hydrogen atom to which it is covalently bonded. The bonding electrons of octahedral

^{*}Fax: +1 505 277 1520.

^{0022-4596/\$ -} see front matter \odot 2006 Elsevier Inc. All rights reserved. doi:10.1016/j.jssc.2006.01.014



Fig. 1. An icosahedron of $B_{12}P_2$ is illustrated. The contours depict accumulation of bonding charge on the icosahedron's triangular faces.



Fig. 2. The structure of $B_{12}P_2$ and $B_{12}As_2$ is depicted.

borane are centered on the triangular faces of its octahedron. Octahedral borane molecules also tend to form dianions.

Boron octahedral and icosahedra are essential units of some insulating refractory solids. For example, CaB₆ is an example of a crystal in which divalent cations (e.g., Ca^{2+}) reside at the center of cubes whose corners are occupied by boron octahedra, $(B_6)^{2-}$. A similar structure is found for $B_{12}P_2$, $B_{12}As_2$ and $B_{12}O_2$. In particular, boron icosahedra, nominally B_{12} dianions, are centered at the eight vertices of a rhombohedron while two cations reside along the rhombohedron's longest diagonal, the *c*-axis. As illustrated in Fig. 2, the respective phosphorus and arsenic cations of $B_{12}P_2$ and $B_{12}As_2$ are each bonded to one another and to three adjacent boron atoms. The oxygen atoms of $B_{12}O_2$ are well separated from one another. As such, each oxygen cation just bonds to the three boron atoms to which it is adjacent [2]. Strong covalent bonds link six boron atoms of each icosahedron to boron atoms of neighboring icosahedra. The remaining six boron atoms of each icosahedron bond to the solid's cations.

The bonding associated with these structures is unusual. In particular, each boron atom of an icosahedron participates in the electron-deficient bonding of its icosahedron as well as in covalent bonding to atoms outside of its icosahedron. All of this bonding is primarily attributed to electrons from these boron atoms' second shell. One of the three second-shell electrons is involved in bonding external to the boron atom's icosahedron. The remaining two electrons from a boron atom's second shell participate in the internal bonding of its icosahedron. Thus, 24 electrons (2×12) are available for an icosahedron's internal bonding.

The internal bonding of an icosahedron is associated with electrons whose wavefunctions extend over its surface [3–6]. As such, these electrons occupy molecular orbitals that encompass the icosahedron's surface. Since the icosahedron is a spheroid, the bonding orbitals on its surface reflect its near spherical symmetry. That is, these molecular orbitals possess s-, p-, d- and f-symmetry with respect to the icosahedron's centroid. However, the crystal field of the icosahedron (its departure from being a true sphere) splits high-lying icosahedral orbitals. Thus, the seven orbitals of f-symmetry are split into states that are four- and three-fold degenerate states. Those states with four-fold degeneracy are of lower energy. Occupation of these orbitals places bonding charge about the centers of the icosahedron's triangular faces.

There are a total of 13 bonding orbitals: 1 *s*-orbital, 3 *p*-orbitals, 5 *d*-orbitals and the above-mentioned 4 orbitals of *f*-symmetry. Filling of these bonding orbitals requires 26 electrons (13×2) . Thus, icosahedra tend to garner two electrons, making them dianions. The associated bi-electron affinity is especially strong because the screening of the nuclear charge is relatively weak. In particular, only each boron atoms' two 1*s* electrons intervene between their nuclear charge and the bonding electrons.

Analogous arguments can be used to understand the internal bonding of a boron octahedron [6]. There are 7 internal bonding orbitals for the octahedron: 1 molecular orbital with *s*-symmetry, 3 molecular orbitals with *p*-symmetry and 3 of 5 molecular orbitals of *d*-symmetry. Filling of these 7 bonding orbitals requires 14 (7×2) electrons. However, only 12 electrons (2×6) are available after the external bonding requirements of a boron octahedron are fulfilled. Therefore, a boron octahedron tends to garner two additional electrons to become dianions.

