

THE BAND STRUCTURE OF DIAMOND

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I. INTRODUCTION

IN recent years important progress has been achieved in the study of the band structure of crystals. The combination of theoretical calculations and experimental methods of investigation has made it possible to obtain, for a number of crystals, reliable information about the structure of the energy bands in wave-vector space and about the magnitudes of the interband transitions in the neighborhoods of the principal points and directions of the Brillouin zone.

It is well known that the singularities of the structure of the energy bands in k-space determine the majority of the physical properties of a crystal. Therefore, even though until comparatively recently band theory had not reached beyond the limits of the interests of a narrow circle of theoretical physicists, just now it is attracting the attention of an ever wider circle of investigators and practical persons.

Among all known crystals, diamond certainly occupies a special position—it is a wide-band semiconductor, being characterized together with its unique hardness by high thermal conductivity, stability with respect to corrosive surroundings even at high temperatures, and small specific heat.

One can count several dozens of articles which are directly devoted to theoretical and experimental investigations of the band structure of diamonds. However, unfortunately these articles are frequently of a sketchy nature; moreover they are scattered among various sources, mainly foreign. It is impossible to name even a single unified article which is devoted to the band structure of diamonds, neither from the domestic articles nor from the foreign works.

The present review article to some extent attempts to fill this vacancy. In addition, the basic physical properties of diamonds are briefly discussed and also the applications of diamonds in the electronics industry and in instrument manufacture.

II. THE STRUCTURE OF DIAMOND

As long ago as the end of the 18th century, it was known that diamonds are composed of carbon atoms. However, the complete structure of diamond was deciphered much later, in 1913, with the aid of x-rays.

The elementary cubic cell of the diamond structure is shown in Fig. 1. Atoms are located at the corners of the cube (for easy visualization, the atoms are represented on the figure in the form of spheres). One atom is also located at the center of each face. Four more atoms are distributed inside the cube. For this, the cube can be imagined to be divided according to volume into eight equal parts, and these four atoms are located at the centers of such "eighths." However, they do not occupy all eight centers but only four of them, so that the "eighths" with occupied centers alternate with the unoccupied ones. A large number of such cubes, laid right next to each other so that they fill a certain space without any gaps, forms the space lattice of the diamond structure. The lattice constant (the edge of the cube of the elementary cell) is equal to 3.57 Å.^[1]

A simple calculation shows that eight atoms occur in each elementary cubic cell, and one cubic centimeter of diamond contains 1.76×10^{23} atoms.^[2]

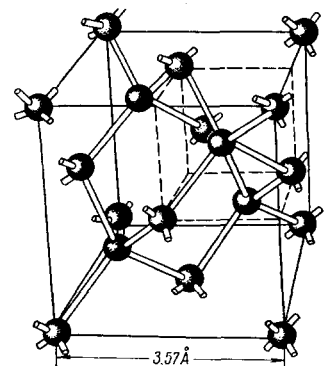


FIG. 1. The elementary cubic cell of the diamond structure. The tetrahedral system of bonds between the atoms in the lattice is shown in the Figure.

It is easy to establish that the structure of diamond consists of two interpenetrating identical face-centered cubic lattices, displaced one with respect to the other along the space diagonal of the cube by a distance equal to one-fourth the length of this diagonal, thus forming one face-centered lattice with a basal plane which contains two atoms with the coordinates $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$.^[3]

The tetravalent carbon atoms in the diamond structure are bound to the four nearest-neighbor atoms, which are distributed in a tetrahedron. A bond is achieved in each of the four directions by using a single valence electron from each atom. Such electron pairs, possessing antiparallel spins, form homopolar or covalent bonds.

Without dwelling in detail on the nature of homopolar forces, we note that a homopolar bond possesses a direction. Therefore, the forces which bond the carbon atoms together are oriented along crystallographic directions. Homopolar forces guarantee a very stable bonding of the atoms in the crystal. This explains, in particular, the unique hardness of diamond.

The cohesive energy E_{coh} of diamond has been calculated according to the formula^[4]

$$E_{\text{coh}} = \frac{\Theta}{2} + \frac{E_{\text{el}}}{N} - E_{\text{fa}}, \quad (1)$$

where Θ denotes the electrostatic energy of one lattice ion due to the interaction with all other lattice ions and the uniform gas of valence electrons, E_{el} is the total energy of the system of valence electrons, N is the number of lattice ions, and E_{fa} is the energy necessary to remove the four valence electrons from the free atom.

The calculated numerical value $E_{\text{coh}} = 6.1$ eV/atom approaches the experimentally determined value for the cohesive energy of diamond, 7.3 eV/atom.^[4]

The distribution of the electron density and of the charges in the diamond lattice has been the object of numerous experimental and theoretical investigations.^[4-10, 126] It has been established that the major portion of the valence electrons is localized in the direction of the bonds between nearest neighbors (1.2 electrons per band^[4]). In this connection the density of the electrons at the center of the bond is roughly twice as large as it is at the midpoint between the bonds. The fact that the diamond lattice^[11] has such an "open" nature facilitates the introduction of atoms of different elements into it during the process of crystal growth.

III. FORMATION OF THE ENERGY BANDS

An isolated carbon atom has the electron configuration $1s^2 2s^2 2p^2$ (see Fig. 2a). However, in such a form it is not yet ready for introduction into the lattice. The point is that in the 2s-shell there is only one orbital in which two paired electrons with oppositely directed spins are located. But unpaired electrons are necessary in order to form the covalent bond. Therefore, one of the electrons of the 2s-shell of a carbon atom which participates in the formation of the diamond lattice goes over into the 2p-shell, which contains three orbitals although there are only two electrons. Such an atom has the electron configuration $1s^2 2s^1 2p^3$ (see Fig. 2b), that is, one valence electron in the 2s shell

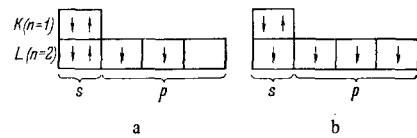


FIG. 2. The electron configuration: a) an isolated carbon atom, b) a carbon atom in the diamond lattice.

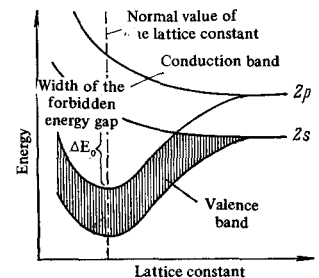


FIG. 3. Diagram showing the formation of the energy bands in diamond.

and three unpaired valence electrons in the 2p shell.

The process of the formation of the band structure of diamond is schematically shown in Fig. 3. As long as the atoms are located at large distances from each other their electric fields do not interact, and therefore their wave functions and energy levels are similar to those which correspond to isolated atoms. However, this system contains N levels of the same energy, where N is the number of atoms.

As the atoms approach the distance which is characteristic of the solid state, their electric fields enter into the interaction. As a result, each level of the previously isolated atom splits into N levels which are very close to each other. The distance between neighboring levels amounts to a very small quantity (of the order of 10^{-22} to 10^{-23} eV). Therefore, one can regard the collection of levels as a continuous band—the energy band.

The forbidden levels of the electrons also merge together into bands—the forbidden bands.

In the 2s- and 2p-shells an isolated carbon atom has eight quantum states, of which only half of them are occupied.

For large values of the lattice constant the lower band (corresponding to the 2s shell) is completely filled, and the upper band (corresponding to the 2p shell) is partially filled. As the atoms approach one another, the eight quantum states of each are distributed equally between the two bands. In this connection the lower band turns out to be completely filled by $s + p$ electrons, but there is not a single electron in the upper portion of the band (if we do not consider the electrons which may happen to hit there as a result of excitation).

At the distance equal to the normal value of the lattice constant, a forbidden energy gap of width ΔE_0 is formed between the lower valence band and the upper conduction band.

A complete description of the energy bands of a crystal, from both the qualitative side as well as from the quantitative side, can be obtained by solving the Schrödinger equation

$$-\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \psi - \frac{\hbar^2}{2} \sum_\alpha \frac{1}{M_\alpha} \nabla_\alpha^2 \psi + \frac{1}{2} \sum_i \sum_j \frac{e^2}{r_{ij}} \psi + U_0(\mathbf{R}_\alpha) \psi + U'(\mathbf{r}_i, \mathbf{R}_\alpha) \psi = E\psi, \quad (2)$$

where r_i and R_α denote, respectively, the coordinates of the electrons and of the nuclei ($i = 1, 2, \dots$; $\alpha = 1, 2, \dots$), $\psi(r_i, R_\alpha)$ is the wave function of the crystal, and E denotes the total energy of the crystal.

The first term in Eq. (2) corresponds to the kinetic energy of the electrons, and the second term in (2) corresponds to the kinetic energy of the nuclei. The factors associated with ψ in the following terms on the left-hand side of (2) correspond, respectively, to the following: the potential energy of the interaction between the electrons, the potential energy of the interaction of the nuclei, and the potential energy of the interaction between the electrons and the nuclei.

However, the complete solution of Eq. (2) is actually a problem which remains incomplete up to the present day, but its approximate solution can be achieved by means of the systematic introduction of a number of notable simplifications.

The first significant approximation is the division of the particles into external or light (valence electrons) and internal or heavy (the atomic cores containing the nucleus with all of the electrons except for the valence electrons). In this connection it is assumed that the atomic core, which is usually called the nucleus for the sake of brevity, is a localized system to a sufficient degree of accuracy. This approximation makes it possible to regard the motion of the electrons at any given instant as occurring in the field of fixed nuclei, and excludes the possibility of energy exchange between the electron and nuclear systems, which is expressed mathematically by representing the wave function in the form of the product of a nuclear wave function times the electronic wave function:

$$\psi(R_\alpha, r_i) = \xi(R_\alpha) \psi_n(r_i, R_\alpha). \quad (3)$$

If (3) is substituted into (2) and the second summation in Eq. (2), containing terms which depend only slightly on the coordinates of the electrons and which are small in comparison with their kinetic energy, is neglected, then Eq. (2) decomposes into two independent equations describing, respectively, the motion of the nuclei and of the electrons. The first equation is not considered in band theory, and the second has the form

$$-\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \psi_n + \frac{1}{2} \sum_i \sum_j \frac{e^2}{r_i r_j} \psi_n + U'(R_\alpha, r_i) \psi_n = E_n(R_\alpha) \psi_n; \quad (4)$$

here the R_α are to be regarded not as variables but as the fixed coordinates of the sites in a lattice of given symmetry, on which the potential energy of the system and the total energy of the electrons depend.

The next assumption consists in replacing the exact configurational interaction between the electrons, acting on each electron, by an average effective field, the so-called self-consistent field. In this connection the double sum $\frac{1}{2} \sum_i \sum_j (e^2/r_{ij})$ in Eq. (4) is replaced by a term of the form $\sum_i U''(r_i)$, i.e., the instantaneous

interaction of each electron with all of the remaining electrons is replaced by a sum of potential terms, each of which describes the energy of the corresponding electron in the self-consistent field. As a result Eq. (4) decomposes into one-electron equations:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + [U(r) - E] \psi(r) = 0 \quad (5)$$

(here the corresponding indices for E and ψ are omitted).

The potential energy $U(r)$ of each individual electron depends on all of the remaining electrons. Therefore, in the general case the investigation of the electronic states of a physical object containing N electrons reduces to the simultaneous solution of N equations of the type (5), which is a hopelessly difficult problem. Fortunately, in the case of a crystal a substantial alleviation of this problem is contained within the crystal itself, namely in one of its remarkable properties—symmetry. In fact, from the identity of the internal field at crystallographically identical points it follows that the potential energy of the electron possesses the same elements of symmetry as the crystal lattice itself, including translational symmetry. Therefore, if the crystalline lattice is in fact the model for the atomic structure of the crystal, then one can go further, namely, one can attempt to create a mathematical model of its electronic structure. Thus arose the concept of Brillouin zones.^[12]

IV. THE BRILLOUIN ZONE

The scope of the present review article does not permit us to discuss in detail the theory of Brillouin zones, all the more since this question has been elegantly described in the book^[13]. Here we shall confine our attention to just a few remarks.

