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COMPOUNDS ISOELECTRONIC WITH DIAMOND AS A BASIS
FOR THE CREATION OF NEW HARD AND SUPER-HARD
MATERIALS

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From considerations of similarity in electronic structure, a procedure has been proposed for predicting new materials with increased hardness. It provides a basis for determining the compositions of compounds isoelectronic with diamond. Computer programs have been developed which make it possible to find the concentrations of the components of binary, ternary, etc. systems isoelectronic with a given system. Various two- and three-component compounds isoelectronic with diamond in the volume of the simplest cells of the crystal have been tabulated as promising substances in the search for new hard and super-hard materials.

A characteristic feature of the electronic structure of diamond, essential for its hardness, is the presence, in the valence level of each carbon atom, of four electrons capable of taking part in the formation of four strong tetrahedrally directed covalent bonds. Thus in the search for new super-hard materials, it is natural to try to reproduce this property of diamond. In a sense, this property is reproduced in another super-hard material - cubic boron nitride BN. The deficit of electrons on the boron atoms is compensated exactly by a corresponding excess of electrons on the nitrogen atoms, so that a crystalline system with the same number of electrons as in diamond is finally obtained (with in this case, the same number of atoms). A significant difference which should be emphasized and which is important for the subsequent discussion is that in boron nitride BN, four electrons are present on one atom only on the average (since the electron density distribution in it does not correspond to the formation of the polar compound $B^- \cdot N^+$; that is, it does not correspond to the complete transfer of one electron from the nitrogen atom to the boron atom).

The next step in the breakdown of the microscopic structure of diamond while preserving the features of its electronic structure important for hardness may be a slight change in the structure of its crystal lattice with preservation of the electronic subsystem as a whole. To explain this, we can consider the following example. We break down the diamond crystal into imaginary ten-atom fragments, remove five carbon atoms from each of these fragments, and then replace them by four nitrogen atoms (the position of the fifth C atom removed remains vacant). Since four N atoms have the same number of valence electrons as five C atoms, the crystal made up of the nine-atom fragments C_5H_4 with one vacancy for every 10 sites will be isoelectronic with the diamond crystal (in all cases we are dealing only with the valence level). There are therefore grounds for

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expecting that a number of its properties, determined primarily by the electronic structure, will be similar to the properties of diamond.

We shall describe as isoelectronic with diamond those compounds which after reduction to a lattice of the diamond type have an average of four electrons per lattice site. In accordance with what has been said above, the existence of the system of tetrahedral saturated covalent bonds characteristic of diamond is possible on the average in these compounds. This feature, and also the fact that all known materials with a high hardness, in particular boron nitride BN, carborundum SiC, boron carbide B_4C , and silicon nitride Si_3N_4 , can be regarded as compounds isoelectronic with diamond in the volume of the simplest cells of the crystal (see below), make it possible to put forward the statement (or hypothesis) that one possible way of creating new super-hard materials lies in the synthesis of multicomponent compounds, isoelectronic with diamond, from atoms with small dimensions and predominantly covalent interatomic (inter-site) bonds. In our view, from what has been said above, the importance of the determination of the compositions of these compounds and the development of an appropriate procedure for this is sufficiently obvious.

Mathematically, the problem of determining the composition of a multicomponent compound isoelectronic with diamond involves the determination of a set of solutions of indefinite equations of the form

$$n_A x + n_B y + n_C z + \dots = 4N, \quad (1)$$

where n_A, n_B, n_C, \dots are the numbers of valence electrons in the atoms of the components, N is an integral positive number, and x, y, z, \dots are the required concentrations. The problem rapidly becomes more complicated with increase in the number of components. We have compiled a set of FORTRAN programs which make it possible to use a computer to determine solutions to equations of type (1) for given characteristics of the components (n_A, n_B, n_C, \dots) and a given value of the average electron concentration for the required compound n_i . The programs can be arbitrarily divided into two groups, one of which carries out the analysis of a random set of values of the concentrations x, y, z, \dots for their similarity to the coordinates of any point of any of the hyperplanes describing the required solid solution or crystal. The programs of this group which have now been compiled make it possible to examine compounds containing from three to 12 components. The other group of programs makes it possible to carry out the search for the concentration of one of the components of the solid solution or crystal, isoelectronic with a given compound, from the fixed values of the concentrations of the other components while moving along the line or hyperplane described by Eq. (1). These programs have been realized (at the present time) for compounds containing from two to five components. More detailed information on the programs, together with their texts, will be published separately.