The high melting temperatures of these solids attest to the strength of their internal bonding. However, X-ray diffraction studies indicate that icosahedra deform in order to accommodate two-atom and three-atom inter-icosahedra chains of significantly different lengths: P–P, As–As, O–O, C–B–C, C–B–B and B–B–B [7]. These solids have been termed "inverted" molecular solids to emphasize that the two-center covalent external bonding is often even stronger and stiffer than that within icosahedra [1]. As such, the application of pressure compresses the boron cages fractionally more than the external bonds [8].

3. "Self-healing" of radiation damage in icosahedral boronrich solids

Since icosahedral boron-rich solids are generally very hard solids with high-melting temperatures, they have been utilized in extreme environments. These solids have been observed to survive extremely well in radiation environments.

The observed radiation tolerance of icosahedral boronrich solids has spurred systematic study of these solids' response to irradiation. High-resolution transmission electron microcopy was used to interrogate several icosahedral boron-rich solids (β -rhombohedral boron and boron carbides) during and after heavy bombardments [9-11]. The damage, clustering of defects and amorphization, expected of common semiconductors was not observed even when bombardments were carried out at a very low temperature, $\sim 12 \text{ K}$ [7]. In particular, high-resolution transmission electron micrographs of β rhombohedral boron showed no significant change following very heavy bombardment with nitrogen ions. The observed moderate swelling of the target was attributed to bombarding ions trapped within the β -rhombohedral boron film. By contrast, this bombardment level, 36 displacements per atom estimated from a TRIM calculation, is at least four orders of magnitude greater than is needed to amorphize boron nitride, BN. The absence of damage after such severe bombardment cannot be attributed to displacing some atoms into established interstitial locations.

To probe the cause of the radiation tolerance without implanting ions, several metal diborides, octahedral boronrich solids and icosahedral boron-rich solids were subjected to heavy electron bombardment [12]. The diborides (e.g. TiB_2) and octahedral boron-rich solids (e.g. CaB_6) were heavily damaged within minutes. However, the icosahedral boron-rich solids ($B_{12}P_2$ and $B_{12}As_2$) showed no signs of damage even after much more prolonged bombardment (several hours).

Conservation of energy and momentum ensures that atoms of all of these solids are readily displaced by the heavy energetic bombardments. The absence of radiation damage in icosahedral boron-rich solids must therefore be ascribed to the easy recombination of the radiationinduced vacancies and interstitials. Thus, boron atoms displaced from icosahedra must readily return.

Such a scenario is plausible if an electron from a departing boron atom is retained by the icosahedron from which it is knocked [12]. Then, Coulomb attraction will foster recombination between a departing boron cation and an icosahedron possessing an extra negative charge as a result of its loss of a boron cation. In addition, the very small size of a boron cation should aid its diffusion and thereby facilitate recombination. This view is supported by the observation that icosahedra which are "degraded" by the loss of an atom do indeed garner an extra negative charge [13]. By contrast, octahedra are not known to survive in a degraded state.

The experiments by the Zuppiroli-group indicate remarkable resistance tolerance of icosahedral boron-rich solids [9–12]. To confirm the self-healing that these experiments imply, additional radiation damage experiments on many icosahedral boron-rich solids have been conducted in collaboration with the Ewing-group at facilities at the University of Michigan and at Argonne National Laboratory using samples provided by T.L. Aselage of Sandia National Laboratories. These bombardments employed some heavy ions as well as energetic electrons. As illustrated by the high-resolution transmission electron micrographs shown in Fig. 3, these recent measurements are consistent with self-healing of radiation damage in icosahedral boron-rich solids.



Fig. 3. Very high-resolution transmission electron microscopy shows no damage to $B_{12}P_2$ after an intense bombardment (10^{18} electrons/cm² s) by 400 keV electrons to a net dose of about 10^{23} electrons/cm². The bombardment is more intense than that from undiluted ⁹⁰Sr (10^{12} electrons/cm² s).

4. Beta-voltaic devices with semiconducting icosahedral boron-rich solids

The ability of icosahedral boron-rich solids to survive extensive irradiation can be exploited in various potential applications. One such application could be the development of high-power, long-lived and high-capacity betavoltaic cells.

Beta-voltaic cells were initially developed in tandem with photo-voltaic cells about half a century ago. Photo-voltaic cells are used extensively to convert the power from electromagnetic radiation into electric power. In a somewhat similar manner beta-voltaic cells convert the power of betaparticles generated from radio-isotopes into electric power.