According to Bloch's theorem, the solution $\psi_k(r)$ of Eq. (5) has the form

$$\psi_k(r) = e^{ikr} u_k(r), \quad (6)$$

where $u_k(r)$ is a periodic function having the period of the direct lattice, and k is the wave vector.

Differentiating expression (6) twice with respect to r and substituting $\nabla^2 \psi$ and ψ into Eq. (5), we obtain the following differential equation for $u_k(r)$:

$$-\frac{\hbar^2}{2m} \nabla^2 u - \frac{\hbar^2}{2m} \cdot 2ik \nabla u + \left[U(r) + \frac{\hbar^2 k^2}{2m} - E \right] u = 0. \quad (7)$$

Equation (7) enables us to determine the energy E as a function of the wave vector k , that is, to determine the function $E(k)$ which is of fundamental significance for the investigation of the electronic states in a crystal. From here it is natural to conclude that it is meaningful to construct a model of the electronic structure of a crystal in k space. Another characteristic property of this model is due to the discrete nature of the electron's energy.

The Brillouin zones are regions in k -space, inside of which the energy E is a quasicontinuous function of k , but E undergoes discontinuities at the boundaries.

The eigenvalues of the energy of an electron, existing in the periodic field of the crystal, are periodic with respect to the reciprocal lattice.^[14] Therefore, in order to obtain an unambiguous labeling of these eigenvalues, it is natural to confine the region of variation of k within the limits of the primitive cell of the reciprocal lattice. Generally speaking one can choose the primitive cell by different methods, but it is most convenient of all to take, as the boundaries of this cell, planes which bisect the lines connecting the point $k = 0$ with the nearest lattice sites of the reciprocal lattice.

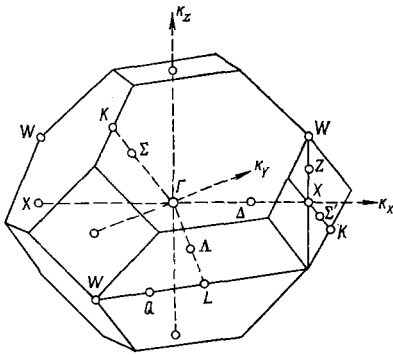


FIG. 4. Brillouin zone.

Such a cell is called the first (reduced) Brillouin zone, or simply the Brillouin zone. This is therefore the mathematical model for the electronic structure of diamond. In what follows we shall start from the fact that the vector \mathbf{k} is reduced to the first zone.

The lattice, which is the reciprocal to a face-centered cubic lattice, is a body-centered cubic. Therefore, the Brillouin zone of diamond is the Wigner-Seitz cell of a body-centered cubic lattice. From elementary geometrical considerations it follows that the Brillouin zone of diamond contains two atoms.

The Brillouin zone of diamond is shown in Fig. 4, where the symmetry axes and the principal symmetry points are indicated. The components of the wave vector \mathbf{k} are taken relative to a Cartesian coordinate system whose origin is located at the center of the zone, the point Γ . This zone possesses complete cubic symmetry with respect to the point Γ . The axis Δ corresponds to the direction $[1\ 0\ 0]$, the axis Λ corresponds to the direction $[1\ 1\ 1]$, and the axis Σ —to the direction $[1\ 1\ 0]$. The following principal symmetry points are of most interest: the point Γ , the centers L of the hexagonal faces, the centers X of the square faces, the points W formed by the intersection of two hexagonal and one square face, and the points K .

The coordinates of these points are as follows:

$$\begin{aligned} \Gamma &= (0, 0, 0), \quad X = \frac{2\pi}{a}(1, 0, 0), \quad L = \frac{\pi}{a}(1, 1, 1), \\ W &= \frac{2\pi}{a}(1/2, 0, 1), \quad K = \frac{2\pi}{a}(3/4, 3/4, 0). \end{aligned} \quad (8)$$

However, the basic problem consists not in determining the shape of the Brillouin zone, since it is determined if the Bravais lattice of the crystal is known, but in calculating the values of the energy as a function of the wave vector \mathbf{k} at each point of the Brillouin zone. Figuratively speaking, the Brillouin zone as it is represented in Fig. 4 can be likened to a topographical map, on which the terrain is indicated by relief and the coordinates of the reference points are given, but the referencing of these points to the terrain is not made (i.e., their height above sea level and so forth is not indicated). The "referencing" of the electronic states to the principal points and to the symmetry axes of the Brillouin zone was brilliantly carried out in^[15], published in 1936.

Using the mathematical apparatus of group theory, the authors of^[15] carried out an analysis of the symmetry of the wave functions in crystals and, on the basis of their investigation, gave a classification of

the electronic states for the principal symmetry points and symmetry axes of the Brillouin zone for cubic lattices, comparable with the well-known classification of the atomic orbitals in spectroscopy. The size of the present article does not permit us to present the complete classification of the electronic states in the Brillouin zone of diamond. The reader can obtain all essential information about this problem both from^[15] as well as from the later articles,^[13,16] and from the particular elements of this classification which we will encounter in the following sections of this article.

V. QUANTITATIVE CALCULATIONS OF THE ENERGY BANDS

The results given in article^[15] lie at the foundation of all subsequent investigations of the electronic states in crystals. However, major difficulties were ahead. In order to make a quantitative calculation of the energy bands of crystals, it was necessary to develop approximate methods of solving the Schrödinger equation, which continued to remain a hard nut to crack, even after being forced into the framework of the Brillouin zone. In addition, reliable initial data and in the first place numerical values of the potential energy $U(\mathbf{r})$ were required. Unfortunately, even up to the present day it is impossible to determine the self-consistent field of the valence electrons in crystals, even if only to that same degree of reliability as this is done for the spherically-symmetric self-consistent field in an atom. In short, there turned out to be too many unknowns in the problem, and nobody was in a position to indicate a unique path which would lead to its solution. It is not surprising that a crystal such as diamond, which is so interesting in many respects, became the touchstone for the testing of different methods of calculating the energy bands.

1. Short Review of the Characteristics of the Different Methods of Calculation

The first description of the electronic structure of diamond, which in its general features is similar to the ideas which exist even up to this day, appeared in 1935.^[17] At the same time, certain erroneous conclusions were contained in article^[17], which was carried out by the method of the Wigner-Seitz cell,^[18] these errors being primarily due to the imperfect calculational techniques of that time. Therefore both^[17] as well as article^[19], which was published almost simultaneously and carried out by using the same method, are only of historical interest at the present time. The next investigation of the band structure of diamond^[20] appeared only after 14 years. It was carried out by using the method of a linear combination of atomic orbitals (LCAO),^[21] based on the possibility of constructing functions of the Bloch type in the form of linear combinations of atomic wave functions, each of which is localized near a certain definite atom.

In the case of diamond the necessity arises to investigate all eight atomic functions describing the 2s level and the triply degenerate 2p level ($2p_x$, $2p_y$, $2p_z$) of each of the two atoms contained in the reduced Brillouin zone, that is, the problem reduces to the solution of an eighth-order secular equation. Unfor-

unately, the value of article^[20] was lessened to a considerable extent by a number of mistakes which were made in the calculations.

The intensive development of computational techniques and the appearance of high-speed electronic computers at the beginning of the 1950's facilitated further progress in the investigation of the band structure of diamond. During the period from 1952 to 1954, several articles devoted to this problem appeared at once.

The assault on the energy bands of diamond started simultaneously along four directions.

a) The method of orthogonalized plane waves (OPW)^[22] appeared as the result of an aspiration to eliminate an inherent defect from the LCAO method, consisting in the fact that outside of the atomic core, where the potential essentially does not vary, the atomic wave functions fall off too rapidly. In other words, the wave functions of the ionized states, i.e., plane waves, are completely excluded from consideration.

The essence of the OPW method consists in the fact that the wave functions of the external electrons, represented in the form of a linear combination of plane waves, are orthogonalized in the quantum mechanical sense with respect to all the wave functions of the electrons in the ionic core.

The calculation of the structure of the energy bands of diamond, carried out by Herman^[23] using the OPW method, gave results which are quite compatible with contemporary ideas.

b) Slater and Koster,^[24] returning to the LCAO method but performing the calculations more correctly, obtained results which are compatible with the results of article^[23] in regard to the main features. However, it should be noted that numerical values of certain parameters, which were obtained by using the OPW method,^[23] were used in^[24].

c) Hall^[25] proposed the method of equivalent orbitals for the calculation of the electronic structure of diamond; this method consists in the fact that orbitals of molecular type (crystal or molecule) are constructed out of orbitals which are localized in separate parts of the system, usually on valence lines. In this connection, as a consequence of the crystal symmetry the localized orbitals break up into groups such that all the orbitals of one group give the same type of charge distribution in space, differing among themselves only in regard to spatial position and orientation. This method requires less computational work than the LCAO method, but gives less accurate quantitative results.

d) Zehler^[26] made an attempt to return to the cellular method, modernizing it by the application of a variational principle (the variational cellular method). However, such a modernization did not give a substantial effect. Subsequently none of the investigators has returned to using the cellular method.

As a result of the investigations performed during the time period under consideration, qualitative and quantitative investigations of the structure of the energy bands of diamond in the symmetry directions of type Δ and Λ were completed to the first approximation. Later work, carried out in the 1950's and at the beginning of the 1960's, was devoted to a more accurate

determination of the numerical values of the energy band parameters in the indicated directions. In this connection, the investigations using OPW,^[27,28] LCAO,^[29] and equivalent orbital methods^[30-34] have developed in parallel.

At the beginning of the 1960's effective methods and apparatus were developed for the investigation of crystals deep inside the intrinsic absorption region. These methods, in conjunction with other experimental methods (cyclotron resonance, measurements of the magnetoresistance, etc.), made it possible to obtain valuable information about the band structure of crystals, including information about regions far removed from the extrema of the valence and conduction bands.

Progress in the experimental investigations turned out to have a favorable influence on theoretical research in regard to investigation of the band structure of diamond. A close linkage between theoretical and experimental methods of investigation is characteristic of the period from the beginning of the 1960's up to the present day. In this connection, investigations are being carried out in the following fundamental directions.

a) Experimental corrections are introduced into investigations which are being carried out by "old" methods, for example, by using the OPW method.^[35]

b) "New" semiempirical methods have been developed, here referring primarily to the so-called empirical pseudopotential method (EPM).^[36] This method arose as a logical consequence of the OPW method. In fact, the physical meaning of the process of orthogonalization consists in the fact that a certain potential, describing the repulsion of the electrons from the ions, is added to the true lattice potential. The total effective potential, which is the sum of these two potentials, has obtained the name pseudopotential. If the pseudopotential is determined by some kind of empirical method, for example, by spectroscopy, then the calculation of the energy bands is appreciably simplified.

The first attempts to calculate the electronic structure of diamond by using the EPM are contained in articles^[37,38]. A fundamental investigation of the band structure of diamond using the EPM is given in articles^[39,40].

