

Quasiamorphous semiconductors

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The experimental data on the electrical, thermal, and optical properties of high-boron compounds and modifications of boron—refractory crystals distinguished by specific and complicated structure—are reviewed. It is shown that depending on the complexity of the crystalline structure the properties of the materials transform, systematically approaching the properties characteristic of amorphous semiconductors; a new class of materials is thus identified—quasiamorphous semiconductors. In the limiting case of the most complicated structures, they can be regarded as natural structural models of amorphous semiconductors.

1. INTRODUCTION

A great deal of attention is now being devoted to modeling of the structure of amorphous semiconductors and establishing for them the relations between the structure, the electronic and vibrational states, and the properties. This is motivated by the increasing interest in the physics and technology of these materials.

The study of amorphous semiconductors is closely related with the study of crystals with artificially induced structural disorder: strongly doped, subjected to different radiation treatments, phases with nonstoichiometric composition and solid solutions, and finely dispersed (poly- and microcrystalline) phases.^{1–5}

In addition to this there exists a special class of materials in which the physicochemical properties of refractory crystals are combined with the characteristic electrical, optical, and thermal properties of amorphous semiconductors. Modifications of boron and high-boron compounds (compounds whose boron content exceeds 90 at. %) belong to this class.^{6–9} The specific nature of the properties of these quasiamorphous, high-boron semiconductors is a result of their complicated crystalline structure, and they can be regarded as natural structural models of amorphous semiconductors.

The crystalline lattices of these materials are constructed based on B_{12} icosahedra (Fig. 1), which give strong covalent bonds with the boron atom having only three valence electrons.¹⁰ However an icosahedron has a fifth-order rotational axis, which makes it impossible to construct a lattice from regular icosahedra: they are deformed somewhat and are coupled with one another by separate atoms or nonicosahedral groups of atoms of boron, metal, or metalloid. In the most complicated lattices the structural units are conglomerates consisting of icosahedra (Fig. 1). Figure 2 shows as an example the structure of a high-boron compound.

Thus the materials studied here are characteristically complex and have diverse crystalline structures: the number N of atoms in a unit cell varies from 12 to 1600. As N increases the internal structure of a cell becomes more complicated: groups of boron atoms with different coordination numbers appear, there is a set of distances between neighboring boron atoms, etc. It should also be noted that the structure is “open”, i.e., there is a large number of crystallographic voids: for β -rhombohedral boron, for example, the spatial filling is only 36%.

Table I gives the crystalline modifications of boron and the compounds which are their structural analogs, as well as

groups of high-boron compounds which are not such analogs. Table I was constructed based on the results of Refs. 10–20. The semiconductor properties of only some of the materials presented in the table have been studied thus far. The characteristic semiconductor properties of crystals belonging to each of the structural types enumerated, however, are already known. It will be shown below that as the crystalline structure becomes more complicated (the number N , regarded as a parameter, increases) the properties of the crystals are transformed, and in the limit of the most complicated structures they become completely identical to the properties of amorphous semiconductors. Starting from this some questions regarding the modeling of the structure of amorphous semiconductors will be studied.

2. CHARACTERISTIC PROPERTIES OF AMORPHOUS SEMICONDUCTORS

In this section theoretical formulas describing the basic properties of amorphous semiconductors will be presented.^{1–4} These formulas are usually used to analyze experimental results, though in so doing certain difficulties arise. Since, below, in studying the properties of quasiamorphous semiconductors, we shall be interested primarily in the transformation of the properties as a function of the degree of structural disorder the expressions presented will be studied precisely from this perspective.

2.1. Electrical properties. The absence of translational symmetry (long-range order) and the presence of a large number of defects (breakdown of short-range order) lead to the existence of a high density of localized states in the mobility gap (the “forbidden band”) of an amorphous semiconductor. The Fermi level ϵ_F lies in the region of these states. At low temperatures the electrical conductivity is determined by the mechanism of conduction with a variable hopping length (hopping conductivity near ϵ_F , known as

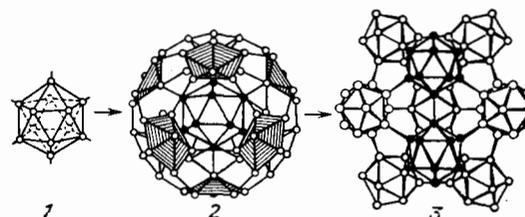


FIG. 1. Structural units. 1) B_{12} icosahedron, 2) $B_{12}(B_6)B_{12}$, 3) $B_{12}(B_{12})_{12}$ (Ref. 10).

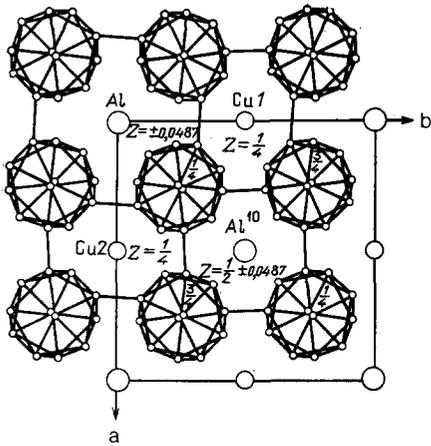


FIG. 2. Crystalline structure of $\text{Al}_{1.00}\text{Cu}_{0.79}\text{B}_{25}$ (projection on a plane perpendicular to the c axis).¹³

Mott's law):

$$\sigma = \sigma'_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right], \quad (1)$$

This formula was derived under the condition that the density of states [$g(\epsilon_F)$] is independent of the energy at the Fermi level and under a number of other simplifying assumptions.¹

According to Ref. 1

$$T_0 = \frac{B\gamma^3}{kg(\epsilon_F)}, \quad (2)$$

where $B \approx 8.4-24.5$, and γ is the damping constant of the wave function of the electron in the localized state (in the simplest case $\gamma = 1/a$, where a is the Bohr radius), which must be known from other experiments if $g(\epsilon_F)$ is to be determined.

In analyzing the data on the electrical conductivity, described by (1), it turns out that σ'_0 differs by an order of magnitude from the theoretical values, but the values of T_0 found from experiments permit calculating $g(\epsilon_F)$ and establishing how its value transforms as an amorphous film of a given material is annealed or as the deposition temperature

of the film is varied. In both cases the degree of disorder of the structure and correspondingly $g(\epsilon_F)$ change; this is reflected in the Mott conductivity. The characteristic values of $g(\epsilon_F)$ usually fall into the range of $10^{18}-10^{20} \text{ eV}^{-1} \cdot \text{cm}^{-3}$.

As is well known, when an amorphous semiconductor is hydrogenated the density of localized states drops considerably, and this is also reflected in the Mott conductivity. In the limiting cases, for example, when the content of hydrogen in amorphous silicon exceeds 5 at. %, $g(\epsilon_F)$ is less than $10^{16} \text{ eV}^{-1} \cdot \text{cm}^{-3}$ and the Mott conductivity is so low that it cannot be observed.¹

When Mott conductivity is realized in strong electric fields the electric conductivity has the form^{1,4}

$$\sigma = \sigma'_0 \exp \left[- \left(\frac{E_0}{E} \right)^{1/4} \right] \quad (3)$$

(nonactivational tunneling), where

$$E_0 = \frac{B\gamma^4}{eg(\epsilon_F)}. \quad (4)$$

Using (2) and (4) together should make it possible to determine $g(\epsilon_F)$ and γ independently, but (3) is usually not observed experimentally: in strong electric fields other mechanisms of nonlinearity of the I-V characteristics (IVC) usually predominate.

In investigations of the IVC of a number of nonhydrogenated amorphous semiconductors the Frenkel-Poole mechanism was identified (thermal-field emission from a Coulomb center). This was established for SiO_2 , boron, and silicon.²¹⁻²³ In this case the dependence of the current density on the intensity of the electric field has the form

$$j \sim \exp \frac{\beta E^{1/2}}{kT}, \quad (5)$$

where $\beta = (e^3 z / \epsilon_0)^{1/2}$ (ze is the charge of the ionized center and ϵ_0 is the static permittivity).