Unlike solar cells (photo-voltaic cells attuned to absorption of solar radiation), beta-voltaic cells do not require an external radiation source. The radio-isotopes that power these devices can be packaged together with the betavoltaic cell to form a self-contained source of electric power. In the absence of degradation, the device provides electric power for the life of the radio-isotope.

Both photo-voltaic devices and beta-voltaic devices utilize the electric field that develops near junctions between materials to separate electron-hole pairs that are generated under irradiation. Whereas absorption of a photon typically generates a single electron-hole pair, an incident energetic beta particle can produce a millimeter long track of 10^5 electron-hole pairs. To capture the energy contained in these pairs beta-voltaic devices employ stacks of junctions. The incident power (W/cm²) from a strong source of beta particles (e.g., 90 Sr) is comparable to that from solar radiation at sea level.

Unfortunately, beta-voltaic devices made with conventional semiconductors tend to suffer very rapid degradation due to radiation damage. In particular, beta-voltaic cells made with silicon and ⁹⁰Sr degrade significantly in a single day, far short of the radioisotope's half-life, 28 years [14,15]. To avoid this degradation, beta-voltaic devices are made with relatively weak radioactive sources. For example, a tritium beta-particle source provides about 1% of the power per atom and about 1% of the net energy capacity per atom as does ⁹⁰Sr. As a result, beta-voltaic cells (as once used in pace makers) have been replaced with long-lived batteries.

The degradation problem can potentially be alleviated by replacing conventional semiconductors with icosahedral boron-rich semiconductors such as doped $B_{12}P_2$ and $B_{12}As_2$ [16]. Indeed, as illustrated in Fig. 3 these semiconductors can sustain far more bombardment without damage than could be produced by even a strong radioisotope.

This replacement, however, is not simple. Beta-voltaic cells operate by the electron-hole pairs generated by incident beta particles being separated by the electric field that exists in the depletion region surrounding a junction with a semiconductor. Efficient, even workable, betavoltaic cells require a significant depletion region. Since the size of the depletion region falls with the carrier density, efficient beta-voltaic devices require a relatively low carrier density. Furthermore, electrons and holes created within the depletion region must be able to diffuse apart before being trapped or recombining. Optimally, the carriers' diffusion length should be comparable to the depth of the depletion region. All told, beta-voltaic cells, like solar cells, require semiconductors with moderate densities of high mobility (>1 cm²/V s) carriers. Fortunately, this situation is thought to exist for holes in B₁₂P₂ and B₁₂As₂; the Hall mobility of B₁₂P₂ at 295 K is reported to be 63 cm²/V s [17].

To date, only p-type $B_{12}P_2$ and $B_{12}As_2$ have been obtained. Indeed, it has been argued that the prevalent defects in simple icosahedral boron-rich semiconductors will render them p-type [18]. Even so, beta-voltaic devices could be based on (Schottky) junctions between p-type icosahedral boron-rich semiconductors and electrical conductors rather than between p- and n-type semiconductors. In any case, a development effort would be required to determine if beta-voltaic devices with these icosahedral boron-rich semiconductors would be viable.

N-type materials can be obtained by heavy incorporation of some transition-metal atoms into β -rhombohedral boron [19]. In addition, some icosahedral boron-rich solids with rare-earth elements (RE) have been reported to be ntype: REB₂₂C₂N and REB₁₇CN [20]. It is unclear if these materials can be made with sufficiently low carrier densities and high enough mobilities to be useful in beta-voltaic cells.

5. 'Boron carbides' electrical properties

Boron carbides are icosahedral boron-rich solids that have been studied very extensively. Insights into a number of fundamental physical phenomena have developed as a result of attempting to understand some of these materials' remarkable properties. In addition, some of boron carbides' distinctive properties have been exploited in devising devices.

Boron carbides are compositionally disordered materials that can exist as a single phase of a wide range of compositions: $B_{12+x}C_{3-x}$ with 0.1 < x < 1.7 [21,22]. The large entropic contribution to the free energy associated with boron carbides' compositional disorder is thought to stabilize the wide single-phase regime of hot-pressed boron carbides [21].