Another semiempirical method is based on the method of equivalent orbitals. Within the framework of this method, the initial parameters are expressed in terms of the experimentally measurable quantities. In this connection, a quite satisfactory description of the valence band of diamond is obtained.^[41] In the recent articles^[42,43] the applicability of such a method to the investigation of the complete structure of the energy bands for diamond is studied.

c) The gradually increasing tempo of the development of calculational techniques has regenerated interest in a method which for a long time had been regarded as unpromising due to the large amount of computational work required for its accomplishment. The topic of discussion is the method of augmented plane waves (APW), which was first proposed in 1937.^[44] The APW method is based on the assumption that the potential is spherically symmetric in a region

Table I

Symbol for the state	Basis function or type of symmetry	Multiplicity of the degeneracy	Compatibility relations between Γ and Δ , Λ , Σ :		
			Δ	Λ	Σ
Γ_1	1	1	Δ_1	Λ_1	Σ_1
$\Gamma_{25'}$	$\{xy, yz, zx\}$	3	$\Delta_2\Delta_5$	$\Lambda_1\Lambda_3$	$\Sigma_1\Sigma_2\Sigma_3$
$\Gamma_{2'}$	xyz	1	Δ_2'	Λ_1	Σ_3
Γ_{15}	$\{x, y, z\}$	3	$\Delta_1\Delta_5$	$\Lambda_1\Lambda_3$	$\Sigma_1\Sigma_3\Sigma_4$

of radius r_S around each lattice site and is constant in the intermediate regions. In general the radius r_S of the spherical region can be chosen arbitrarily; however, the spheres must not overlap. Therefore, usually r_S is selected for such a calculation in such a way that it will be somewhat smaller than the radius of the Wigner-Seitz sphere. In this connection, the radial Schrödinger equation is solved exactly inside each sphere of radius r_S . Exact solutions in the form of plane waves are also found in the regions outside of the spheres. Finally, by matching these solutions on the surface of each sphere, the solution of the Schrödinger equation is obtained for the entire crystal.^[45]

Up to the present day, the most complete conception of the structure of the energy bands in diamond has been obtained^[46] with the aid of the APW method; we shall return to this later.

2. Diagrams of the Energy Bands

The energy band structure of a crystal is usually represented in the form of diagrams, showing the dependence of the electron energy on the magnitude of the wave vector k in the directions of the symmetry axes of the Brillouin zone.

The starting point for the construction of such a diagram is the center of the band, i.e., the symmetry point Γ , where $k = 0$, and the limiting points in the directions Δ , Λ , and Σ are X, L, and K, respectively, the points at which k has its maximum value in the given direction.

The characters of the fundamental states at the point Γ together with the compatibility relations are given in Table I.

The structure of the energy bands for diamond is shown graphically on Fig. 5 for the direction Δ , Λ , and Σ . Each curve, being a graph of the function $E(k)$ in the appropriate direction, corresponds to a particular band of energy levels. Two diagrams are actually shown in the figure. The first diagram, located on the left-hand side of the figure and bounded by vertical lines on which the energies of the states at the points L and X are plotted, depicts the structure of the energy bands in the directions Λ and Δ . The second diagram, which is located on the right-hand side of the figure, depicts the structure of the energy bands in the direction Σ .

At the center of the Brillouin zone the state Γ_1 , corresponding to the lowest point of the valence band, is the combination of s-functions which are symmetric with respect to the midpoint of the line joining the two atoms. The state $\Gamma_{25'}$, representing the symmetric combination of the p-functions of the two atoms, corre-

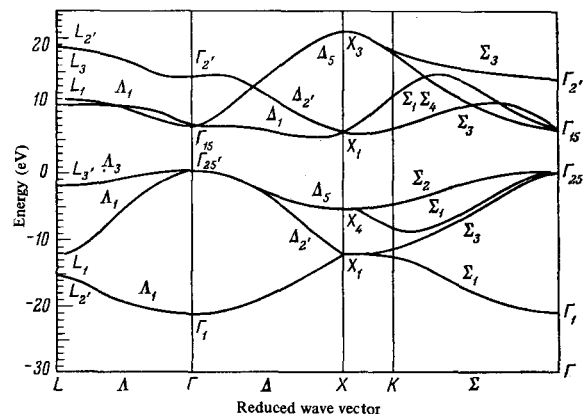


FIG. 5. Structure of the energy bands of diamond. ^[35] The function $E(k)$ is depicted graphically for each of the three directions Λ , Δ , and Σ .

sponds to the top of the valence band. The lowest state Γ_{15} of the conduction band for $k = 0$ is represented by the antisymmetric combination of the same functions. The next state $\Gamma_{2'}$ of the conduction band corresponds to the antisymmetric combination of the s-functions.

First of all let us consider the diagram for the directions Λ and Δ .

The lowest curve shown on Fig. 5 corresponds to the s-band of the valence band. One electron per atom is contained in this band. Starting from the point with minimum energy at $k = 0$, the curve rises either to the left upon increasing k in the direction Λ or to the right upon increasing k in the direction Δ . The two upper curves of the valence band represent bands of p-type levels. One of these bands contains two electrons per atom, but the other only contains one electron per atom. In the direction Δ one of these bands in the vicinity of $k = 0$ is described by an inverted parabola, which flattens out with increasing k , smoothly descending to a meeting with the s-band at the point k_{max} . In this direction the second p-band attains the maximum value of k at a larger value of the energy than the first. In the interval from $k = 0$ to k_{max} the curve, representing the second p-band, changes its slope. In the direction Λ the lower p-band changes its slope in the interval from $k = 0$ to k_{max} and reaches its maximum value at a larger value of the energy than the s-band. The energy of the upper p-band changes relatively little in the interval from $k = 0$ to k_{max} .

The occupation of the valence band by the electrons takes place in the following order. At first the lowest s-band is completed, filling up sooner in the direction Λ than in the direction Δ . After the s-band is filled, the electrons can immediately cross into the p-band, which joins with the s-band in the direction Δ . Thus, there is no forbidden gap between the two sets of energy levels in the valence band. Although such a gap exists in the direction Λ , as a result of the fact that in other directions the bands join with each other, a single continuous band of levels of a mixed s-p type appears.

In contrast to the valence band, in the conduction band the two p-bands are located below and the s-band is above. In the Λ direction both p-bands overlap with each other. In the Δ direction, the s-band changes its slope in the interval between $k = 0$ and k_{max} , and at

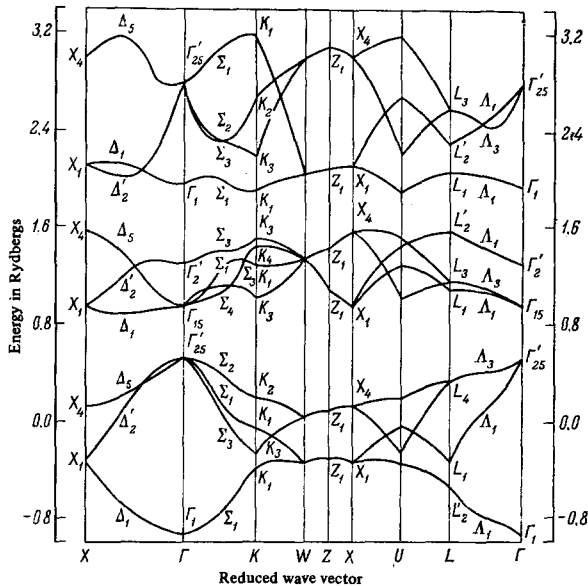


FIG. 6. Structure of the energy bands in diamond, calculated by using the APW method. [46] The energy bands along the principal symmetry directions are indicated. The coordinates of the vectors k are given in Table II.

the point k_{\max} it joins with the p-band. Thus, the conduction band is also continuous. The s-band can contain one electron per atom, and there can be three electrons per atom in the two p-bands. These four states together with the four states of the valence band form the bands of energy levels which correspond to the initial eight levels of an isolated carbon atom (see Fig. 3).

As is evident from Fig. 5, the state of maximum energy in the valence band occurs at $k = 0$, but the minimum energy Δ_1^m of the conduction band is displaced in the Δ direction. In general the six equivalent Δ directions correspond to six identical minima.

As is clear from the right-hand side of Fig. 5, the characteristic property of the band structure of diamond in the Σ direction consists in the fact that in the valence band and in the conduction band there are four separate energy bands, each of which contains one electron per atom. In this connection, the three lower bands of the conduction band are interwoven with each other.

The results of a more detailed investigation of the band structure of diamond [46] are shown in Figs. 6 and 7, where the energy bands along the principal symmetry directions and along the minor symmetry directions, respectively, are depicted.

Numerical designations have been introduced for those symmetry points for which no generally accepted notation [15] exists. The characteristics of the twenty symmetry points for which the calculations were carried out are given in Table II.

As is clear from Fig. 6, the qualitative picture of the valence band and of the lower energy bands in the conduction band, which is obtained as the result of the investigation [46], basically agrees with the results of [35]. Moreover, the work [46] made it possible to explain the interesting property of the conduction band in diamond, consisting in the fact that there is a forbidden gap be-

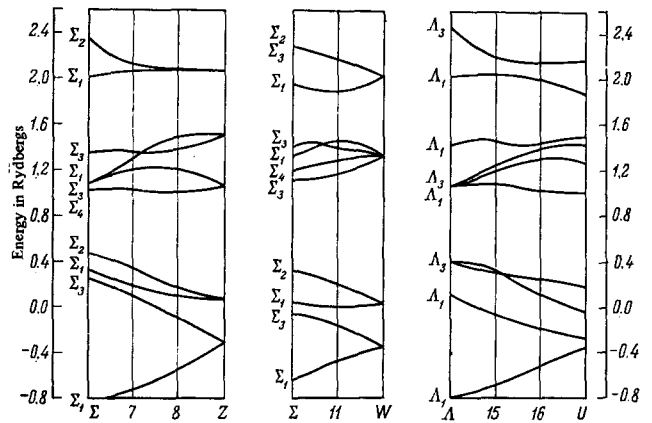


FIG. 7. Structure of the energy bands for diamond, calculated by using the APW method. [46] The energy bands along the minor symmetry directions are shown. The coordinates of the k vectors are given in Table II. The two Σ points, reading from left to right, are $(\pi/4a)(220)$ and $(\pi/4a)(440)$.

Table II

Name of the principal symmetry point	$4(\alpha/\pi)k$	Weight factor	Name of the principal symmetry point	$4(\alpha/\pi)k$	Weight factor
Γ	000	1	Λ_1	640	24
Δ	200	6	W	840	6
Δ	400	6	K	660	4
Δ	600	6	Λ	222	8
X	800	3	15	422	24
Σ	220	12	16	622	24
7	420	24	U	822	8
8	620	24	18	442	24
Z	820	12	Q	642	24
Σ	440	12	L	444	4

tween the first four levels in the conduction band and the following levels.

The graphs of the energy bands, which were considered above, have been constructed without taking the influence of the spin into consideration, i.e., by starting from the assumption that two electrons with oppositely directed spins can be placed in two states which are described by one and the same spatial wave function ψ . The spin-orbit interaction may remove the degeneracy of these states.

In diamond the upper boundary of the valence band corresponds to a state with three-fold orbital degeneracy. However, if spin is taken into consideration, then the degeneracy turns out to be six-fold. The spin-orbit interaction partially lifts the degeneracy, splitting the p-levels into the four-fold degenerate $p_{3/2}$ levels and the doubly degenerate $p_{1/2}$ levels. Here the four-fold degenerate $p_{3/2}$ state corresponds to a larger energy than that of the doubly degenerate $p_{1/2}$ state.

The splittings of all of the states of the type Γ considered above are in accordance with the character tables shown in Table III, where D^{-1} is the operator which transforms the single group into the double group.

A diagram of the energy bands for diamond, with the spin-orbit effects taken into account, is shown in Fig. 8. [47] In diamond the spin-orbit splitting of the valence band is estimated to be 0.006 eV, which is almost a thousand times smaller than the minimum width of the forbidden gap.