In the opposite case, for hydrogenated amorphous silicon ($a\text{-Si:H}$), in investigations of the IVC the space-charge limited current (SCLC) mechanism was identified.²⁴ In this case the IVC have the form

$$I \sim V^{(T_c/T)+1}, \quad (6)$$

TABLE I. Modifications of boron and high-boron compounds.

Structural type	Analog materials
α -rhombohedral boron, $R \bar{3}m$ ($N=12$)	B_{13}P_2 , B_{13}As_2 , boron carbide B_3Si , B_9O , B_{12}S_2 , $\text{B}_{12}\text{C}_2\text{Al}$, $\text{B}_{40}\text{C}_4\text{Al}$, $\text{B}_{12}\text{C}_2\text{Si}$
α -tetragonal boron, $P4_2/nmm$ ($N=50$)	$\beta\text{-AlB}_{12}(\text{Al}_3\text{C}_2\text{B}_{48})$, BeB_{12} , NiB_{26} , $\text{B}_{50}\text{N}_{1-2}$, B_{50}C_2 , B_{50}C , AlB_{154} , $\text{Ti}_{1,3-2}\text{B}_{50}$, $\text{Ti}_{-2}\text{Ni}_{-1,5}(\text{B}_{12})_4$, $\text{V}_{1,5-1,5}\text{B}_{50}$, $\text{Ti}_{1,2,7}\text{N}_{1,30}\text{B}_{48}$, $\text{Ti}_{0-2}\text{C}_2\text{B}_{2-0}\text{B}_{48}$, $\text{V}_{-1,5}\text{N}_{-0,5}\text{B}_{1,5}(\text{B}_{12})_4$, $\text{V}_{0-2}\text{C}_2\text{B}_{2-0}\text{B}_{48}$, $\text{Al}_{1,0}\text{Cu}_{0,79}\text{B}_{25}$, $\text{AlBe}_{0,8}\text{B}_{24}$
β -rhombohedral boron, $R \bar{3}m$ ($N=105$)	SiB_{14} , ZrB_x ($\sim 18 \leq x \leq 40$), $\text{Ga}_{1,5}\text{B}_{108}$, ScB_{-38} , ZnB_{51} , CrB_{41} , MnB_{23} , FeB_{49} , $\text{Cu}_{4,5}\text{B}_{104}$, $\text{Cu}_{4,5}\text{B}_{105}$, CuB_{29} , $\text{Cu}_2\text{Al}_{2,7}\text{B}_{104}$
β -tetragonal boron, $P4_22_12$ ($N=200$)	$\alpha\text{-AlB}_{12}$, $\text{Al}_{1,1}\text{Be}_{0,7}\text{B}_{22}$, BeB_6 , LiB_{10}
YB_{98} , $Fm\bar{3}c$ ($N=1800$)	MB_{98} (M — all are rare earths except Eu, La, Ce, Pr, Nd)
NaB_{15} , $I\bar{4}3m$ ($N=50$)	MgAlB_{14} , LiAlB_{14}

Two additional types of structures are given in Ref. 16: $\gamma\text{-AlB}_{12}$ ($P2_12_12$) and AlB_{10} (or AlC_2B_8)—hexagonal close packing of B₆ icosahedra, orthorhombic structure. Data on B_3Si are presented in Ref. 17 (orthorhombic structure, $Pnmm$, $N=289$: 43 Si atoms and 246 boron atoms in a unit cell).

where T_c is the characteristic parameter of the energy dependence of the density of states, given in the form

$$g(\varepsilon) \sim \exp \frac{\varepsilon}{kT_c}. \quad (7)$$

For the mechanism of hopping conduction along localized states the Hall mobility is characteristically low²⁵:

$$\mu_H \ll 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}, \quad (8)$$

and does not correspond to the true magnitude of the mobility of the current carriers. The mobility μ_H differs sharply in order of magnitude from the mobility from magnetoresistance, if it is also defined formally, making the assumption that the experimental quantity $\Delta\rho/\rho \sim (\mu_{\Delta\rho/\rho} H)^2 \mu_H$ also differs sharply in magnitude from the drift mobility (μ_D).

Another characteristic property is that the electric conductivity depends on the frequency of the electric field¹:

$$\sigma(\omega) = \frac{1}{3} \omega \pi e^2 k T g^2(\varepsilon_F) \gamma^{-5} \left(\ln \frac{\nu_{ph}}{\omega} \right)^4, \quad (9)$$

where ν_{ph} is the phonon frequency.

The expression (9) can be written in the form

$$\sigma \sim \omega^2. \quad (10)$$

If the frequency of the phonon $\nu_{ph} = 10^7 \sim 10^{13}$ Hz and ω is of the order of 10^4 s^{-1} , then s varies from 0.4 to 0.8. It is noted in Ref. 1 that the values of $g(\varepsilon_F)$ obtained for amorphous semiconductors from the experimental data using (9) are much too high.

We shall study the thermo-emf S in the region where conduction with a variable hopping length is realized:

$$S \sim \left(\frac{d \ln g(\varepsilon)}{d\varepsilon} \right)_{\varepsilon=\varepsilon_F}. \quad (11)$$

Different theoretical works disagree about the temperature dependence of S .¹ It should be noted that it is experimentally very difficult to determine the exact temperature dependence of the thermo-emf because the materials have a quite high resistance in this range and the values of S are low (of the order of tens of $\mu\text{V} \cdot \text{K}^{-1}$).

At high temperatures a transition occurs from hopping conduction along localized states at the Fermi level to conduction along delocalized states of the conduction or valence band of the amorphous semiconductor, where the mobility of the current carriers is an order of magnitude higher (several to tens of $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$).¹ In this case

$$\sigma \sim \exp \left(- \frac{\Delta E}{kT} \right), \quad (12)$$

$$S \sim A + \frac{\Delta E}{kT}, \quad (13)$$

where

$$\Delta E = (\varepsilon_{c,v} - \varepsilon_F)_{T=0} \quad (14)$$

($\varepsilon_{c,v}$ is the edge of the conduction or valence band, $A \approx 1-2$).

Since in this case S is usually of the order of hundreds of $\mu\text{V} \cdot \text{K}^{-1}$, when the mechanism of conduction changes it grows simultaneously with exponential growth of σ . It should be noted, however, that the values of ΔE found from experiment and from (12) and (13) do not agree; this is explained by the exponential increase in μ as the tempera-

ture T increases. The reasons for this are still under discussion.²⁶

Amorphous semiconductors also have the characteristic electrical properties of being insensitive to doping, the drift mobility depends exponentially on the temperature, and the relaxation time of the photoconductivity is long.

The insensitivity of the electrical properties to doping (hydrogenated amorphous semiconductors are obvious exceptions) occurs for several reasons: $g(\varepsilon_F)$ is large and in order to obtain an appreciable shift in ε_F a large number of electrons supplied by impurity atoms is required; not all impurity atoms are electrically active; and self-compensation can occur.¹

The exponential dependence of the drift mobility, like the long-time relaxation of the photoconductivity, is a consequence of the presence of a high concentration of traps—localized states of current carriers. The relaxation of photoconductivity usually cannot be described by one time constant.

The density of the localized states of an amorphous semiconductor and the fact that the mobility is low for conduction along these states were mentioned above. The electronic states in bands, conversely, are delocalized, and here the mobility is an order of magnitude higher (states lying above the mobility edge). However the form of $g(\varepsilon_F)$ of the delocalized states of an amorphous semiconductor differs considerably from the form of $g(\varepsilon_F)$ of a crystal: the sharp features resulting from the existence of Brillouin zones vanish. Sometimes the curve $g(\varepsilon_F)$ is almost completely structureless.¹ This is also a characteristic property of amorphous semiconductors and is a result of the absence of long-range order. This is illustrated, in particular, by the results of Ref. 27, where it is shown that the form of $g(\varepsilon_F)$ for the valence band of silicon is transformed as the crystalline state transforms into an amorphous state. The method of x-ray emission spectroscopy, which we later also used to study quasiamorphous semiconductors, was employed here.

2.2. Thermal properties. The theory of the thermal properties of amorphous semiconductors is much less developed than the theory of electrical properties. There are also many fewer experimental studies. Nonetheless the basic features of the thermal properties, associated primarily with the absence of long-range order, can be enumerated.