As illustrated in Fig. 4, boron carbides' icosahedra reside at the corners of its rhombohedral cell. Three-atom chains occupy the longest diagonal of each rhombohedron. Compositional disorder occurs as carbon atoms replace boron atoms at a number of locations within this structure. In particular, most icosahedra are thought to contain a single carbon atom. The locations of carbon atoms within different icosahedra are not ordered relative to one another. Thus, icosahedral carbon atoms are distributed among various icosahedral sites. Carbon atoms can also exist within the three-atom inter-icosahedral chains. Three



Fig. 4. The structure of a boron carbide is illustrated.

types of three-atom chain are envisioned: C–B–C, C–B–B and B–B–B. Altering the carbon concentration changes the distribution of three-atom chains. As the carbon concentration is reduced C–B–C chains tend to be progressively replaced by C–B–B chains. Upon lowering the carbon concentration further C–B–B chains are replaced by B–B–B chains.

Since C–B–C and B–B–B chains are envisioned as positively charged while C–B–B chains are neutral, the number of charge carriers, holes, on icosahedra simply equals the number of C–B–B chains [22]. Thus, the carrier density peaks near a carbon concentration of 13 atomic percent where most chains are C–B–B chains.

Despite their high carrier densities, boron carbides manifest the thermally facilitated electronic transport of semiconductors rather than the thermally impeded transport of metals. In particular, the boron carbides' charge carriers localize and move by thermally assisted hopping between icosahedra.

Disorder facilitates the collapse of charge carriers from moving freely ("itinerant" transport) to hopping between severely localized states [23]. Succinctly stated, disorder slows a carrier sufficiently so that atoms can relax about it. This atomic relaxation is associated with "self-trapping," the phenomenon by which a charge carrier becomes bound (trapped) within a potential well produced by atomic displacements that the carrier's presence induces [24]. Thus, carriers in ordered icosahedral boron-rich solids (e.g., $B_{12}P_2$ and $B_{12}As_2$) manifest itinerant transport while carriers in boron carbides move by thermally assisted hopping.

Detailed studies of boron carbides' electronic transport are consistent with expectations from a temperatureindependent high-density of self-trapped holes [22,25]. Namely, the electrical conductivity rises with temperature, achieving an Arrhenius behavior as the temperature increases toward that characterizing the atomic vibrations. The activation energy ($\sim 0.16 \text{ eV}$) of this Arrhenius conductivity is independent of the carbon concentration. Hall effect measurements confirm a low thermally activated Hall mobility consistent with that of small-polaronic carriers [26,27].

Despite the very high carrier densities ($\sim 10^{21} \text{ cm}^{-3}$) measurements of the magnetic susceptibility and the e.s.r. indicate a relatively small spin density, $\sim 10^{19} \text{ cm}^{-3}$ [28,29]. This finding implies that the carriers form singlet pairs (singlet bipolarons).

For bipolaron formation, the energy lowering associated with the pair's interaction with atomic displacements must overcome its Coulomb repulsion. The Coulomb repulsion associated with bringing holes from adjacent icosahedra to pair on a single icosahedron is modest: $\sim (e^2/2\epsilon R - e^2/3\epsilon R) \sim 0.15 \text{ eV}$, where ϵ is the dielectric constant (~10) and R is the radius of an icosahedron (~0.18 nm). The first contribution to the repulsion energy is the energy of distributing two holes on the surface of an icosahedron and the second contribution is the Coulomb repulsion between holes on adjacent icosahedra.

The frontier internal bonding orbitals of an icosahedron within which the holes are to pair are four-fold degenerate. Therefore, to pair as a singlet, rather than as a triplet (Hund's rule), requires symmetry-breaking atomic displacements. Such displacements can lift the electronic degeneracy, mix the singlet states and stabilize some singlets. Two types of singlet bipolaron are possible [30]. With a strong enough electron-lattice interaction between the holes and symmetry-breaking atomic displacements, the singlet pair may be bound with a potential well established by nearly static symmetry-breaking atomic displacements. Such a singlet bipolaron is a "conventional bipolaron." Alternatively, a singlet may be stabilized by the lowering of atomic vibration energy associated with the singlet changing between different electronic configurations in response to symmetry-breaking vibrations. The latter situation describes the formation of a "softening bipolaron" [30]. In Fig. 5 the free energy of a singlet formed in a model system is plotted against the electron-lattice interaction associated with a symmetry-breaking vibration. The two distinct minima of the free energy correspond to parameters for which a softening bipolaron and a conventional bipolaron are most likely to form. For singlet-bipolaron formation, the appropriate minimum must be deep enough so that the singlet bipolaron is stable against both dissociation and triplet formation.