Upon a transition to elements with large atomic

Table III

Γ (single group):	Γ_1	Γ_2	$\Gamma_{25'}$	Γ_{15}
$D^1 \times \Gamma$ (double group):	Γ_6	Γ_7	$\Gamma_7 + \Gamma_8$	$\Gamma_6 + \Gamma_8$

Table IV. Energy at the Symmetry Points, in eV

Symmetry points	37 1959	28 1963	29 1964	36 1966	39 1966 r.	35 1966	41 1967	30 1968
Γ_1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\Gamma_{25'}$	21.9	23.2	20.9	19.6	27.7	22.0	18.0	
Γ_{15}	28.0	28.7	26.9	25.4	35	29.1		
Γ_2	37.5		35.3	30.5	39.8	35		
X_4^1	10.5	9.1	10.5	8.1	9	11		
X_4^2	15.2	14.7	16.4	14.4	20.6	15.2		
X_4^3	29.0	27.8	28.1	25.5	33.5	27		
X_4^4			46.6	35	33.5			
L_2^1	5.6	5.5	4.9	5.2	5.1	5.7		
L_1^1	11.7	8.4	13.6	8.0	12.3	8		
L_3^1	17.2	17.8	17.9	17.2	23.9	18.5		
L_2^2	30.9	31.2	26.1	27.5	34.8	30.1		
L_3^2	30.9	28.0	25.3	28.2	36.2	34.5		
$\Gamma_{25'} \rightarrow \Delta_1^m$					5.4	5.47		5.26
$\Gamma_{25'} \rightarrow \Gamma_{15}$	6.1	5.5	6.0	5.8	7.3	7.1		7.33
$X_4^1 \rightarrow X_4^2$	14.2	13.1	11.7	11.1	12.9	11.8		12.9
$L_3^1 \rightarrow L_1^1$	13.7	13.4	8.2	10.3	10.9	11.4		10.88
$K_2 \rightarrow K_3^2$				11.0				13

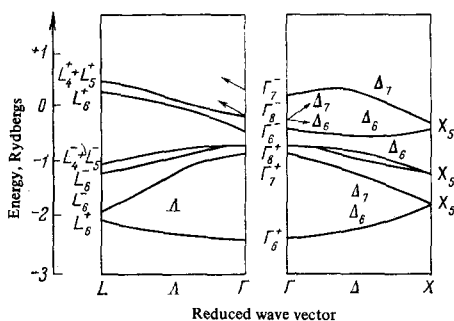


FIG. 8. Structure of the energy bands for diamond with the spin-orbit effects taken into account. [47] For clarity of illustration, the spin-orbit splitting is shown using an enlarged scale.

numbers, the spin-orbit splitting increases appreciably. For comparison, we note that for silicon and germanium the spin-orbit splitting amounts to 0.04 and 0.29 eV, respectively. But even in diamonds, spin-orbit effects can play a definite role in certain special cases, for example, in connection with experiments involving holes if their effective temperature does not exceed 50°K. However, for convenience in calculations, at the beginning the spin-orbit splitting is usually neglected, and then when there is need for them the appropriate corrections are introduced, taking the spin-orbit interaction into account.

3. Comparison of the Results of Different Investigations

An analysis of the theoretical investigations of the band structure of diamond, carried out by different authors using different methods, indicates that the most reliable results are given in articles [28, 29, 35, 37, 39, 40, 41, 46]. Qualitatively the results of these articles are in good agreement with each other, except for isolated unessential details.

A summary of the quantitative results of these arti-

cles is given in Table IV, where in addition to the values of the energy in eV at the symmetry points, the energy values for the fundamental transitions are also given. The literature reference and the year of publication are indicated at the top of each column. For articles in which the numerical values of the energy are not indicated, the values were obtained from the corresponding graphs.

From Table IV it is seen that a specific points certain discrepancies exist between the energy values determined in different articles. The values for the transition energies are in substantially better agreement, especially according to the data given in the latest articles [35, 39, 40] where experimental corrections have been introduced into the theoretical calculations by using one method or another.

VI. INVESTIGATION OF THE BAND STRUCTURE BY OPTICAL METHODS

The edge of the intrinsic absorption band for diamond is equal to $\sim 2250 \text{ \AA}$, which corresponds to an energy $\sim 5.5 \text{ eV}$. It is impossible to attribute this value to the direct (vertical) transition $\Gamma_{25'} \rightarrow \Gamma_{15}$ from the valence band to the conduction band, since according to the latest articles [35, 39, 40], whose data must be regarded as the most reliable, the energy of the transition $\Gamma_{25'} \rightarrow \Gamma_{15}$ is equal to $\sim 7.3 \text{ eV}$. On the other hand, this value identifies well with the energy of the indirect (nonvertical) transition $\Gamma_{25'} \rightarrow \Delta_1^m$ from the valence band to the conduction band. As is well known, such transitions occur only with the participation of phonons.

A detailed study of the optical transmission spectra of several diamonds in the vicinity of the intrinsic absorption edge has been carried out by Clark et al. [48] over the range from 5.0 to 6.0 eV and at many temperatures between 90 and 600°K. As a result of the analysis of the absorption peaks, six phonon energies were recognized. Three of these turned out to be

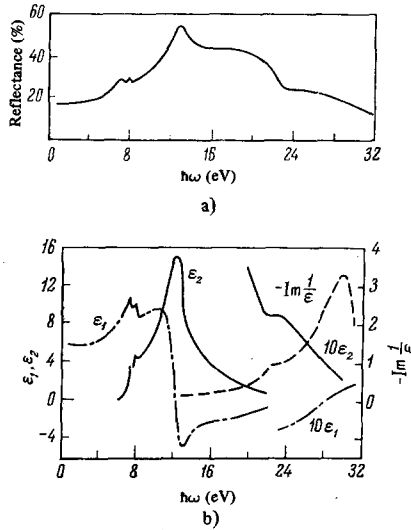


FIG. 9. Graphs of the fundamental optical constants for diamond.

greater than the Raman energy, $(\hbar\omega)_{\text{Raman}} = 0.167$ eV, and represent combinations of two or more phonons having the following energies:

- 1) $(\hbar\omega)_{\text{TO}} = 0.143$ eV (transverse optical phonon);
- 2) $(\hbar\omega)_{\text{LO,LA}} = 0.132$ eV (longitudinal optical, longitudinal acoustic phonons);
- 3) $(\hbar\omega)_{\text{TA}} = 0.083$ eV (transverse acoustical phonon).

The presence of only three phonons with $\hbar\omega < (\hbar\omega)_{\text{Raman}}$ indicates that the lowest minimum of the conduction band is close to the boundary of the reduced zone in the $[100]$ direction (the symmetry point X_1).^[48] At X_1 the longitudinal acoustical and optical phonons are degenerate. The transition $\Gamma_{25'} \rightarrow X_1$ is not forbidden by the selection rules for any type of phonon.

A comparison of the data^[48] with the theoretically calculated values^[35] and with the measured values of $(\hbar\omega)_{\text{LO}}$ and $(\hbar\omega)_{\text{LA}}$ in the infrared region^[49] forces us to assume that the minimum of the conduction band is removed from X/dT by a distance equal to between 5 and 25% of the distance to the center of the Brillouin zone. A transverse optical phonon obviously does not play any role in indirect transitions. The energy (ΔE_g) of the indirect transition from the valence band to the conduction band is estimated to be 5.47 eV at 295°K, and the temperature dependence of (ΔE_g) is expressed by the following formula:

$$(\Delta E_g)/dT = -5.4 \pm 0.5 \times 10^{-5} \text{ eV/deg K.} \quad (9)$$

The binding energy of the indirect exciton is 0.07 eV.^[48]

A description of the experimental techniques and the results of the investigations of the band structure of diamonds by using optical methods are presented in the original and review articles^[50-57]. A typical reflectance spectrum of a type-IIa diamond over a broad range up to the far ultraviolet is shown in Fig. 9 (a), and the real ϵ_1 and imaginary ϵ_2 parts of the complex dielectric constant ϵ and also the energy-loss function, $-\text{Im}(1/\epsilon)$, for a type-IIa diamond are shown in Fig. 9 (b).^[56]

In Table V a summary is given of the basic results

Table V. Interband Energy Differences in Diamond

Transition	Energy (eV)			
	Experimental Values [48,56]	Theoretical Values		
		38	39	40
$\Gamma_{25'} \rightarrow \Delta_1^m$	5.47	5.47	5.4	5.26
$\Gamma_{25'} \rightarrow \Gamma_{15}$	7.3	7.1	7.3	7.33
$\Sigma_2 \rightarrow \Sigma_3$	} 12.2	11.8	12.9	12.9
$X_1^1 \rightarrow X_1^1$				
$\Gamma_{25'} \rightarrow \Gamma_1$	23	22	27.7	

of the experimental investigation of the band structure of diamonds by using optical methods, in comparison with the latest results of theoretical calculations.

As is clear from the table, the experimental results basically confirm current ideas about the energy band structure of diamond, although certain discrepancies exist between the numerical values of specific parameters obtained theoretically and experimentally. Just now it is difficult to indicate the cause of these discrepancies. In any event one would expect that with the continued improvement of techniques in both theoretical and experimental investigations, these discrepancies will become smaller.

From what has been said it is clear that the energy bands of diamond have to sufficient degree a complex structure, which is responsible for all the diverse transitions of the charge carriers from one state to the other both inside the isolated ellipsoidal regions as well as between these regions, and which is consequently responsible for the large number of optical transitions (both vertical as well as nonvertical) involving the participation of phonons.

In this connection it should be taken into account that hitherto we have considered the band structure of diamond with a perfect lattice. In actual fact the picture described above is considerably complicated in view of the presence of a large number of energy levels inside the forbidden energy gap. In order to trace how these levels are produced, it is first of all necessary to become acquainted with the fundamental varieties (types) of diamonds and their principal physical properties.

VII. FUNDAMENTAL PHYSICAL PROPERTIES

A classification of diamonds was first proposed in 1934 by Robertson et al.^[58] who, by studying crystals of diamond, distinguished among them type-I and type-II diamonds, differing one from the other first of all by their optical properties. It was found that the type-II diamonds, which are rarely found in nature, are transparent in the ultraviolet region up to $\lambda = 2250 \text{ \AA}$. For the more frequently occurring type-I diamonds, the absorption edge is shifted toward the side of longer wavelengths (approximately 3000 \AA). In the infrared region type-I diamonds have an absorption band near 8 μ . This band is not present for type-II diamonds.

If it is taken into consideration that the wavelength of 2250 \AA , the absorption edge for type-II diamonds, corresponds to an energy ~ 5.5 eV, which is approximately equal to ΔE_g —the width of the forbidden gap in diamonds associated with nonvertical transitions, then it becomes clear that the cited authors of article^[58]

quite intuitively (the numerical value of ΔE_g only became known two decades later^[23]) followed the correct path.

According to current ideas, the classification^[58] can approximately be formulated as follows: Type-II diamonds have a band structure which approximates, to this or the other extent, the band structure of a perfect diamond, and all remaining diamonds belong to type I. Therefore, it is quite natural that the overwhelming majority of subsequent investigators have still not digressed from the classification given in^[58], but have only further developed it.

For a long time, no satisfactory explanation of the differences between the two types of diamonds existed. In 1944 Raman put forward a hypothesis which attempted to explain this difference as due to the presence of two types of lattices.^[59] However, the theory^[59] did not obtain experimental verification.

In 1959 Kaiser and Bond^[60] carried out investigations of the gas content in diamond, as a result of which they were able to observe a relatively large concentration of nitrogen (up to 4×10^{20} atoms/cm³) in type-I diamonds. A substantial amount of nitrogen was not found in type-II diamonds. Meanwhile the following residual impurities were observed in both types of diamonds: aluminum, calcium, silicon, and certain other elements.

Subsequent investigations^[61] confirmed the conclusion of^[60] that nitrogen is the principal impurity in diamond, producing a substantial violation of the periodicity of its lattice.

It was established that type-I diamonds contain 0.025 to 0.25 % nitrogen, and type-II diamonds contain less than 0.001 % nitrogen. Therefore, it was agreed upon to call type-I diamonds "nitrogen diamonds" and type-II diamonds "nitrogenless."