The thermal conductivity of an amorphous semiconductor is low. Writing formally

$$\kappa = \frac{1}{3} C v l, \quad (15)$$

where C is the heat capacity, v is the velocity of sound, and l is the phonon mean free path length, gives l of the order of interatomic distances. In this case the concept of a "phonon" is no longer applicable: heat transfer is represented in terms of the exchange of energy quanta between neighboring atoms, i.e., $l(T) = \text{const}$. Indeed, it has been established experimentally for a number of amorphous materials that κ is constant at high temperatures, when $C(T) = \text{const}$. At low temperatures, when C increases, the behavior of an amorphous semiconductor is of the form¹

$$\kappa \sim T^n \quad (1, 8 < n < 2).$$

Among the anomalies in the thermal properties we can also mention the anomalously high heat capacity at low temperatures and the fact that there is no correlation between

the value of the thermal conductivity and the thermal expansion.

2.3. Optical properties. The characteristic features of the optical properties of an amorphous semiconductor also follow from the specific nature of its structure.

One characteristic feature is that Urbach's rule for the absorption coefficient near the characteristic absorption edge holds:

$$\alpha \sim \exp(\Gamma \hbar \omega), \quad (16)$$

i.e., there is a long-wavelength absorption tail.

For a large number of amorphous semiconductors the values of the parameter Γ determined experimentally at $T = 300$ K fall into the range $\sim 5-15$ eV⁻¹.

The theory links the existence of a long-wavelength tail with disordering of the structure.³ Absorption of light in a "random" field is studied, and different frequency dependences are obtained for α depending on the form of the potential of this field. For Coulomb (no correlation in the arrangement of point charges) and smooth (on the average quite smoothly varying in space) fields

$$\alpha = \alpha_m \exp\left(-\frac{E_g - \hbar \omega}{\bar{W}}\right), \quad (17)$$

where α_m is virtually independent of the frequency.

The characteristic energy in the expression (17) is

$$\bar{W} \equiv \frac{1}{\Gamma}. \quad (18)$$

For amorphous semiconductors the frequency dependence α usually has the form (17). It should also be noted that the parameter \bar{W} increases as the temperature increases $\bar{W} \sim T$ (above some critical temperature) and as the degree of static "disorder" of the structure increases.^{1,3}

The characteristics of the IR absorption and Raman scattering spectra of amorphous semiconductors are determined by the fact that owing to the breakdown in the quantum-mechanical selection rules interaction with vibrations that are inactive in the corresponding crystalline semiconductors is allowed. Thus the fine structure of the spectra characteristic for a crystal is absent for the corresponding amorphous material. The IR absorption spectrum reproduces, to within a factor that depends on the frequency, the vibrational density of states.

3. PROPERTIES OF QUASIAMORPHOUS SEMICONDUCTORS

3.1. Electrical properties and conduction mechanism. β -rhombohedral boron has been known now for a long time as a semiconductor with low carrier mobility ($\mu_H < 1$ cm²·V⁻¹·s⁻¹),²⁵ but its nature has not been understood. Indeed attempts at explaining the low mobility in β -rhombohedral boron based on existing ideas (small-radius polarons, extrinsic compensated semiconductors, molecular crystals) have been unsuccessful.⁶ It has been suggested that conduction occurs along the so-called "boron impurity in boron"—atoms with high coordination numbers (8 and 9), which constitute about 13% of all atoms in the lattice (the remaining atoms have a coordination number of 6). In a number of studies it was observed that the electric conductivity depends on the temperature, which dependence was interpreted as satisfaction of Mott's law [formula (1)].⁶

Merely the satisfaction of this law cannot, however, serve as a basis for comparing β -rhombohedral boron with an amorphous semiconductor: conductivity with a variable hopping length is observed, as is well known, in extrinsic compensated semiconductors also. Random compensation could not be excluded, since the crystals of β -rhombohedral boron were comparatively impure.

For β -rhombohedral boron a dependence $\sigma(\omega)$ of the type (10) has been observed, and it has been noted that the values of μ_H do not correspond to the values of $\mu_{\Delta\rho/\rho}$. In addition, the electric conductivity and thermo-emf characteristically both increased as the temperature was increased, the activation energy of the electric conductivity was of the order of tens of eV, and it was observed experimentally that the drift mobility increases with the temperature also.⁶

The concept of quasicrystallinity of β -rhombohedral boron,⁶ based on the characteristics of its crystalline structure (large and structurally complicated unit cell), required experimental proof. Such proof could be the following: 1) establishment of a correlation between the degree of complexity of the lattice (the number N) of a number of high-boron semiconductors and their electrical properties; 2) identification of the same electrical properties for them that are characteristic for amorphous semiconductors.

Thus both the number of objects of study and the range of electrical properties studied had to be expanded. Further, to prove quasicrystallinity it was necessary to study from the same perspective the thermal and optical properties, which also had to be sensitive to the characteristic features of the crystalline structure. Such studies were performed for a significant number of high-boron semiconductors.

The experimental dependence of the mobility μ_H on the number of atoms in a unit cell (N) has now been determined (Fig. 3).⁸ One can see that for $N = 12$ (simple lattice) $\mu_H \approx 100$ cm²·V⁻¹·s⁻¹, and starting with $N \geq 50$ the materials can be classified as semiconductors with low mobility. The form of the curve $\mu_H(N)$ is the same as that of the curve $\mu(\varepsilon)$ near the mobility threshold of the amorphous semiconductor, where the mobility is observed to increase by an order of magnitude.¹

Figure 3 demonstrates the transition of μ_H from "band" to "hopping" mobility for a number of semiconductors with gradually increasing complexity of the crystalline structure. A change in the conduction mechanism can also be observed in the case of strong doping of a semiconductor with $N \geq 50$, when the Fermi level reaches the level of the

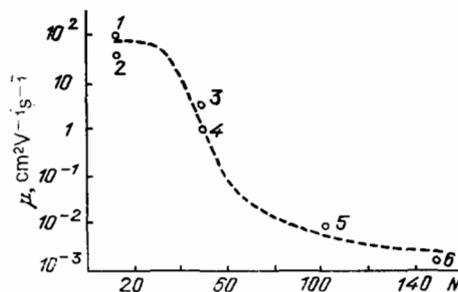


FIG. 3. The dependence of the Hall mobility ($T = 300$ K) on the number N of atoms in the unit cell.^{6,8} 1) α -rhombohedral boron, 2) $B_{13}P_2$, 3) $MgAlB_{14}$, 4) β - AlB_{12} , 5) β -rhombohedral boron, 6) α - AlB_{12} .

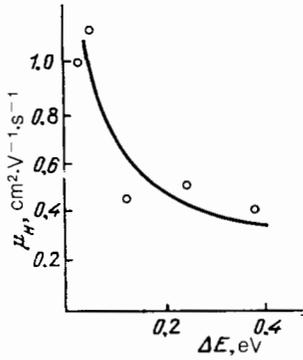


FIG. 4. The dependence of the Hall mobility of β -rhombohedral boron ($T = 300$ K) on the activation energy of electrical conductivity (ΔE decreases as the degree of doping increases).⁶

mobility threshold ε_v (all semiconductors are of the p -type). Figure 4 shows the dependence $\mu_H(\Delta E)$ for β -rhombohedral boron $\Delta E = (\varepsilon_v - \varepsilon_F)_{T=0}$. The transition from conduction along localized states to conduction along delocalized states of the conduction band is also observed as the temperature is increased. This is demonstrated in Fig. 5. At sufficiently low temperatures Mott's law for electric conductivity (1) holds, and the thermo-emf is low. As the temperature is raised a region is observed where S grows rapidly with exponential growth of σ with an activation energy ~ 0.1 eV, after which there is a section where S drops and σ increases. At the highest temperatures intrinsic conductivity is observed: the thermal width of the gap $\sigma \sim \exp(-E_g^T/2kT)$ corresponds well to E_g^{opt} .

Thus three independent methods by which the hopping mechanism is replaced by conduction along delocalized states are realized: with simplification of the crystalline structure ($N \lesssim 50$), with strong doping, and at high temperatures for semiconductors with a complicated crystalline structure ($N \gtrsim 50$).