The existence of a conventional bipolaron is always associated with a photo-absorption band. That is, conventionally self-trapped carriers can always be excited from their ground state. However, a photo-absorption band may not occur with a softening bipolaron [30]. Then stabilization of the bipolaron is primarily due to a reduction of the free energy of atomic vibrations rather than to lowering a carrier's energy. No carrier-induced photo-absorption band has been observed in boron carbides [31].

The Seebeck coefficient is the entropy transported with a charge carrier divided by its electrical charge.



Fig. 5. The free energy of a singlet pair formed amongst degenerate electronic states is plotted against the strength of the carriers' electron–lattice interaction with symmetry-breaking atomic deformations that lift the electronic degeneracy. Two energy minima are evident. With sufficiently strong coupling, the energy of the singlet pair is low enough that it is likely to form a "conventional bipolaron." The minimum at weaker coupling defines a region in which formation of a "softening bipolaron" is most likely.

A carrier-induced change of vibration entropy, as occurs with a softening bipolaron, will make a distinctive contribution to its Seebeck coefficient [32]. By contrast, the predominant contribution to the Seebeck coefficient from conventional carriers is simply the change in carriers' entropy-of-mixing upon addition of a carrier. Thus, large carrier densities imply small conventional Seebeck coefficients.

The Seebeck coefficients of boron carbides are very large despite their large carrier densities [33]. In addition, boron carbides' Seebeck coefficients depend only weakly on carrier density. These anomalous features are in accord with expectations for a softening bipolaron [32]. In particular, carrier-induced softening produces two effects for carriers that move by phonon-assisted hopping. First, carrier-induced softening produces a region of enhanced vibration entropy that travels with the carrier. Second, additional heat is transported with a carrier since carrierinduced softening causes the energy transfers associated with the hopping process to occur preferentially at occupied sites. In Fig. 6 the predictions for carrier-induced softening [32] are compared with observations for boron carbides [33].

Thermal transport in boron carbides is also surprising. Despite boron carbides being hard and stiff with very high sound velocities ($\sim 10^6$ cm/s), thermal diffusion can be extremely slow [34,35]. In particular, reducing boron carbides' carbon content to about 13 atomic percent lowers the thermal diffusivity to about 0.01 cm²/s, an extremely small value [35].

Finally, it should be noted that Werheit and students have opposed the view that the predominant charge carriers in boron carbides are bipolarons or even polarons. In particular, Werheit associates dc transport in boron carbides with a low density of high-mobility carriers. By contrast, my collaborators and I envision dc transport in boron carbides being associated with a high density of lowmobility carriers that move by thermally assisted hopping.

It is therefore useful to summarize experimental evidence for bipolaron hopping. First, a very low thermally activated mobility ($\ll 1 \text{ cm}^2/\text{Vs}$) is found when the dc conductivity is divided by the number of paired holes that are introduced by replacing carbon atoms with boron atoms: x/2 of $B_{12+x}C_{3-x}$ for x < 1. Second, measurements of the Hall mobility reveal a very low thermally activated Hall mobility that is consistent with the predictions for polaron or bipolaron hopping [26,27]. The mobility deduced from the Hall effect is the intrinsic mobility, unaffected by trapping, since the magnetic field through the Lorentz force does not deflect a trapped (stationary) charge carrier. Third, the density of localized (hopping type) carriers is orders of magnitude greater than the density of observed spins, implying that the carriers pair as singlets thereby forming singlet bipolarons [28,29]. Fourth, the conductivity as a function of x reaches its maximum at x = 1, when the hopping conductivity, proportional to the product of the probabilities of sites being occupied (x/2)and of being vacant (1 - x/2), has its peak [22]. Fifth, the conductivity rises with increasing frequency and temperature in accord with predictions and common experience for hopping-type transport [31,36]. In particular, polarization currents associated with the hopping of localized carriers rise with increasing frequency and temperature [37]. These currents peak at the carbon concentration for which bipolaron concentration is at its maximum, 13 atomic percent carbon.