Later type-I diamonds were divided into two subtypes: Type Ia containing nitrogen impurities in the form of different aggregations (platelets),^[61] and Type Ib in which the nitrogen occurs in a dispersed paramagnetic form.^[62,63]

One more variety of diamonds was found somewhat earlier, in 1952.^[64] The topic of discussion is now the so-called semiconducting diamonds which, in contrast to all other types of diamonds which are good insulators (specific resistivity from 10^{14} to 10^{16} ohm-cm), have a small specific resistivity (of the order of 10^2 to 10^6 ohm-cm). Since with regard to their other properties these diamonds are very similar to type II diamonds, it was decided to distinguish two groups among the nitrogenless diamonds: Type IIa (insulators) and type IIb (semiconductors).

And, finally, a group of diamonds has been isolated whose absorption edge occurs between the limits of transparency for type-II diamonds and the transparency limits for type-I diamonds (i.e., in the region between 2260 and 2950 Å). These diamonds have obtained the name "intermediate". As the latest investigations^[65] showed, in regard to their basic properties "intermediate" diamonds are very similar to type-IIa diamonds.

At the same time it is necessary to note that one cannot always draw a sharp boundary between diamonds of the two basic types. This in turn is explained by the extremely nonuniform distribution of nitrogen impuri-

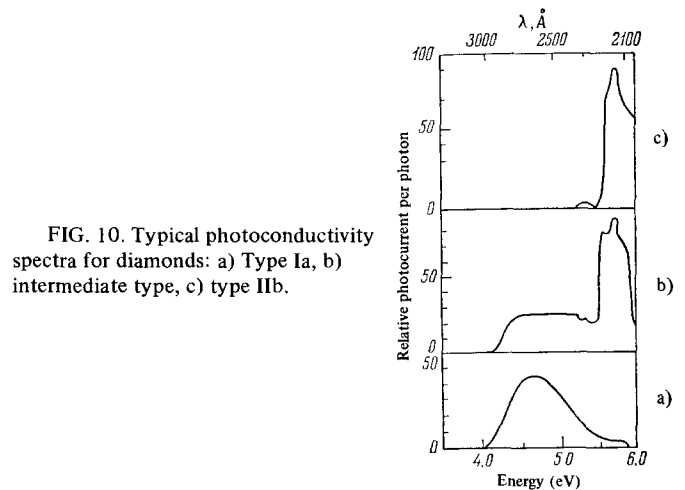


FIG. 10. Typical photoconductivity spectra for diamonds: a) Type Ia, b) intermediate type, c) type IIb.

ties both in the volume as well as in specific planes and directions of the crystal.^[66-68,127] Diamonds are known in which one part of the diamond possesses the properties of a type-I diamond, and the other part has the properties of a type-II diamond.^[11] The hypothesis was put forward in^[69] that during the process of formation, under certain conditions the diamonds at first grew like type-II diamonds, but later they were covered with an envelope of type-I diamond. Therefore, in optical studies one cannot always obtain the correct idea about the type of diamond.

Investigation of the photoconductivity can give more reliable information about the type of crystal. The different properties of the photoconductivity of the two types of diamonds were mentioned a long time ago in article^[58]. In subsequent articles^[70-76] the photoconductivity of diamonds has been thoroughly investigated.

Because of the relatively large number of defects and impurities in the diamond lattice, the frequency dependence of the photoconductivity of diamonds has a rather complicated nature. The photoconductivity is observed to be extremely negligible over individual segments in the visible and near-infrared parts of the spectrum. However, in the ultraviolet part of the spectrum associated with the transition from 3000 Å towards the side of shorter wavelengths, the photocurrent begins to increase sharply. For type-IIa diamonds, the maximum photocurrent occurs in the vicinity of 2250 Å, which roughly corresponds to the absorption edge for diamonds of this type. In addition, in individual samples a second distinct maximum is observed in the vicinity of 2550 Å.^[71] The fundamental maximum of the photocurrent in type-Ia diamonds occurs in the neighborhood from 2700 to 2800 Å.

For wavelengths smaller than 2200 Å, an abrupt decrease of the photocurrent is observed for both types of diamonds. The maximum photocurrent excited in type-IIa diamonds, other conditions being equal, is approximately one to two orders of magnitude larger than the photocurrent in type-Ia diamonds. It is obvious that this is explained by the fact that the presence of nitrogen platelets reduces the lifetime and lessens the mobility of the charge carriers.^[71] Typical photoconductivity spectra for various types of diamonds are shown in Fig. 10.

The temperature dependence of the electrical conductivity of diamonds has been investigated in the region from 50 to 700°C.^[77-79] The measurements showed that in the range of temperatures from 220 to 600°C the curve showing the dependence of the logarithm of the electrical conductivity ($\ln \sigma$) on the value of the reciprocal, $1/T$, of the absolute temperature can be divided into three segments: From 220 to 340°C, from 340 to 480°C, and from 480 to 600°C; on each of these segments there is rather good agreement with an exponential dependence of the electrical conductivity on the temperature, although the slopes of the corresponding portions of the curve are different. Upon heating the diamond above 600°C, the temperature dependence of the electrical conductivity no longer obeys an exponential law. This segment of the curve contains alternating minima and maxima. At low temperatures (up to 220°C) the electrical conductivity increases slowly with increasing temperature. In connection with repeated measurements, the electrical conductivity decreases.

The activation energy of various diamonds, determined from the graph of the dependence of $\ln \sigma$ on $1/T$, varied from 2 to 2.8 eV.

Pogodaev,^[77] who was investigating the temperature dependence of the specific resistivity of x-ray irradiated and nonirradiated diamond samples, conjectured that the low-temperature conductivity of diamonds is electronic, but the high-temperature conductivity is due to holes.

The majority of diamonds belong among the number of substances which possess the ability to luminesce under the influence of ultraviolet irradiation. In this connection a dark blue or pale blue luminescence is characteristic for type-Ia diamonds, and a greenish-yellow luminescence is characteristic for type-IIa diamonds. According to present-day ideas, the blue luminescence in diamond is caused by the recombination of electrons and holes separately trapped at nitrogen donors and aluminum acceptors of variable mutual separation,^[75, 128] and the greenish-yellow luminescence is associated with a structure factor.^[80]

In contrast to the case of photoluminescence, all diamonds without any exceptions possess the ability to luminesce under the influence of X-rays. This property, in particular, is utilized in devices for the automatic separation of diamonds from other minerals.

One of the most interesting types of luminescence is electroluminescence, a process in which the direct conversion of electrical energy into light occurs.

Two different types of electroluminescence exist. Electroluminescence of the first type occurs upon direct contact of the electrodes, to which a constant or variable voltage is applied, with the excited diamonds. In this connection it is as if a "sprinkling" or injection of charges into the crystal occurs.

In order to excite this type of luminescence, the diamond under investigation is clamped between two electrodes, where one of the electrodes—the fixed one has a planar shape, and the position of the second electrode, filled out in the shape of a spike, changes during the performance of the experiment. It is curious that the maximum luminescence effect is observed only when the electrode, having the shape of a spike, is

located at a certain discrete point on the surface of the diamond. Under the described conditions all of the type-IIa diamonds luminesce, but of the type-I diamonds only a few more than half luminesce. The luminescence of type-IIa diamonds differs, other conditions being equal, by having a large intensity in comparison with the luminescence from type-I diamonds.^[81]

Electroluminescence of the second type is observed in diamonds placed in an alternating electric field, but insulated from the electrodes. This is the so-called intrinsic electroluminescence (the Destriau effect).

The following relation exists between the brightness of the electroluminescence and the electric voltage field:

$$\beta = ke^{-b/\sqrt{U}} \quad (10)$$

where β denotes the intensity of the electroluminescence, k and b are constants, and U is the applied voltage.

It has been established that electroluminescence of the second type is observed primarily in diamonds containing impurities.^[82]

VIII. SEMICONDUCTING DIAMONDS

Interest in semiconducting diamonds (type IIb) is primarily due to the fact that they provide the possibility to relatively easily study the electrical properties and certain characteristic features of the band structure. The point is that in ordinary diamonds, which possess a large specific resistivity, such exceedingly weak currents are excited that it is difficult to detect them even by using the most modern equipment. Another difficulty which arises in connection with electrical measurements is related to the creation of a barrier layer between the electrode and the crystal, as a consequence of the large differences between the specific resistivities of the electrode and of the sample. In the case of semiconducting diamonds, this difference is considerably smaller. This is why literally each newly found sample of this rarest variety is subjected to thorough investigation.^[82-91]

In regard to their optical properties, semiconducting diamonds are very similar to type-IIa diamonds: The transmission limits in the ultraviolet region approximately coincide for the two types. In connection with the investigation of the optical absorption spectra in the infrared region, additional absorption maxima are observed in the infrared region, which are characteristic only of type-IIb diamonds. In connection with the effect of short-wavelength ultraviolet radiation on type-IIb diamonds, a bright and prolonged phosphorescence appears, which is strongly quenched by long wavelength ultraviolet light.

As a result of the determination of the sign of the Hall coefficient in type-IIb diamonds, the hole nature of their conductivity has been established. The simultaneous measurement of the Hall coefficient and the specific resistivity showed that the mobility of the charge carriers in type-IIb diamonds is approximately 1550 cm²/V-sec. The density of charge carriers is given by $n_g = 7 \times 10^{13}$ holes/cm³, i.e., it is approximately the same as for germanium. It has been established that rectification of the current takes place

at the contact between a silver probe and a type-IIb diamond. In this connection, in the vicinity of 130°K a change in the sign of the rectification occurs, which once again is characteristic of a p-type semiconductor.

In connection with investigations of semiconducting diamonds using the method of thermal annealing, it has been observed that the concentration of acceptor levels remains constant over a wide range of temperature from 500 to 2500°C.^[92] Hence follows the conclusion that the acceptor centers are rigidly fastened in the lattice. This confirms the hypothesis that the acceptor levels in diamond are formed by trivalent atoms (such as aluminum or boron), which are located in the lattice at substitutional sites. Analysis by using the method of neutron activation showed that aluminum may be responsible for the acceptor levels in type-IIb diamonds.^[88]

As a result of the investigation of the photoconductivity in the infrared region and the thermoluminescence of natural diamonds of type IIb and synthetic diamonds doped with aluminum and boron,^[76] it has been established that the aluminum acceptor levels are located at a distance of 0.373 eV from the upper boundary of the valence band. Boron may be responsible for the other acceptor levels, which are located at a distance of 0.20 eV from the upper boundary of the valence band.

According to^[92] the forbidden energy gap in type-IIb diamond contains N_a acceptor levels and N_d donor levels located above the acceptor levels, where $N_a > N_d$. The hole conductivity is realized by means of electron transitions into the $(N_a - N_d)$ unfilled acceptor levels.

It is well known that in the production of semiconductors (for example, germanium and silicon), their conductivity is established due to the introduction of a strictly measured-out number of impurities under rigidly controlled conditions. It is quite obvious that the probability for the spontaneous occurrence of such a process in nature is exceedingly small. This explains the uniqueness of semiconducting diamonds.

The observation of a change in the specific resistivity of diamond in a transverse magnetic field is of definite interest in connection with investigations of the band structure.

According to^[84], in fields up to 4000 G the change in the specific resistivity $(\Delta\rho/\rho_0)$ is proportional to the square of the transverse magnetic field, where it obeys the well known equation

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho(H) - \rho(0)}{\rho(0)} = 3.8 \cdot 10^{-17} \mu^2 H^2, \quad (11)$$

where $\rho(H)$ denotes the specific resistivity in the magnetic field, $\rho(0)$ is the specific resistivity in the absence of the magnetic field, and μ is the Hall mobility.