It should be noted that in the last few years the electrical properties and the mechanism of conduction in boron carbide—the structural analog of α -rhombohedral boron ($N = 12$)—have been under intensive study. Boron carbide, which is a semiconductor with low mobility, does not conform to the law shown in Fig. 3. The reason for this lies in the fact that boron carbide is a phase with variable composition. The concomitant disorder of the structure is responsible for the specific nature of the conduction mechanism: as is assert-

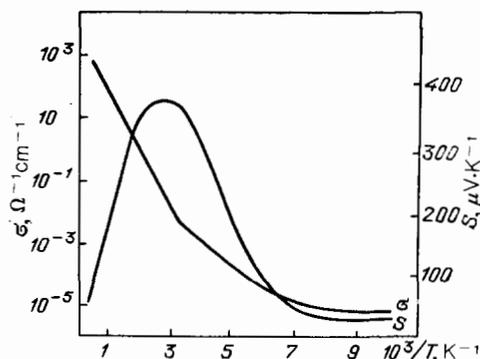


FIG. 5. The temperature dependence of the electrical conductivity σ and thermo-emf S of GdB_{66} .⁹

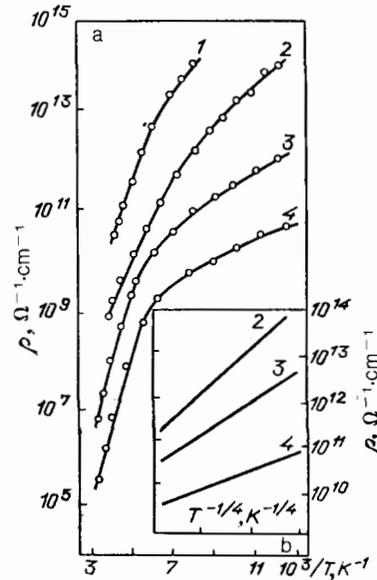


FIG. 6. a) Temperature dependence of the resistivity; 1) $(\text{Be, Al})\text{B}_{12}$, 2) $\beta\text{-AlB}_{12}$, 3) β -rhombohedral boron, 4) $\alpha\text{-AlB}_{12}$.⁷ b) The same in Mott coordinates.

ed in Refs. 28–33, conduction in boron carbide is realized by small bipolarons. In Refs. 34–37 other possible reasons for structural disorder in samples of boron carbide were analyzed starting from the characteristics of their preparation (the presence of free carbon, pores, and boundaries between grains). It is shown, in particular, that at high frequencies, when the grain boundaries do not affect charge transfer a characteristic temperature dependence of the electric conductivity of the form (1) is observed.

3.2. *Electron density of states.* Conduction with variable hopping length is realized at low temperatures for all semiconductors with $N \gtrsim 50$. Figure 6 shows the temperature dependences of the resistivity in both standard and Mott coordinates for a number of semiconductors with different values of N . It follows from these data that as N increases, T_0 decreases. If the values of γ for the materials studied are close, then the values of $g(\varepsilon_F)$ increase as N increases. The picture shown in Fig. 6 is similar to that observed for amorphous semiconductors when $g(\varepsilon_F)$ is varied by lowering the annealing temperature or lowering the film deposition temperature: in both cases $g(\varepsilon_F)$ increases.¹

To calculate $g(\varepsilon_F)$ from (3) it is necessary to know the value of γ . Assuming that γ is of the order of $(10 \text{ \AA})^{-1}$, we obtain $g(\varepsilon_F) \approx 10^{19} - 10^{20} \text{ eV}^{-1} \text{ sec}^{-3}$, as in amorphous semiconductors. This choice of γ seems reasonable. Indeed, if conduction occurs along delocalized states of an amorphous semiconductor, then according to Ref. 1

$$\sigma = \sigma_{\text{min}} \exp \frac{\varepsilon_F - \varepsilon_v}{kT}, \quad (19)$$

where

$$\sigma_{\text{min}} = 0,026 \frac{e^2}{\hbar a}, \quad a \gtrsim 2/\gamma \quad (20)$$

(a is the distance between the centers of localization). Since

$$(\varepsilon_F - \varepsilon_v) = (\varepsilon_F - \varepsilon_v)_{T=0} - \gamma_0 T, \quad (21)$$

where γ_0 is the temperature coefficient of the gap, to calculate σ_{min} from the experimental values of σ and ΔE it is

necessary to know γ_0 . This quantity is known for β -rhombohedral boron, if it is assumed that γ_0 equals half the temperature coefficient of ϵ_g .³⁸

The value of σ_{\min} was calculated for undoped, single-crystalline β -rhombohedral boron in the same temperature range where the transitions $\epsilon_v - \epsilon_F$ (19) are realized and $\Delta E = 0.5$ eV.⁸ In addition $a = 10$ Å. It should be noted, however, that similar calculations for the compounds MB_{66} , whose structure is significantly more complicated than that of β -rhombohedral boron, do not give reasonable values of a : they are anomalously high. We shall discuss below a possible reason for this discrepancy. In any case, the data for MB_{66} do not conform to the general pattern, and for this reason they are not presented in Fig. 6 together with the data on the temperature dependences of the resistivity for other semiconductors.

It is of interest to evaluate $g(\epsilon_F)$ from other experiments, in particular, from the field dependences of the electrical conductivity, if they conform to the law (3). However nonactivational tunneling in strong electric fields has been identified only for β -rhombohedral boron.³⁹ A detailed study of the IVC for α - AlB_{12} made it possible to identify for this material the Frenkel-Poole effect, as in the case of amorphous boron. For $(Be,Al)B_{12}$ the SCLC mechanism was identified. It should be noted that with an appropriate choice of material for the contacts the SCLC mechanism has also been established for β -rhombohedral boron.⁴⁰

It can be concluded based on what was said above that the mechanism of nonlinearity of the IVC of $(Be,Al)B_{12}$ and β -rhombohedral boron is analogous to the mechanism of nonlinearity of the IVC of amorphous hydrogenated silicon.²⁴ At the same time, for α - AlB_{12} there is a corresponding analogy to nonhydrogenated silicon, boron, and SiO_2 .²¹⁻²³

Values of $g(\epsilon_F)$ can also be obtained from data on the frequency dependences of the electrical conductivity, according to (9). Such data exist for β -rhombohedral boron and $B_{14}Si$.^{6,41} To obtain these estimates it is necessary to know the values of ν_{ph} and γ . Setting $\nu_{ph} \approx 500$ cm^{-1} and $\gamma \approx (10 \text{ Å})^{-1}$, we obtain for β -rhombohedral boron the value $g(\epsilon_F) \approx 10^{20}$ $eV^{-1} cm^{-3}$, which exceeds the value obtained from analysis of the experimental data based on (1) and (2) (of the order of 10^{19} $eV^{-1} cm^{-2}$). The result obtained from (9) is insensitive to the value of ν_{ph} . As already pointed out above, for amorphous semiconductors the value of $g(\epsilon_F)$ determined from (9) is usually greater than the value determined based on (1) and (2) using the corresponding experimental data, i.e., the situation is analogous to Ref. 1.

The value of $g(\epsilon_F)$ for β -rhombohedral boron obtained using the dependence $\sigma(E)$ and the formulas (3) and (4) is also significantly higher than the value obtained from (1) and (2).⁶

Information about the form of the density of states of the valence band of some of the semiconductors studied was obtained by the method of x-ray emission spectroscopy.⁴² This method permits judging the partial density of all occupied states.^{27,42}

Figure 7 shows the spectra reflecting the energy distribution of the density of states within the valence band for two compounds MB_{66} .⁴³ The spectra obviously do not have the sharp features characteristic of the spectra of crystals, including also crystals of borides and modifications of boron

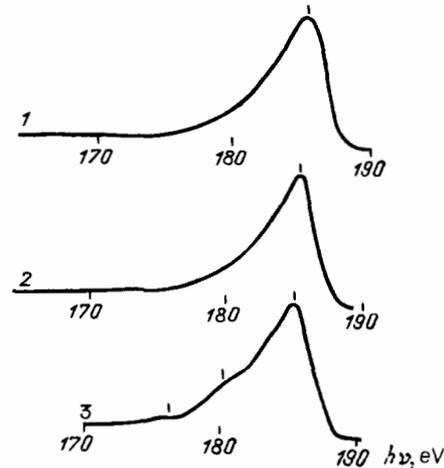


FIG. 7. X-ray emission spectra. 1) GdB_{66} , 2) DyB_{66} , 3) amorphous boron.

with simpler crystalline lattices (MB_{66} have the most complicated lattices of all materials studied: the number of atoms in the unit cell N equals 1600). The spectra of MB_{66} , as well as the spectrum of amorphous boron, which is also presented in Fig. 7, are structureless.