By contrast, Werheit envisions most of the holes, introduced by replacing carbon atoms with boron atoms, being trapped. Current is then associated with untrapped carriers that move with high mobility. From their analysis



Fig. 6. The Seebeck coefficient measured on a boron carbide over a wide temperature range is shown on the upper figure. The lower figure shows the two contributions to the Seebeck coefficient for hopping carriers arising from carrier-induced softening plotted against the temperature divided by the characteristic phonon temperature, Θ .

of their measurements of the frequency dependence of the electrical conductivity, Werheit and associates conclude that the charge carriers are high-mobility free carriers at all but low temperatures [38]. They estimate a 100 nm room-temperature mean-free-path for these free carriers, a value comparable to that of the carriers in the highest purity crystalline silicon. This mean-free-path corresponds to a mobility of almost $4000 \text{ cm}^2/\text{V}$ s upon taking the charge carrier effective mass to be the free-electron mass. Similar measurements by other groups are taken as indicative of boron carbides having low-mobility hopping type carriers [31,36].

6. Devices based on boron carbides

Boron carbides' unusual transport has practical applications. The thermally activated hopping conductivity, anomalously large Seebeck coefficients and extremely slow thermal transport all contribute to boron carbides having a surprisingly large thermoelectric figure-of-merit, $Z \equiv \sigma S^2/\kappa$, at high temperatures. Here σ denotes the electrical conductivity, S represents the Seebeck coefficient and κ indicates the thermal conductivity. For this reason, boron carbides are used as p-type thermoelectrics in special high-temperature applications.

Boron carbides can also be used as neutron detectors [39]. In particular, ¹⁰B is an excellent absorber of thermal neutrons. Therefore, thermal neutrons cannot penetrate far (much more than a millimeter) into a boron carbide enriched with ¹⁰B before being absorbed. Upon absorbing a neutron, ¹⁰B decays into ⁷Li and ⁴He, thereby heating the material in the immediate vicinity of the neutron absorption. A temperature difference is thereby established between the face of a boron carbide upon which neutrons are incident and the back face that opposes it. This temperature difference can be monitored using boron carbides' large Seebeck effect. That is, the voltage developed between the material's front and back faces is the product of the temperature difference and the material's Seebeck coefficient. Boron carbides' exceptionally large

Seebeck coefficient results in an unexpectedly sensitive probe of neutron absorption.

Radiation damage arising from the decay of ¹⁰B is minimized by the self-healing that characterizes icosahedral boron-rich solids. The effect of whatever damage is produced on the Seebeck measurement is also limited by boron carbides' high carrier density and the exceptionally weak dependence of boron carbides' Seebeck coefficient on carrier density. All told, boron carbides may serve as simple, small and robust neutron detectors.

References

- [1] D. Emin, Physics Today, vol. 40, AIP, New York, January 1987, p. 55.
- [2] T.L. Aselage, D.R. Tallant, D. Emin, Phys. Rev. B 56 (1997) 3122.
- [3] H.C. Longuet-Higgins, M. de V. Roberts, Proc. R. Soc. London Ser. A 230 (1955) 110.
- [4] W.N. Lipscomb, Boron Hydrides, Benjamin, New York, 1963.
- [5] A.J. Stone, Polyhedron 3 (1984) 1299.
- [6] D. Emin, D.G. Evans, S.S. McCready, Phys. Stat. Solidi B 205 (1998) 311.
- [7] B. Morosin, A. Mullendore, D. Emin, G.A. Slack, in: D. Emin, T.L. Aselage, C.L. Beckel, I.A. Howard, C. Wood (Eds.), Boron-Rich Solids, American Institute of Physics, New York, 1986, p. 70.
- [8] G.A. Samara, D. Emin, C. Wood, Phys. Rev. B 32 (1985) 2315.
- [9] T. Stoto, L. Zuppiroli, J. Pelissier, Radiat. Eff. 90 (1985) 161.
- [10] T. Stoto, N. Houssean, L. Zuppiroli, B. Kryger, J. Appl. Phys. 68 (1990) 3198.
- [11] L. Schmirgeld, L. Zuppiroli, M. Brunel, J. Delafon, C. Templier, in: D. Emin, T.L. Aselage, C.L. Beckel, I.A. Howard, C. Wood (Eds.), Boron-Rich Solids, AIP Conf. Proc. No. 231, AIP, New York, 1991, p. 630.
- [12] M. Carrard, D. Emin, L. Zuppiroli, Phys. Rev. B 51 (1995) 11270.
- [13] M.F. Hawthorne, C.C. Young, P.A. Wegner, J. Am. Chem. Soc. 87 (1965) 1818.
- [14] W.G. Pfann, W. van Roosbroek, J. Appl. Phys. 25 (1954) 1422.
- [15] P. Rappaport, Phys. Rev. 93 (1954) 246.
- [16] T. L. Aselage, D. Emin, US Patent # 6,479,919, 2002.