It has been established that the effect in a transverse field is at least three times larger than the effect in a longitudinal field. With the anisotropy of the crystal taken into account, this indicates in particular that at least one valence level in diamond does not have a spherical energy surface. The coefficient of the specific resistivity in a longitudinal field, $(\Delta\rho/\rho \cdot H^2)_{\text{long}}$, actually does not depend on the value of the magnetic field below 6000 Oe, but it decreases with the field in stronger fields.^[85]

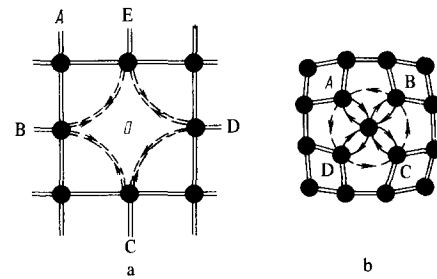


FIG. 11. Diagrams showing the formation of defect bonds: a) vacancy, b) carbon atom in an interstitial position.

Cyclotron resonance experiments in semiconducting diamonds^[88] made it possible to determine the masses of the light m_l^* and heavy m_h^* holes at the edge of the valence band: $m_l^* = 0.7 m_0$ and $m_h^* = 2.2 m_0$. For the band which is split-off as a result of the spin-orbit effect, $m^* = 1.06 m_0$. The effective mass of an electron at the edge of the conduction band is given by $m = 0.2 m_0$, where m_0 is the free electron mass.

IX. CHARACTERISTIC PROPERTIES OF THE BAND STRUCTURE OF A REAL DIAMOND

Various violations of the lattice periodicity are observed in a real crystal. These violations do not cause any changes in the structure of the valence band or of the conduction band, but only lead to the appearance of energy levels inside the forbidden energy gap, which will be investigated below.

1. Lattice Defects

If one of the carbon atoms is removed from the diamond lattice, for example, as the result of thermal motion, then a so-called 0 vacancy is produced (see Fig. 11a). As is clear from the Figure, here the bonds of the atoms such as A remain unbroken. However, imperfect (defect) bonds are formed on four atoms, namely atoms B, C, D, and E since the vacancy will not be in a state which is able to provide the four electrons required for the completion of the four normal bonds of these four atoms.

Unpaired electrons can behave in a different way: Each of them may remain bound to its own nucleus, they can enter into the orbits of atoms having unoccupied bonds, and, finally, they tend to form a quasicovalent defect bond with the unpaired electrons of the two nearest defect atoms, as shown in Fig. 11 (a). Investigation of the wave equations of motion of such electrons shows there is a certain probability for all of these possibilities. However, in any of the cases under consideration the unpaired electron is less tightly bound to the lattice than the electron forming the normal bond. As a consequence each of the atoms B, C, D, and E exists in a state which is closer to the free atom than the atom forming the normal bond. Thus, these atoms are responsible for the creation of energy levels lying above the top of the valence band and below the conduction band, that is, inside the forbidden energy gap. The joining of two vacancies and the formation of the so-called divacancies involves the

appearance of new energy levels, and the coupling of a sufficiently large number of divacancies causes the formation of internal surfaces (cavities) in diamonds.

Even the surface of a perfect diamond can be treated as the boundary between an ideal lattice and an infinite number of vacancies. The bonding of the atoms on the surface of the lattice obviously cannot be tetrahedral, and the most likely possibility is that the atoms maintain three normal bonds, and the remaining unpaired orbitals form imperfect bonds, which also leads to the formation of additional energy levels inside the forbidden energy gap.

The situation which arises in connection with the appearance of a carbon atom at an interstitial position is shown in Fig. 11 b. As a result each of the atoms A, B, C, and D turns out to be directly bound not to four but to five nearest neighbors. Now four valence bonds are insufficient to maintain the normal interaction with all of the neighbors. The natural consequence of the situation which is thus created is—the formation of unpaired imperfect bonds.

One more factor which causes a violation of the periodicity of the lattice is the presence of dislocations—that is, displacements of the atomic planes which arise as a result of mechanical stresses during the process of the crystal's growth. Due to the effect of the dislocations, part of the bonds may turn out to be deformed and some of them are broken, which in the final analysis leads to the formation of new energy levels inside the forbidden energy gap.

A number of authors have carried out theoretical investigations of the electronic states of such defects in the diamond lattice as single vacancies,^[93-96] divacancies,^[97] and interstitial carbon atoms.^[98]

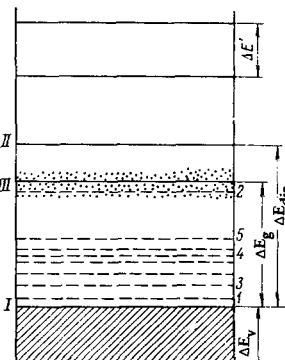
Unfortunately, at the present time it is impossible to artificially produce crystals containing defects of one arbitrary type. Therefore, the results of articles^[93-98] can only be approximately interpreted by comparing the results of the theoretical calculations with the experimental data.

Thus, in the absorption spectrum of irradiated type-I diamond which is given in article^[99], a broad band is observed between 1.65 and 2.4 eV with an intense line at 1.673 eV, this band being known as the GR 1 absorption band, and there is an intense band in the ultraviolet spectrum beginning at 2.8 eV and extending to 4 eV. In accordance with article^[96] single neutral vacancies are responsible for the GR 1 absorption band. The structure of the ultraviolet band is more complicated. However, the quantitative calculation presented in article^[97] gives reason to conjecture that at least part of this band is due to transitions of the electrons immediately surrounding a neutral divacancy.

An investigation of the surface states of diamond by using the method of equivalent orbitals^[100] (the MO-LCAO method) showed that the presence of unsaturated bonds associated with the surface carbon atoms causes the formation of an energy band in the middle of the forbidden gap, where the number of states in this band is equal to the number of surface carbon atoms.

Champion^[11] proposed the following simplified scheme for the energy bands in diamond, which we

FIG. 12. Diagram showing the band structure of diamond with the energy levels due to lattice defects taken into consideration. [11] The widths are as follows: valence band $\Delta E_v \approx 20$ eV, the forbidden energy gap for indirect transitions is $\Delta E_g = 5.47$ eV, the forbidden gap for direct transitions is $\Delta E_{dir} = 7.3$ eV, and $\Delta E'$ denotes the forbidden gap between the first four levels and the following levels in the conduction band.



have reproduced in Fig. 12 with certain improvements which have been introduced on the basis of the results of later work.

An ideal crystal of infinite extent should not contain energy levels between the upper boundary I of the valence band, which is completely filled, and the bottom II of the completely empty conduction band, with the exception of empty exciton levels III located near the intrinsic absorption edge.

In a real crystal energy levels appear inside the forbidden energy gap, indicated on Fig. 12 by the dashed lines, where the appearance of these extra levels is due to the presence of lattice defects.

Dislocations are responsible for the energy levels 1 near the top of the valence band, and for the energy levels 2 which are found very close to the bottom of the conduction band.

Single vacancies are responsible for the energy levels 3 which are located somewhat above the levels 1, but still rather close to the top of the valence band. With an increase in the number of vacancies new levels 4 appear, approaching the middle of the forbidden gap.

The presence of interstitial carbon atoms at interstitial positions does not significantly alter the picture of the distribution of the energy levels inside the forbidden gap, unless the increase in the number of levels in the vicinities of 1 and 3 is considered. Finally, the levels 5 which are located approximately in the middle of the forbidden gap are caused by the effect of the surface.

According to^[11] the energy levels considered above, caused by the presence of lattice defects, are normally occupied.

2. Impurity Levels

Unfortunately, the theoretical investigation of impurity states in diamond is still in a rudimentary state. Little is known about the electronic structure of impurities in the diamond lattice. Questions about the interaction of the impurities, the conditions of their binding in the lattice, have not been touched upon. All information about the impurity levels is derived from experimental data on photoconductivity, optical absorption, radioactive irradiation, and experiments connected with the investigation of certain other properties of natural and synthetic diamonds of various types.^[75,77,101-105,129,130]

A summary of the known (to one or the other degree of approximation) energy levels inside the forbidden

Table VI

Element	Type of impurity	E_A (eV)	E_D (eV)
Nitrogen	D, C	0.373	4.05
	D, C		1.7
Aluminum	A	0.35	
	A		
Beryllium	A	0.2	
	A		
Boron	A	0.35	
	A		
Cadmium	A, C	2.55	
	C		
Lithium	C		0.29
Traps for holes	C, C		0.94
Traps for electrons	A, C	2.1	

Conventional notation: A—acceptor, D—donor, C—center for the capture of electrons and holes.

energy gap in diamond, these levels being caused by impurities, is given in Table VI.^[105]

As is clear from Table VI, the majority of the known levels are acceptor levels. From this one can conclude that the conductivity in diamond is primarily due to holes. Nitrogen produces deep donor levels, which cannot have a substantial influence on the conductivity.

From the point of view of band structure, the basic difference between the two types of diamonds consists in the following.

Type-I diamonds contain a relatively large number of impurities (of these, the major impurity is obviously nitrogen), and therefore there is a correspondingly large number of energy levels, caused by these impurities, inside the forbidden gap. These impurities are quite randomly distributed and may cancel each other (in the case of an identical number of donor levels and acceptor levels) or may produce centers for the capture of holes and electrons. Incidentally, the impurity levels turn out to have a definite influence of the electrical properties of type-I diamonds. From theoretical calculations it follows that the specific resistivity of a crystal, having a forbidden energy gap of the same width as diamond, should be equal to 10^{70} ohm-cm.^[11]

Type-IIa diamonds contain a relatively small number of impurities and correspondingly a smaller number of energy levels inside the forbidden gap, associated with the impurities, than type-I diamonds do. In return they have a relatively large number of energy levels produced by lattice defects (primarily due to dislocations^[106]). Although these levels also turn out to have an influence on the specific resistivity of the crystal, they obviously do not have any substantial effect on the other properties of diamond as a semiconductor. The value of type-II diamonds as a raw material for the electronics industry is determined by this fact.

X. APPLICATIONS OF DIAMONDS IN THE ELECTRONICS INDUSTRY AND IN INSTRUMENT MANUFACTURE

One of the fundamental shortcomings of semiconducting devices is the substantial temperature dependence of their characteristics. Thus, germanium triodes and diodes (for germanium $\Delta E_0 = 0.8$ eV) turn out to be practically useless for employment in electronic circuits when the surrounding temperature is

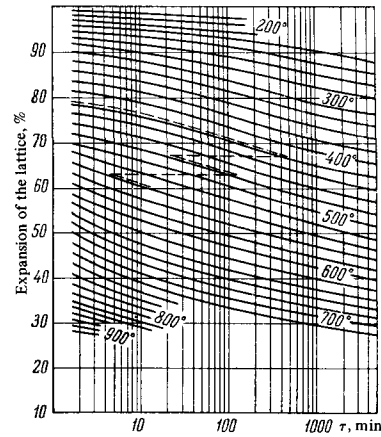


FIG. 13. Nomogram for the determination of the temperature with the aid of temperature indicators made out of diamond, irradiated until the lattice expansion amounts to $\Delta v_0/v_0 = 4.87\%$.^[113] The expansion of the lattice is plotted on the axis of ordinates, and the time is plotted on the axis of abscissas using a logarithmic scale.

above 60°C . For silicon the width of the forbidden band is somewhat larger ($\Delta E_0 = 1.1$ eV). Therefore silicon semiconducting devices can operate in particular cases at temperatures up to 200°C . The necessity for the creation of highly-stable semiconducting devices, capable of operating at higher temperatures, has stimulated a search for materials with larger forbidden energy gaps. From this point of view, diamond is an ideal material.