3.3. Doping and modification. Semiconductors with a complicated crystalline structure are comparatively insensitive to the introduction of impurities. It has been established that their electrical properties can be altered appreciably only with an impurity content of the order of several at. %.⁶ The latest data on the effect of impurities on the resistance of β -rhombohedral boron were obtained in Ref. 44 and are presented in Fig. 8. With regard to the insensitivity to doping these materials are similar to amorphous semiconductors.

It should be noted that p -type conductivity is characteristic of all undoped semiconductors, and the introduction of most impurity elements does not change it. This means that the Fermi level lies closer to ϵ_v than ϵ_c . A possible explanation of this fact is that there exists an electronic deficit of bonds in the crystalline lattice,¹⁰ as a result of which all impurity atoms give up their electrons to form bonds. This proposition is supported by data on the effect of impurities on some mechanical properties.⁴⁵

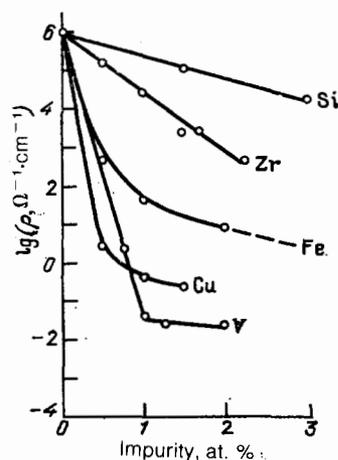


FIG. 8. The dependence of the resistivity ρ of β -rhombohedral boron on the degree of doping ($T = 300$ K).⁴⁴

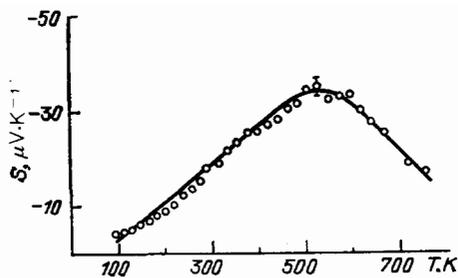


FIG. 9. Temperature dependences of the thermo-emf of β -rhombohedral boron doped with iron ($\text{FeB}_{20.5}$).⁴⁶

Figure 9 shows data on the thermo-emf of β -rhombohedral boron with Fe impurity, which changes the sign of the thermo-emf. This result was obtained in Refs. 46–48 by doping β -rhombohedral boron and B_{14}Si with vanadium, nickel, and chromium. Since the content of these impurities is somewhat higher than that of boron atoms with coordination number 9 (2%), “boron impurity in boron”²⁶ is thought to be an effect of compensation.

Data from Mössbauer spectroscopy⁴⁹ suggests that iron in the lattice of β -rhombohedral boron is in the states Fe^{2+} and Fe^{3+} . From here it is concluded that Fe is a donor impurity. However the data of Ref. 50 on β -rhombohedral boron doped with Fe do not agree with the data of Ref. 49. In addition, at high temperatures the sign of the thermo-emf changes. Thus the question of the effect of impurities consisting of 3d elements remains, in our opinion, unsolved. It is emphasized in Ref. 44 that stable n -type conductivity cannot yet be obtained by doping. We note that in Ref. 44 the thermo-emf of doped β -rhombohedral boron was studied in the temperature range where conduction was realized along delocalized states.

Investigation of the effect of impurities on the electrical properties of α - AlB_{12} also revealed an insensitivity to doping: σ and S could be varied only by introducing several at. % impurities.⁶ Some data on doping of MgAlB_{14} with nickel up to 1 at. % are presented in Ref. 8. The samples had p -conductivity. Attempts to dope GdB_{66} and other compounds MB_{66} were unsuccessful: adding Fe, Se, and other elements in quantities of up to several at. % gave a two-phase material.

In connection with the question of the effect of impurities on the electrical properties of quasicrystalline semiconductors we shall examine the results of Ref. 51: the quantities σ and T_0 (2), determined for crystals of β -rhombohedral boron which were not specially doped but whose impurity

composition differed significantly were insensitive to this composition. From here it may be concluded that the centers of localization are not related with impurity atoms; their existence is determined by the specific nature of the crystalline structure of β -rhombohedral boron.

We shall examine some other results of the modification of the electrical properties of quasicrystalline semiconductors. In so doing, purely qualitative analogies between them and the results of the modification of the properties of amorphous semiconductors, in particular, amorphous silicon, will be pointed out.

We shall discuss the effect of high-temperature ($T \gtrsim 1000$ K) annealing on the properties of α - AlB_{12} .⁶ It has been established that such annealing increases the electrical conductivity and decreases the parameter T_0 [see (2)], i.e., it increases the density of localized states. In addition, as will be shown below, the intensity of the Urbach absorption tail increases. Annealing in this case has the opposite effect to that of annealing of an unhydrogenated amorphous semiconductor, in particular, amorphous silicon. In the latter, annealing reduces the density of states in the mobility gap owing to a reduction in the number of structural defects (broken silicon-silicon bonds) as well as owing to a decrease in the degree of disorder of the structure.

It can be conjectured that the effect of annealing in the case of α - AlB_{12} is determined by the modification of the structure: annealing probably leads to redistribution of the aluminum atoms between nonequivalent positions (the α - AlB_{12} lattice contains five such positions; Table II), which increases the “disorder”. This suggestion was made when differential thermal analysis did not reveal any phase transition on annealing.

An analogous modification of the structure is apparently responsible for the electrical memory effect observed for α - AlB_{12} .⁶ Since pinching of the current leads to strong heating of the sample in a local region a low-resistance channel should form as a result of electrical breakdown, and the sample transforms into a state with a low-resistance memory.

The opposite effect is observed when α - AlB_{12} is modified with beryllium, though one would expect that the introduction of beryllium should increase the degree of “disorder” in the structure. The distribution of Al atoms in the lattice also apparently plays a role in this case: Be replaces Al in some positions while other positions of Al remain occupied (see Table II). This modification of the structure of α - AlB_{12} leads to a reduction of “disorder”: The intensity of the Urbach tail drops, the electrical conductivity drops, there is no extended section of Mott conductivity, and the SCLC

TABLE II. The distribution of metal atoms in positions of the crystalline lattices of $\text{Al}_{11}\text{Be}_{0.7}\text{B}_{22}$ and α - AlB_{12} .¹⁴

Atom	Position	Degree of filling, %	
		$\text{Al}_{11}\text{Be}_{0.7}\text{B}_{22}$	α - AlB_{12}
Al (1)	8b	35.1 (6)	71.7 (7)
Al (2)	8b	29.1 (7)	49.1 (3)
Al (3)	8b	38.7 (7)	24.0 (6)
Al (4)	8b	0	15.0 (3)
Al (5)	8b	0	2.1 (5)
Be (1)	8b	46 (3)	0
Be (2)	4a	42 (6)	0

mechanism is characteristic for the IVC.^{39,52} It is obvious that the effect of introducing beryllium into α -AlB₁₂ can be phenomenologically compared with the effect of hydrogenation of semiconductors such as amorphous Si, Ge, and others.¹

3.4. Photoconductivity. Most high-boron semiconductors with a complicated crystalline structure do not exhibit significant photoconductivity. This is apparently linked with the large number of localized states—trapping centers for photocarriers, as in the case of unhydrogenated amorphous semiconductors.¹

The spectral dependence of the photoconductivity of LiAlB₁₄—a semiconductor with a comparatively simple structure ($N = 50$)—was recently studied in Ref. 53.