- [17] R.A. Burmeister, P.E. Greene, Trans. Met. Soc. AIME 239 (1967) 408.
- [18] D. Emin, J. Solid. State Chem. 177 (2004) 1619.
- [19] G.A. Slack, J.H. Rosolowski, C. Hejna, M. Garbauskas, J.S. Kasper, in: H. Werheit (Ed.), Proceedings of the Nineth International Symposium on Boron, Borides and Related Compounds, Universitat Duisburg, 1987, p. 132.
- [20] T. Mori, T. Tanaka, J. Solid State Chem., this volume.
- [21] D. Emin, Phys. Rev. B 38 (1988) 6041.
- [22] T.L. Aselage, D. Emin, S.S. McCready, Phys. Rev. B 64 (2001) 054302.
- [23] D. Emin, M.-N. Bussac, Phys. Rev. B 49 (1994) 14290.
- [24] D. Emin, in: Physics Today, vol. 35, AIP, New York, June 1982, p. 34.
- [25] C. Wood, D. Emin, Phys. Rev. B 29 (1984) 4582.
- [26] C. Wood, in: D. Emin, T.L. Aselage, C.L. Beckel, I.A. Howard, C. Wood (Eds.), Boron-Rich Solids, American Institute of Physics, New York, 1986, p. 20670.
- [27] D. Emin, in: C.L. Chien, C.R. Westgate (Eds.), The Hall Effect and its Applications, Plenum Press, New York, 1980, p. 281.
- [28] L.J. Azevedo, E.L. Venturini, D. Emin, C. Wood, Phys. Rev. B 32 (1985) 7970.
- [29] O. Chauvet, D. Emin, L. Forro, L. Zuppiroli, T.L. Aselage, Phys. Rev. B 53 (1996) 14450.
- [30] D. Emin, Phys. Rev. B 61 (2000) 6069.
- [31] G.A. Samara, H.L. Tardy, E.L. Venturini, T.L. Aselage, D. Emin, Phys. Rev. B 48 (1993) 1468.
- [32] D. Emin, Phys. Rev. B 59 (1999) 6205.
- [33] T.L. Aselage, D. Emin, S.S. McCready, R.V. Duncan, Phys. Rev. Lett. 81 (1998) 2316.
- [34] J.H. Gieske, T.L. Aselage, D. Emin, in: D. Emin, T.L. Aselage, C.L. Beckel, A.C. Switendick, B. Morosin (Eds.), Boron Rich Solids, American Institute of Physics, New York, 1991, p. 376.
- [35] D. Emin, in: R. Freer (Ed.), The Physics and Chemistry of Carbides, Nitrides and Borides, Kluwer Academic Publishers, London, 1990, p. 691.
- [36] L. Zuppiroli, N. Papandrou, R. Kormann, J. Appl. Phys. 70 (1991) 246.
- [37] D. Emin, Phys. Rev. B 46 (1992) 9419.
- [38] R. Schmechel, H. Werheit, J. Solid State Chem. 133 (1997) 335.
- [39] D. Emin, T.L. Aselage, J. Appl. Phys. 97 (2005) 013529.