At the present time by the creation of electron-hole transitions in a diamond crystal it has been possible to obtain high quality semiconductor triodes.^[107] According to reports by the foreign press, a method of synthesizing diamonds has been found in the USA, making it possible to obtain relatively large (in size) diamond crystals, suitable for the production of transistors.

One of the promising areas for the utilization of diamonds is in the measurement of temperature. If ordinary thermoresistors can be used only up to a temperature of 200°C , then thermoresistors based on diamonds are designed for temperatures up to 1000°C .^[108] At the present time thermoresistors based on natural type-IIb diamonds are being developed in the USA.^[109] However, the creation of such devices is of rather theoretical value in view of the extreme rarity of natural semiconducting diamonds. Better prospects for the bulk manufacture of diamond thermoresistors are being uncovered in connection with the creation of semiconducting diamonds by doping natural crystals and the production of synthetic semiconducting diamonds.^[101, 102, 110-112, 131, 132]

In the USSR a temperature indicator based on powdered diamonds has been developed—an original device for making temperature measurements in places which are difficult to reach.^[113] The principal of operation of this temperature indicator is based on the fact that a certain dependence exists between the density of diamond irradiated by neutrons and the temperature, and also the annealing time. The monitored temperature is determined according to a special nomogram, obtained experimentally on the basis of data concerning the expansion of the lattice during the

period of the measurements and the annealing time (see Fig. 13). The temperature indicator made out of irradiated diamond is designed for use in the region from 10 to 1000°C and makes it possible to carry out measurements for time intervals ranging from a few minutes to hundreds of hours. The diameter of the indicator is 1 mm and the length is 5 mm. If the diamond powder is poured directly into an opening in the element to be monitored, then the volume which it occupies amounts to only 0.2 mm³.

The first developments in the area of diamond thermoresistors and semiconducting triodes date back to the beginning of the 1960's. Somewhat earlier diamonds obtained recognition as detectors in nuclear radiation counters.^[114]

A diamond conduction counter has the following fundamental advantages: a) the ability to count even at room temperature; the possibility, owing to its small size, to use it as a point counter; c) the linear dependence of the amplitude of the counting pulse on the energy of the detected particle; d) a very good resolution time ($\tau = 0.01$ microsec).

The electron density of diamond is 3000 times larger than the density of air and is close to the electron density of the tissue in the human body. Therefore, the penetrating ability of radiation with respect to diamond and with respect to the human body is roughly the same. This indicates good prospects for the use of diamond counters in medicine, where they can also be applied for intracavity studies.

It should be noted that not all, by far, diamonds can be used as crystal counters. A large number of articles^[115-120] has been devoted to the investigation of the counting properties of diamonds and to methods for the selection of "counting" diamonds. Finally, the criteria for the selection of diamonds for conduction counters have not yet been established; on the basis of accumulated statistical data, one can conclude that it is necessary to select the counting diamonds among the type-II diamonds.

Although diamond counters will never completely displace other types of counters, they are irreplaceable for a number of special applications. The further development of diamond conduction counters, perhaps, will proceed along the path leading to the creation of electron-hole $n - p$ and $p - n$ junctions in diamond crystals.

Another property of diamonds, which governs the possibility of their use as nuclear radiation detectors, consists in their ability to luminesce under the influence of radioactive radiation.

Upon the passage of a charged particle through a diamond, a short-lived light flash appears (scintillation). In a scintillation counter the light pulse is converted into an electric signal with the aid of a photoelectric multiplier. The signal from the discharge of the photoelectric multiplier through an amplifier then enters a discriminator, which does not allow small noise signals to pass. The output of the discriminator through a recounting block is connected to a registering device.

The luminescence (blue or yellowish-green) of a diamond is so intense that any source of radiation with an energy up to several thousand electron volts can be

detected with the aid of a photomultiplier of arbitrary type and the usual electronic apparatus.

In contrast to conduction counters, for diamond scintillation counters a correspondence between the type of diamond and its counting ability has not been established.^[121, 122]

Investigations^[123] carried out recently in the USA indicate that the power of semiconductor devices can be substantially increased by using type-IIa diamonds for cooling (heat removal). Crystals applicable for this purpose had sizes ranging from 0.05 to 0.2 carats.

The selected crystals were polished, and then metallized by spraying titanium, platinum, and gold on two parallel planes. The semiconducting diodes, which were also metallized by these metals, were joined by the method of thermal compression or were soldered to the surface of the diamond. In one of the experiments, involving a silicon diode mounted on a type-IIa diamond, a power of around 3 watts was obtained, which exceeds by a factor of 4 the maximum power which can be obtained from a similar diode mounted on a copper heat-exchanger.^[133]

In another case, a gallium arsenide diode laser mounted on a type-IIa diamond operated in the continuous lasing regime when the temperature of the heat exchanger was equal to -68°C . Upon mounting the diode laser on a copper heat exchanger, the temperature of the heat exchanger associated with similar operation of the laser had to be lowered to -123°C . Thus, the laser with the diamond heat exchanger can be cooled by dry ice instead of liquid nitrogen, which is required for the copper heat exchanger. The conjecture has been expressed^[123] that diamond, being used as a heat exchanger, can cause a revolution in the technology of the manufacture of semiconductor devices for cases when the dissipation of heat is limited by intrinsic heat extractions.^[133]

Diamond is practically the only substance which transmits radiation over a broad range from 0.3 to 1000 μ . Therefore it is an ideal material to use as a window for infrared radiation detectors. Since type-I diamonds have additional absorption bands in the infrared region, then type-II diamonds are used in practice as windows in infrared radiation detectors.^[124]

The application of diamonds as a radiation monitor (dosimeter) for ultraviolet radiation is also of specific interest.^[125] The promising outlook for the application of diamonds in this area is determined by their long-lived storage capability, due to the large width of the forbidden gap. Type-II diamonds, which are to be used as radiation monitors for ultraviolet radiation, are subjected to a certain dosage of neutron irradiation as a preliminary treatment.

The cited examples do not, by far, exhaust all of the possibilities for the utilization of diamonds in electronics technology and device construction. The immediate future will show whether diamonds occupy the same place in this area as they now occupy in the instrument industry. All the prerequisites exist for this (to happen).

¹R. W. G. Wyckoff, *Crystal Structures*, Interscience Publishers, 1963.

²G. S. Buberman, *Fizikaalmazov* (Physics of

- Diamonds), "Znanie", M. 1968.
- ³C. Herring, J. Franklin Inst. 233, 525 (1942).
 - ⁴K. H. Bennemann, Phys. Rev. 139, A482 (1965).
 - ⁵R. Brill, Z. Elektrochem. 63, 1088 (1959).
 - ⁶H. C. Bolton and J. W. Heaton, Proc. Phys. Soc. (London) 78, 239 (1961).
 - ⁷L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).
 - ⁸Iza Goroff and Leonard Kleinman, Phys. Rev. 164, 1100 (1967).
 - ⁹J. C. Phillips, Phys. Rev. 166, 832 (1968).
 - ¹⁰Richard J. Weiss and Walter C. Phillips, Phys. Rev. 176, 900 (1968).
 - ¹¹F. C. Champion, Electronic Properties of Diamond, London, 1963.
 - ¹²L. Brillouin, J. Phys. Radium 1, 377 (1930).
 - ¹³H. Jones, The Theory of Brillouin Zones and Electronic States in Crystals, North-Holland Publishing Co., 1962 (Russ. Transl., Mir, M. 1968).
 - ¹⁴J. M. Ziman, Principles of the Theory of Solids, Cambridge, 1964 (Russ. Transl., Mir, M. 1966).
 - ¹⁵L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
 - ¹⁶G. F. Koster, Solid State Physics 5, 173 (1957).
 - ¹⁷G. E. Kimbal, J. Chem. Phys. 3, 560 (1935).
 - ¹⁸E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).
 - ¹⁹F. Hund and B. Mrowka, Sachs. Akad. Wiss., Leipzig 87, 185, 325 (1935).
 - ²⁰A. Morita, Science Repts. Tôhoku Univ. 33, 92 (1949).
 - ²¹F. Bloch, Z. Physik 52, 535 (1928).
 - ²²Conyers Herring, Phys. Rev. 57, 1169 (1940).
 - ²³Frank Herman, Phys. Rev. 88, 1210 (1952); 93, 1214 (1954).
 - ²⁴J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
 - ²⁵G. G. Hall, Phil. Mag. 43, 338 (1952).
 - ²⁶V. Zehler, Ann. Physik 13, 229 (1953).
 - ²⁷L. B. Rédil, Proc. Roy. Soc. (London) A270, 373, 383 (1962).
 - ²⁸F. Bassani and M. Yoshimine, Phys. Rev. 130, 20 (1963).
 - ²⁹H. A. Kellner, Acta Phys. Australia 18, 48 (1964).
 - ³⁰G. G. Hall, Phil. Mag. 3, 429 (1959).
 - ³¹A. I. Gubanov and A. A. Nran'yan, Fiz. Tverd. Tela 1, 1044 (1959) [Sov. Phys.-Solid State 1, 956 (1960)].
 - ³²A. A. Nran'yan, Fiz. Tverd. Tela 2, 474, 1650 (1960) [Sov. Phys.-Solid State 2, 439 (1960)].
 - ³³D. Stocker, Proc. Roy. Soc. (London) A270, 397 (1962).
 - ³⁴N. V. Cohan, D. Pugh, and R. H. Tredgold, Proc. Phys. Soc. (London) 82, 65 (1963).
 - ³⁵F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, J. Phys. Soc. Japan, Suppl. 21, 7 (1966).
 - ³⁶James C. Phillips and Leonard Kleinman, Phys. Rev. 116, 287 (1959).
 - ³⁷Leonard Kleinman and James C. Phillips, Phys. Rev. 116, 880 (1959).
 - ³⁸F. Bassani and V. Celli, J. Phys. Chem. Solids 20, 64 (1961).
 - ³⁹W. Saslow, T. K. Bergstresser, and Marvin L. Cohen, Phys. Rev. Letters 16, 354 (1966).
 - ⁴⁰Luis R. Saravia and David Brust, Phys. Rev. 170, 683 (1968).
 - ⁴¹A. A. Levin, Ya. K. Syrkin, and M. E. Dyatkina, Fiz. Tekh. Poluprov. 1, 687 (1967) [Sov. Phys.-Semi-cond. 1, 574 (1967)].
 - ⁴²A. A. Levin and A. A. Dyatkina, Zh. Struk. Khim. 9, 531 (1968).
 - ⁴³A. A. Levin, Dokl. Akad. Nauk SSSR 181, 1168 (1968).
 - ⁴⁴J. C. Slater, Phys. Rev. 51, 846 (1937).
 - ⁴⁵T. L. Louck, Augmented Plane Wave Method, Benjamin, 1967.
 - ⁴⁶R. Keown, Phys. Rev. 150, 568 (1966).
 - ⁴⁷C. Kittel, Quantum Theory of Solids, Wiley, 1963 (Russ. Transl., Nauka, M. 1967).
 - ⁴⁸C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) A277, 312 (1964).
 - ⁴⁹J. F. Angress, A. R. Goodwin, and S. D. Smith, Proc. Roy. Soc. (London) A308, 111 (1968).
 - ⁵⁰D. M. Rossel, Brit. J. Appl. Phys. 16, 119, 1359 (1965); 17, 1313 (1966).
 - ⁵¹J. C. Phillips, Solid State Physics 18, 55 (1965) (Russ. Transl., Mir, M. 1968).
 - ⁵²J. Tauc, Progress in Semiconductors (London) 9, 87 (1965) (Russ. Transl., Mir, M. 1967).
 - ⁵³H. R. Philipp and E. A. Taft, Phys. Rev. 127, 159 (1962).
 - ⁵⁴W. C. Walker and J. Osantowski, Phys. Rev. 134, A153 (1964).
 - ⁵⁵H. R. Philipp and E. A. Taft, Phys. Rev. 136, A1445 (1964).
 - ⁵⁶R. A. Roberts and W. C. Walker, Phys. Rev. 161, 730 (1967).
 - ⁵⁷N. R. Whetten, Appl. Phys. Letters 8, 135 (1966).
 - ⁵⁸R. Robertson, J. J. Fox, and A. E. Martin, Phil. Trans. Roy. Soc. London A263, 463 (1934).
 - ⁵⁹C. V. Raman, Proc. Indian Acad. Sci. 19, 189 (1944).
 - ⁶⁰W. Kaiser and W. L. Bond, Phys. Rev. 115, 857 (1959).
 - ⁶¹A. B. Lang, Proc. Phys. Soc. (London) 84, 871 (1964).
 - ⁶²H. B. Dyer, F. A. Raal, L. du Preez, and J. H. N. Loubser, Phil. Mag. 11, 763 (1965).
 - ⁶³L. du Preez and F. A. Raal, Diamond Research, Suppl. Ind. Diam. Rev. 6 (1965).
 - ⁶⁴J. F. H. Custers, Physica 18, 489 (1952); Physica 20, 183 (1954).
 - ⁶⁵Yu. L. Orlov and G. S. Buberma, v sbornike "Novye dannye o mineralakh SSSR" (in the collection: New Data about Minerals of the USSR), bulletin 22, Nauka, 1971.
 - ⁶⁶M. Seal and H. Wasmund, Diamond Research, Suppl. Ind. Diam. Rev. 29 (1969).
 - ⁶⁷N. D. Samsonenko, Fiz. Tverd. Tela 6, 3086 (1964) [Sov. Phys.-Solid State 6, 2460 (1965)].
 - ⁶⁸Yu. L. Klyuev, A. N. Rykov, and L. Ya. Khozak, in the collection: Almazy (Diamonds), M., No. 2, 8 (1969).
 - ⁶⁹S. Talansky and M. Raule-Cope, Diamond Research, Suppl. Ind. Diam. Rev. 2 (1969).
 - ⁷⁰T. L. Moss, Photoconductivity in the Elements, London, 1952.
 - ⁷¹E. A. Konorova, L. A. Sorokina, and S. A. Shevchenko, Fiz. Tverd. Tela 7, 1092 (1965) [Sov. Phys.-Solid State 7, 876 (1965)].
 - ⁷²P. J. Dean, E. C. Lightowlers, and D. R. Wight, Phys. Rev. 140, A352 (1965).
 - ⁷³E. C. Lightowlers and A. T. Collins, Phys. Rev.