The kinetics of the photoconductivity of β -rhombohedral boron was studied in a number of works,^{54–56} where the existence of a long relaxation time was observed. The character of this relaxation is similar to that observed for amorphous semiconductors with a high density of trapping centers whose energy is distributed around E_g (Fig. 10a).

Investigations of thermally stimulated currents made it possible to determine the parameters of some localized states in the gap of β -rhombohedral boron.^{57–59}

Oscillations of the photocurrent at low temperatures and in strong electric fields were observed in Ref. 57 (Fig. 10b). Temperature-induced and IR quenching of photoconductivity were also observed.^{55,57} All these results can be interpreted on the basis of Rose's model,⁶⁰ which is often employed to analyze the photoelectric properties of amorphous semiconductors, in particular, amorphous hydrogenated silicon.⁶¹

3.5. Thermal conductivity. The electronic component does not make an appreciable contribution to the thermal conductivity of high-boron semiconductors owing to their low electrical conductivity.

The thermal conductivity κ of the crystalline lattice of the materials studied changes in a regular fashion as the number of atoms in the unit cell increases, i.e., as the degree of complexity of the crystalline structure increases (Fig. 11), and approaches in magnitude the thermal conductivity of amorphous boron.

The character of the temperature dependence of the thermal conductivity changes as the crystalline structure becomes more complex. In Ref. 62 it was pointed out that there exists a wide temperature range ($T \gtrsim 450$ K) in which the

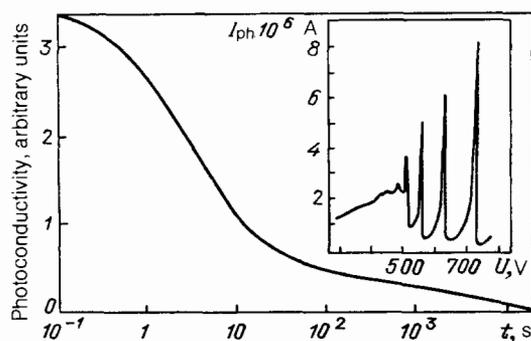


FIG. 10. The relaxation of the photoconductivity of β -rhombohedral boron ($T = 300$ K).⁵⁶ The oscillations of the photocurrent of β -rhombohedral boron are shown in the inset ($T = 107$ K).⁵⁷

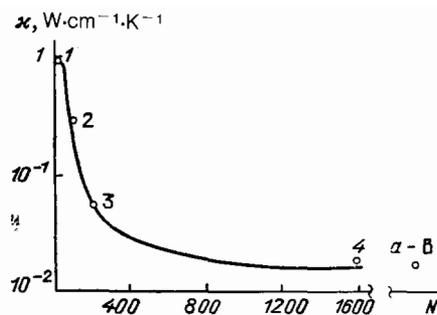


FIG. 11. The thermal conductivity as a function of the number N of atoms in a unit cell ($T = 300$ K).⁸ 1) B₁₃P₂, 2) β -rhombohedral boron, 3) α -AlB₁₂, 4) GdB₆₆ (the thermal conductivity of amorphous boron is also shown in the figure).

thermal conductivity of β -rhombohedral boron is constant, which is not characteristic for crystals. At sufficiently low temperatures, however, there is a section where the thermal conductivity drops as the temperature increases, like the thermal conductivity of crystals.

It was later established that the temperature behavior of the thermal conductivity changes as the crystalline structure of high-boron semiconductors becomes more complicated: for α -AlB₁₂ ($N \approx 200$) the thermal conductivity is constant starting at lower temperatures⁶³ and for MB₆₆ ($N \approx 1600$) the thermal conductivity does not drop anywhere as the temperature is increased.⁶⁴

The data on the thermal conductivity of YB₆₆, obtained at the lowest temperatures, are very interesting: the temperature dependence is close to the form $\kappa \sim T^2$, as is characteristic for amorphous semiconductors⁶⁵ (Fig. 12). It is obvious that κ does not depend on the variation of the composition in the region of homogeneity near YB₆₆. For boron carbide—also phases of variable composition, but with a simpler crystalline structure—the thermal conductivity does depend on the composition,⁶⁵ indicating that the scattering of phonons by structural defects is significant.

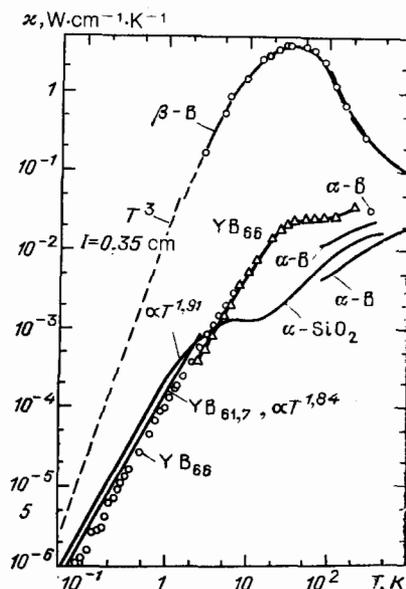


FIG. 12. The temperature dependences of the thermal conductivity of β -rhombohedral boron, YB_{66(61.7)}, amorphous boron (α -B), and SiO₂.⁶⁵

Thus the mechanism of heat transfer in compounds with a complicated crystalline structure is obviously similar to that in an amorphous material.

Data on the high velocity of sound in the materials studied— $v \approx 10^6$ cm/s—are of undoubted interest.⁶⁶ This is because the elastic moduli of these refractory crystals are high and the density of the crystals is low.

The low density of crystals of high-boron semiconductors, in its turn, is due not only to the low atomic weight of boron but also the “openness” of the crystalline structure, previously observed as a characteristic property inherent to these materials.

As emphasized above the crystals studied have a low thermal conductivity.^{62–67} In Ref. 62 the thermal conductivity of β -rhombohedral boron was determined using the well-known Leibfried–Shleman formula for crystals: the computed value of the thermal conductivity is much greater than the experimental value. Based on this it was concluded in Ref. 62 that the mechanism of heat transfer is not standard. The Leibfried–Shleman formula, however, very rarely gives values of the thermal conductivity that agree satisfactorily with the experimental values. In this connection the fact that there is no correlation between the values of the thermal conductivity and the coefficient of thermal expansion is obviously more significant.

Based on the anomalously low value of the thermal conductivity for the crystal one would expect that the coefficient of thermal expansion would be anomalously high, but, as one can see for the example of β -rhombohedral boron, this is not observed.³⁸ The situation here is similar to that for an amorphous material: for SiO_2 , in particular, at room temperature $\alpha \approx 10^{-2}$ $\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$, and the coefficient of thermal expansion (linear) is $\sim 0.7 \cdot 10^{-6}$ K^{-1} , i.e., both values are small.

3.6. Optical absorption tails. A characteristic property of an amorphous semiconductor is the Urbach absorption tail [formulas (16–18)].

A long-wavelength tail at the intrinsic absorption edge was observed for β -rhombohedral boron in Refs. 68–69, and the intensity of the tail increased with the temperature.

A temperature dependent absorption tail was later observed for boron carbide in Ref. 70. In Ref. 6 it was suggested that the existence of this tail is associated with the disordered structure of boron carbide as a phase with variable composition, which is now taken into account in the analysis of electric and thermal transport phenomena.^{28–37}

A temperature-dependent absorption coefficient in the region of the tail was also observed for $\alpha\text{-AlB}_{12}$.⁷¹

We shall examine the results obtained for β -rhombohedral boron, $\alpha\text{-AlB}_{12}$, GdB_{66} , as well as amorphous boron on the spectral dependence of the absorption coefficient at room temperature in order to determine the characteristics of the change in the parameter Γ (16)–(18). These results are presented in Fig. 13.

The values of γ for amorphous boron, GdB_{66} , and $\alpha\text{-AlB}_{12}$ equal 5.2 eV⁻¹, 5.9 eV⁻¹, and 6.6 eV⁻¹, respectively, i.e., the absorption coefficient has a tendency to drop more rapidly as the “distance” from the amorphous material increases.

The data for β -rhombohedral boron do not follow this trend.

First, at room temperature the absorption coefficient is

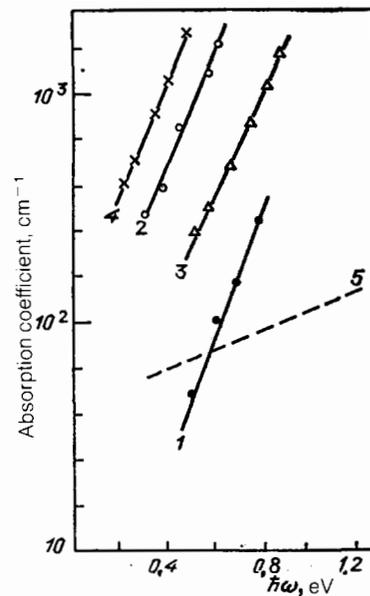


FIG. 13. The long-wavelength tails of the optical absorption. 1) $\alpha\text{-AlB}_{12}$, 2) GdB_{66} , 3) amorphous boron, 4) annealed $\alpha\text{-AlB}_{12}$, 5) β -rhombohedral boron. $T = 300$ K (1–4) and 540 K (5).

so low ($10\text{--}30$ cm^{-1}) that it is virtually impossible to determine its frequency dependence.

Second, the experimental data on the absorption coefficient at high temperatures gives values of the characteristic energy \bar{W} which are anomalously high for the Urbach tail; this is illustrated in Fig. 13. It is found that $\bar{W} \sim 1$ eV.

Thus the temperature dependence of the absorption coefficient of β -rhombohedral boron should be determined by some other factors unrelated with the Urbach rule. Thus the tails α observed for β -rhombohedral boron must be connected with transitions of electrons to the band of localized states, displaced from ϵ_v by 0.5 eV, along which hopping conductivity occurs at low temperatures.⁶⁹

It should also be noted that $\beta\text{-AlB}_{12}$ also does not have an appreciable optical absorption tail at $T = 300$ K.⁷

It can thus be concluded that Urbach tails of optical absorption are characteristic only for materials with the most complicated crystalline structure ($N > 105$).

We shall now consider the data for annealed crystals of $\alpha\text{-AlB}_{12}$ and for $(\text{Be}, \text{Al})\text{B}_{12}$ (modified $\alpha\text{-AlB}_{12}$). Indeed, high-temperature annealing of $\alpha\text{-AlB}_{12}$ increases the density of localized states in the mobility gap and the introduction of Be reduces it, in accordance with which the electrical properties change. Data on the long-wavelength absorption tails confirm that this is a result of the modification of the structure—decrease or increase in the degree of “disorder”: introducing Be into $\alpha\text{-AlB}_{12}$ decreases the intensity of the absorption tail while high-temperature annealing increases it (see Fig. 13).

3.7. IR absorption spectra. We shall now discuss the form of the IR absorption spectra for a number of semiconductors with a different number of atoms in the unit cell (for α -rhombohedral boron the form of the spectrum is presented based on the transmission data).⁷² Figure 14 demonstrates its transformation as the crystalline lattice becomes more complicated: the number of IR absorption bands increases gradually and for GdB_{66} the spectrum becomes structureless, like for amorphous boron.^{6,53,73–76}

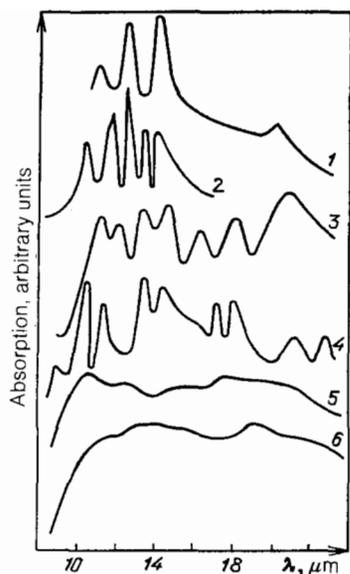


FIG. 14. The form of the IR absorption spectra. 1) α -rhombohedral boron,⁷² 2) LiAlB_{14} ,⁵³ 3) β -rhombohedral boron,⁶ 4) α - AlB_{12} ,³⁹ 5) GdB_{66} , 6) amorphous boron.⁷⁵

The large number of bands in the spectra of the materials studied, their high intensity (α up to $\sim 10^3 \text{ cm}^{-1}$), and the existence of a quite strong continuous background of absorption by the lattice have been repeatedly observed.^{68,6,74} In addition, it should be noted that the dispersion of the permittivity is significant,⁶ which also indicates the existence of an ion-ion component of the bond owing to the nonuniform distribution of the electron density in the complicated lattice. From here follows the appearance of a dipole moment accompanying vibrations and, as a consequence, strong IR absorption. Indeed, IR absorption spectra that are close in character are observed for β -rhombohedral boron, α - AlB_{12} , and $(\text{Be}, \text{Al})\text{B}_{12}$.^{6,39,74} At the same time LiAlB_{14} , which has a significantly simpler lattice, does not have so many strong bands; this agrees with the data on the quite uniform electron density.⁵³

The IR absorption bands of β -rhombohedral boron and α - AlB_{12} are observed against a very strong continuous background. For more complicated crystalline structure (MB_{66}), as already mentioned above, there are no absorption bands, i.e., the spectrum becomes completely continuous, as in the case of amorphous boron. Thus for β -rhombohedral boron and α - AlB_{12} , not all vibrational states are "amorphized" (the quantum-mechanical selection rules ensuring the existence of distinct absorption bands operate), whereas for MB_{66} they are completely "amorphized."

4. MODELING OF THE STRUCTURE OF AMORPHOUS SEMICONDUCTORS

In the preceding section we presented data on the electrical, thermal, and optical properties of high-boron semiconductors. Based on their properties these materials fall between crystalline and amorphous semiconductors. The properties, which change in a regular fashion as the crystalline structure becomes more complicated, become in the limit of the most complicated structures indistinguishable from the characteristic properties of an amorphous semiconductor (quasiamorphous semiconductors).

We shall compare the structure of the crystalline lattices of high-boron semiconductors with the structure of existing models of amorphous semiconductors.

One of the first structural models of amorphous semiconductors was the model of Grigorovich, who proposed it for silicon and germanium.⁷⁷ The structure was represented in the form of spatial packing consisting of pentagonal dodecahedra, connected by some diamond-like units. It is obvious that the crystalline lattice of high-boron semiconductors exhibits a certain similarity with Grigorovich's model. The lattices of high-boron semiconductors are constructed from deformed icosahedra, in most cases connected with one another by groups of isolated atoms. In Grigorovich's model the pentagonal dodecahedra (amorphons) are also coupled by groups of isolated atoms; otherwise it is impossible to achieve sufficiently close spatial packing.

Another outward similarity between the structure of high-boron semiconductors and that of amorphous semiconductors is that in both cases the structures are "open." Indeed, the density of an amorphous body is usually 3–15% lower than that of the corresponding crystal.¹ The low spatial filling of the lattices of high-boron semiconductors and therefore their low density were mentioned above.

Two groups of models are currently used for amorphous semiconductors: models with a continuous random network and microcrystalline models. For some critical sizes of the crystallites the microcrystallite model should be indistinguishable from the continuous random network model.

A characteristic feature of all continuous random network models is the fact that they contain at least 100 atoms: this is the only way that the experimentally determined radial distribution function of the atoms of a given amorphous structure can be made to agree with the function computed for the model of this structure.¹ In other words, at distances equal to several average interatomic distances long-range order vanishes.

We shall compare the structure of the continuous random network model with the structure of the unit cells of crystals of quasiamorphous semiconductors. First, these elementary cells also contain hundreds of atoms. Second, within a unit cell the parameters of short-range order also vary (the coordination numbers, the bond lengths, and the angles between the bonds), but in a manner different from that in the models. In the models one of these parameters (usually the angle between the bonds) changes systematically so that long-range order vanishes at a distance of several bond lengths. In the unit cells of crystals of high-boron semiconductors the atoms can be divided into groups with different short-range order parameters. For example, for β -rhombohedral boron ($N = 105$) the coordination numbers of the atoms are 6, 8, and 9, and the interatomic distances vary in the range 1.70–1.92 Å.¹⁰ In the lattices of MB_{66} ($N = 1600$) the interatomic distances B–B vary over an even wider range (Fig. 15).^{10,78} Such variations in the elements of short-range order are sufficient for the properties of the crystal to be identical to the characteristic properties of an amorphous semiconductor.