- 151, 685 (1966).
- ⁷⁴P. A. Crowther and P. J. Dean, *J. Phys. Chem. Solids* 28, 1115 (1967).
- ⁷⁵P. Denham, E. C. Lightowers, and P. J. Dean, *Phys. Rev.* 161, 762 (1967).
- ⁷⁶E. C. Lightowers, A. T. Collins, P. Denham, and P. S. Walsch, *Diamond Research, Suppl. Ind. Diam. Rev.* 11, (1968).
- ⁷⁷K. N. Pogodaev, *Fiz. Tverd. Tela* 2, 1450 (1960) [*Sov. Phys.-Solid State* 2, 1317 (1961)].
- ⁷⁸K. N. Pogodaev and E. S. Viditus, *Izv. Akad. Nauk SSSR, ser. fiz.* 25, 373 (1961).
- ⁷⁹I. S. Rozhkov, K. K. Abrashev, A. F. Konstantinova, and B. A. Toritsyn, *Geol. i Geofiz.*, No. 2, 138 (1965).
- ⁸⁰G. O. Gomon, *Almazы (Diamonds), "Mashinostroenie"*, M. 1966.
- ⁸¹V. V. Pologrudov, Yu. G. Penzin, and É. É. Penzina, *Optika i Spektroskopiya* 17, 230 (1964).
- ⁸²J. K. Prior and F. C. Champion, *Proc. Phys. Soc. (London)* 80, 349 (1962).
- ⁸³Alfred G. Redfield, *Phys. Rev.* 94, 526 (1954).
- ⁸⁴P. T. Wedepohl, *Proc. Phys. Soc. (London)* B70, 177 (1957).
- ⁸⁵R. T. Bate and R. K. Williardson, *Proc. Phys. Soc. (London)* 74, 363 (1959).
- ⁸⁶A. Halperin and J. Nahum, *J. Phys. Chem. Solids* 18, 297 (1961).
- ⁸⁷P. J. Kemmey and E. W. J. Mitchell, *Proc. Roy. Soc. (London)* A263, 420 (1961).
- ⁸⁸Conrad J. Rauch, *Phys. Rev. Letters* 7, 83 (1961).
- ⁸⁹E. Lightowers, *Diamond Conference, Bristol, 1963*.
- ⁹⁰R. H. Wentorf, Jr. and K. A. Darrow, *Phys. Rev.* 137, A1614 (1965).
- ⁹¹P. T. Wedepohl, *J. Phys. C (Proc. Phys. Soc.)* 1, 1773 (1968).
- ⁹²S. M. Horszowski, *J. Phys. Chem. Solids* 30, 669 (1969).
- ⁹³C. A. Coulson and M. J. Kearsley, *Proc. Roy. Soc. (London)* A241, 433 (1957).
- ⁹⁴T. Yamaguchi, *J. Phys. Soc. Japan* 17, 1359 (1962).
- ⁹⁵J. Friedel, M. Lannoo, and G. Leman, *Phys. Rev.* 164, 1056 (1967).
- ⁹⁶M. Lannoo and A. M. Stoneham, *J. Phys. Chem. Solids* 29, 1987 (1968).
- ⁹⁷C. A. Coulson and F. P. Larkins, *J. Phys. Chem. Solids* 30, 1963 (1969).
- ⁹⁸T. Yamaguchi, *J. Phys. Soc. Japan* 18, 368 (1963).
- ⁹⁹C. D. Clark, R. W. Ditchburn, and H. B. Dyer, *Proc. Roy. Soc. (London)* A237, 75 (1956).
- ¹⁰⁰J. Koutecký and M. Tomášek, *Phys. Rev.* 120, 1212 (1960).
- ¹⁰¹V. S. Vavilov, M. I. Guseva, E. A. Konorova, V. V. Krasnopevtsev, V. F. Sergienko, and V. V. Titov, *Fiz. Tverd. Tela* 8, 1964 (1966) [*Sov. Phys.-Solid State* 8, 1560 (1966)].
- ¹⁰²N. N. Gerasimenko, L. V. Lexheiko, and L. S. Smirnov, in the collection: *Sinteticheskie almazy (Synthetic Diamonds)*, Kiev, bulletin 2, 39 (1970).
- ¹⁰³R. G. Farres, *Solid State Commun.* 7, 685 (1969).
- ¹⁰⁴R. R. Uraly, H. J. Logie, and F. R. N. Nabarro, *Proc. Phys. Soc. (London)* 78, 256 (1961).
- ¹⁰⁵G. S. Buberman, *Élektricheskie svoïstva almazov (Electrical Properties of Diamonds)*, v sb. "Almazы" (in the collection: *Diamonds*), M., No. 2, 5 (1968).
- ¹⁰⁶*Diamond News* 28 (12), 22 (1965).
- ¹⁰⁷Yu. V. Shmartsev, Yu. A. Valov, and A. S. Borshevskii, *Tugoplavkie almazopodobnye poluprovodniki (Hard Diamond-like Semiconductors)*, "Metallurgiya", M. 1964.
- ¹⁰⁸*Electrotechnik (Wurzberg)*, No. 8, 16 (1963).
- ¹⁰⁹G. B. Rodgers and F. A. Raal, *Rev. Sci. Instr.* 31, 663 (1960).
- ¹¹⁰French patent No. 1341561, 23 September 1963.
- ¹¹¹English patent No. 1101563, 31 January 1968.
- ¹¹²A. I. Prikhna, V. M. Ustintsev, and É. B. Vishnevskii, in the collection: *Sinteticheskie almazy (Synthetic Diamonds)* (Kiev), bulletin 5, 21 (1969).
- ¹¹³V. A. Nikolaenko, V. I. Karpukhin, and S. I. Alekseev, *ibid.* 5, 11 (1969).
- ¹¹⁴W. F. Cotty, *Ind. Diam. Rev.* 16, No. 182, 12; No. 183, 31; No. 184, 54; No. 186, 93; No. 187, 114; No. 188, 133; No. 189, 152; No. 190, 174 (1956).
- ¹¹⁵N. G. Trott, *Proc. Roy. Soc. (London)* 220, 498 (1953).
- ¹¹⁶Ch. Allemand and I. Rossel, *Helv. Phys. Acta* 27, 519 (1954).
- ¹¹⁷K. W. Taylor, *Proc. Phys. Soc. (London)* A69, 593 (1956).
- ¹¹⁸F. C. Champion and B. Dale, *Proc. Roy. Soc. (London)* A234, 419 (1956).
- ¹¹⁹E. A. Afanas'eva and E. A. Konorova, *Fiz. Tverd. Tela* 5, 2556 (1963) [*Sov. Phys.-Solid State* 5, 1866 (1964)].
- ¹²⁰Yu. L. Orlov and E. A. Afanas'eva in the collection: *Novye dannye o mineralakh SSSR (New Data about Minerals of the USSR)*, bulletin 17, 105 (1966).
- ¹²¹I. E. Ralph, *Proc. Phys. Soc. (London)* A73, 233 (1959); 76, 688 (1960).
- ¹²²R. J. Dean, P. I. Kennedy, and I. E. Ralph, *Proc. Phys. Soc. (London)* 76, 670 (1960).
- ¹²³*Ind. Diam. Rev.* 28, 301 (1968).
- ¹²⁴*Ind. Diam. Rev.* 26, 112 (1966).
- ¹²⁵K. Miyshita, H. K. Henisch, and J. Toole, *Solid State Electronics* 10, 193 (1967).
- ¹²⁶P. M. Raccah, R. N. Euwema, D. J. Stukel, and T. C. Collins, *Phys. Rev.* B1, 756 (1970).
- ¹²⁷Yu. A. Klyuev, A. N. Rykov, Yu. A. Dedenkov, and V. M. Zubkov, *Dokl. Akad. Nauk SSSR* 189, 771 (1969) [*Sov. Phys.-Doklady* 14, 1133 (1970)].
- ¹²⁸V. E. Il'in, E. V. Sobolev, and O. P. Yur'eva, *Fiz. Tverd. Tela* 7, 2156 (1970) [*Sov. Phys.-Solid State* 7, 1735 (1970)].
- ¹²⁹E. V. Sobolev, Yu. A. Litvin, N. D. Samsonenko, V. E. Il'in, S. V. Lenskaya, and V. P. Butuzov, *Fiz. Tverd. Tela* 10, 2266 (1968) [*Sov. Phys.-Solid State* 10, 1789 (1969)].
- ¹³⁰E. V. Sobolev, V. E. Il'in, É. I. Gil'bert, and S. V. Lenskaya, *Fiz. Tverd. Tela* 11, 247 (1969) [*Sov. Phys.-Solid State* 11, 200 (1969)].
- ¹³¹L. F. Vereshchagin, O. G. Revin, V. N. Slesarev, I. N. Seifi-Khusainov, and A. S. Chmykhov, *Dokl. Akad. Nauk* 192, 1015 (1970) [*Sov. Phys.-Doklady* 15, 566 (1970)].
- ¹³²G. N. Bezrukov, V. P. Butuzov, N. I. Gerasimenko, L. V. Lezheiko, Yu. A. Litvin, and L. S. Smirnov, *Fiz. Tekh. Poluprov.* 4, 693 (1970) [*Sov. Phys.-Semicond.* 4, 587 (1970)].
- ¹³³*Diamond News and S. A. Jeweller* 33 (4), 5 (1970).

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