The structure of the continuous random network model and the internal structure of the unit cell of crystals of high-boron semiconductors are to a certain extent similar. However the dimensions of the model can, in principle, be in-

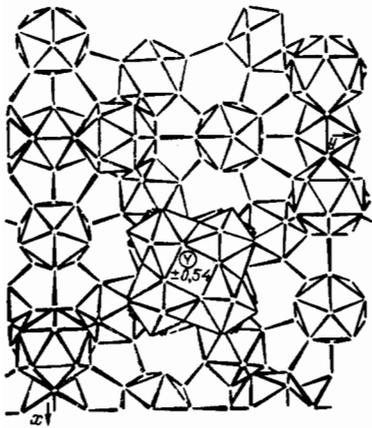


FIG. 15. Fragment of the structure of YB_{66} .⁷⁸

creased to infinity, and the lattice constant of the most complicated crystals is $a_0 \approx 23\text{--}25 \text{ \AA}$. Thus it is not necessary to model an amorphous body as a crystal with infinite unit cells: as shown experimentally, for the formation of the characteristic macroscopic properties it is irrelevant whether or not long-range order is present at distances $\sim 20 \text{ \AA}$ (if the variations of the short-range order parameters in the corresponding element of the structure are significant).

The established values of a_0 are identical to the critical dimensions of the crystallites ($\delta \approx 20 \text{ \AA}$), for which the electrical properties of films of hydrogenated silicon transform from the characteristic "amorphous" properties to the crystalline properties.⁵

If an $\alpha\text{-Si:H}$ film with $\delta < 20 \text{ \AA}$ is regarded as a microcrystallite model of an amorphous semiconductor, then the conditions for this model to be indistinguishable from the model of a continuous random network may be regarded as determined. Apparently films of a hydrogenated semiconductor are especially suitable for being regarded as a microcrystallite model: in this case the defects (broken bonds) in regions of the microcrystallite near the boundaries are passivated by hydrogen atoms, as a result of which band bending in the regions is minimized. The existence of boundaries then leads only to vanishing of long-range order.

We note that for $\delta \approx 20 \text{ \AA}$ a microcrystallite of boron contains about 1000 atoms, which is very close to the number of atoms in a unit cell of MB_{66} crystals.

5. CONCLUSIONS

Analysis of the electrical, thermal, and optical properties of high-boron semiconductors has made it possible to identify them as a new class of materials—quasiamorphous semiconductors. On the one hand these materials are chemically stable crystals with a high melting point and high hardness, while on the other they also exhibit the characteristic properties of amorphous semiconductors.⁷⁹ For this reason, being unique materials, they are of undoubted interest for the physics of semiconductors and solid-state physics.

We emphasize that quasiamorphous semiconductors cannot be modeled in the same manner as the comparatively recently discovered quasicrystals—metallic alloys, obtained by means of rapid solidification ($\sim 10^6 \text{ K}\cdot\text{s}^{-1}$), which have an icosahedral cluster structure and orientational ordering. Based on this, their structure is often modeled in the form of

a Penrose mosaic,⁸⁰ and quite a number of such materials is now known: Al_6Mn ($[x] = ,^x$), Al_4Mn [83], $Al_{94-x}Si_xMn_x$ ($x = 14, 16, 18, 22, 24,$ and 26) [84], $Mg_{32}(Al,Zn)_{49}$ [85], Mg_4CuAl_6 [86], $Al_{13}Fe_{14}$ [87], $(Ti_{1-x}V_x)_2Ni$ ($z = 0\text{--}0,3$) [88], $Al_{86}M_4$ ($M = \text{Co}, V, Ni, Ti, Cu$) [89] and others. It is believed that structurally they fall between crystals and amorphous solids,^{80–89} which is what gives them their name.

An analogy between the structures of quasicrystals and high-boron phases was pointed out in Ref. 90. It is obvious, however, that the analogy lies only in the fact that in both cases the basic unit is an icosahedron; the quasicrystals are low-temperature phases, whose structure, unlike that of the crystal, does not have translational symmetry. Moreover, it has been proposed recently that quasicrystals are a mixture of noncrystalline and poorly crystallized finely dispersed phases ("nanocomposites").⁹¹ Indeed, in many cases several phases have been observed in quasicrystals,^{84,92–94} so that the nature of the structure of these materials remains controversial.

Icosahedral clusters have also been observed in the amorphous modification of boron.^{95,96} As is well known, icosahedral packing is in general the most efficient packing with formation of atomic clusters. In this respect amorphous boron is close to quasicrystals of metallic alloys. The existence of B_{12} icosahedra in crystalline materials is nonetheless not a necessary condition for the appearance of properties characteristic for amorphous semiconductors. Indeed α -rhombohedral boron^{8,97,98} and $B_{13}P_2$ are ordinary crystals, but as their crystalline structure becomes more complicated (N increases) their properties gradually transform ($\beta\text{-AlB}_{12}$, $MgAlB_{14}$, β -rhombohedral boron, $\alpha\text{-AlB}_{12}$, $B_{14}Si$, etc.^{7,8,99–104}) until they become indistinguishable from the properties of amorphous semiconductors (MB_{66} , where M is a rare-earth element (r.e.e.) (Refs. 9, 75, 105–108).

The question of the nature of the "disorder" in such crystals must be studied separately, because based on the standard ideas localization of electronic states is impossible with an ideal periodic structure, no matter how large the periodicity constant a_0 is.

From the viewpoint of possible Anderson localization¹ it is necessary to determine the reason for the appearance of fluctuations in the potential field of the crystal. In Ref. 109 they were attributed to the isotropic composition: boron has two isotopes, B^{10} and B^{11} ($\sim 20\%$ and $\sim 80\%$ of natural boron, respectively). For Anderson localization, however, in this case it is necessary to assume supernarrow electronic bands: $\sim 10^{-4}\text{--}10^{-5} \text{ eV}$.¹⁰⁹

The assumption of narrow bands in a semiconductor with a large lattice constant and complicated unit-cell structure appears in itself to be reasonable: completely equivalent atoms are located next to one another at distances of the order of tens of average interatomic distances, and the overlapping of the corresponding wave functions will be small. In this case the distortions of the potential field of the crystal owing to thermal oscillations or the presence of uncontrollable impurities should be less important than usual. This explanation of the existence of "disorder" in lattices that do not have the most complicated structure can probably be accepted: judging from the Urbach tails, the absorption characteristics, and the IR absorption spectra such semicon-

ductors with $N \approx 100-200$, based on their properties, are only partial analogs of amorphous semiconductors. It should be noted that the calculations of the distances between the centers of localization for them based on the formulas (19) and (20) appear to be completely reasonable, indicating that the concept of minimum metallic conductivity in the form (20) is applicable, i.e., in accordance with the Anderson localization criterion.

When N is increased by an order of magnitude for semiconductors with a more complicated crystalline structure the electrical, optical, and thermal properties become completely analogous to the corresponding properties of amorphous semiconductors: the "disorder" in the structure appears to be sufficient for this. In this case Anderson's approach is not applicable; this is confirmed, in particular, by calculations of the value of a (the distance between the centers of localization) using the formula (20). It is precisely these materials (N is of the order of thousands of atoms in a unit cell) that should be regarded as the natural structural models of amorphous semiconductors.

Thus to model the structure of an amorphous semiconductor elements containing hundreds of atoms are studied. In so doing three different cases are singled out:

1) the parameters of short-range order vary continuously and in a manner so that at a distance equal to several average interatomic distances the long-range order vanishes (the model of a continuous random network);

2) the parameters of short-range order are conserved within the indicated structural element and long-range order vanishes at the boundary (microcrystallite model); and

3) the parameters of short-range order vary within a unit cell of the crystal and long-range order, naturally, exists (the unit cell of a crystal of high-boron semiconductor is the natural model).

In spite of the fundamental differences in the structure of all these three models they describe objects with the same properties, characteristic for an amorphous semiconductor. The first two models have been known for a long time and are widely known, and the third model was first substantiated in Ref. 110.

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