The solution of the problem for two-component compounds is relatively simple. As an example, we can examine boron carbide $B_x C_y$ in more detail. We change to a notation which is more convenient for the subsequent treatment:

$$B_n C_{N-l}(p/N), \quad (2)$$

which indicates that the compound being considered can be obtained by removing l carbon atoms from each N -atom fragment of the diamond crystal and introducing into it n boron atoms. The quantity p , defined as $n-l$, is the number of defects formed in the original N -atom cell of the ideal diamond crystal, and the ratio $p/N \equiv a$ provides a measure of the defect character (nonstoichiometry) of the new crystal relative to the original. The previous values of the concentrations x and y are obviously n/N and $(N-l)/N$ respectively. The requirement that the compound $B_x C_y$ be isoelectronic with diamond imposes the following restriction on the values of n and l : $4l = 3n$. Taking account of this feature in the determination of p , we have $p = n/4$ and the following general equation for boron carbides isoelectronic with diamond:

$$B_{4p} C_{N-3p} (p/N)_x \quad (3)$$

where p , since x and y are positive, may take integral positive values from 1 to $N/3$. Using Eq. (3), we can readily determine the formula of boron carbide isoelectronic with diamond and having the required degree of nonstoichiometry, and subsequent variation of the values of N and p within the given limits generates families of these compounds.

By means of arguments of the same type, it is possible to obtain equations analogous to Eq. (3) for other two-component systems from the elements of the second period, isoelectronic with diamond. The corresponding information is given in Table 1. It may be noted that, although the chemical formulae contain only the symbols of the elements of the second period, they may equally well contain the corresponding elements of other periods (for example, H in place of Li, or Si in place of C). The values of x and y are renormalized (without loss of generality) in such a way that they remain integral (see the example discussed in detail for $B_x C_y$). As before, the measure of the nonstoichiometry a is equal to $(x + y - N)/N$.

TABLE 1. Chemical Formulae of Two-Component Compounds Isoelectronic with Diamond

System	x	y	a	Restrictions
B_xC_y	4p	N-3p	p/N	$1 \leq p < N/3$
N_xC_y	4p	N-5p	-p/N	$1 \leq p < N/5$
Be_xC_y	2p	N-p	p/N	$1 \leq p < N$
O_xC_y	2p	N-3p	-p/N	$1 \leq p < N/3$
Li_xC_y	4p	N-p	3p/N	$1 \leq p < N$
F_xC_y	4p	N-7p	-3p/N	$1 \leq p < N/7$
Li_xB_y	(3p-N)/2	(3N-p)/2	p/N	$N/3 < p < 3N$
Be_xB_y	3p-N	2(N-p)	p/N	$N/3 < p < N$
Li_xN_y	(5p+N)/4	(3N-p)/4	p/N	$-N/5 < p < 3N$
Be_xN_y	(5p+N)/3	2(N-p)/3	p/N	$-N/5 < p < N$
B_xN_y	(5p+N)/2	(N-3p)/2	p/N	$-N/5 < p < N/3$
Li_xO_y	2(3p+N)/5	(3N-p)/5	p/N	$-N/3 < p < 3N$
Be_xO_y	(3p+N)/2	(N-p)/2	p/N	$-N/3 < p < N$
B_xO_y	2(3p+N)/3	(N-3p)/3	p/N	$-N/3 < p < N/3$
N_xO_y	2(3p+N)	-5p-N	p/N	$-N/3 < p < -N/5$
Li_xF_y	(7p+3N)/6	(3N-p)/6	p/N	$-3N/7 < p < 3N$
Be_xF_y	(7p+3N)/5	2(N-p)/5	p/N	$-3N/7 < p < N$
B_xF_y	(7p+3N)/4	(N-3p)/4	p/N	$-3N/7 < p < N/3$
N_xF_y	(7p+3N)2	-(5p+N)/2	p/N	$-3N/7 < p < -N/5$
O_xF_y	7p+3N	-6p-2N	p/N	$-3N/7 < p < -N/3$

Of particular interest among the large variety of compounds isoelectronic with diamond are the stoichiometric combinations, for which $x+y+z+\dots=N$, that is $a=0$, since they permit, in principle, the construction of a defect-free diamond-like structure. If we restrict ourselves to two-component systems, the only possible combinations are BN, BeO, LiF, BeN₂, B₂O, LiN₃, B₃F, Be₃F₂, Li₂O₃. Attention was previously drawn to these substances by Hall [1], who called them "periodic compounds."

Among the nonstoichiometric compounds, we are interested primarily in cases where the quantity N appearing in the equation is a multiple of the number of atoms in the unit cell of the diamond crystal (or equal to it). In the first place, in this situation it is obviously possible in principle to produce a new crystal structure by the simple replacement of the unit cells by others. In the second place, in accordance with what has been said above, it is this situation that corresponds to the existing hard materials B₄C, Si₃N₄, etc. The unit cell of diamond (in the sense adopted in solid state theory) contains two atoms and is shown in Fig. 1. There are seven corresponding nonstoichiometric compounds isoelectronic with diamond: Li₄C(+3/2), Be₂C(+1/2), Li₂B₂(+2/2), Li₅B(+4/2), BeB₂(+1/2), Li₃N(+2/2) and Li₂O(+1/2). The next largest elementary volumes which can be regarded as structural units of the diamond crystal are the four-atom rhombohedron and the eight-atom cube, represented in Fig. 2 (anisotropic crystals are not dealt with here). The structural units of larger volumes can be obtained by the isotropic expansion of these unit cells. For example, from eight two-atom rhombohedra (see Fig. 1) it is possible to construct a sixteen-atom (N=16) rhombohedron, the length of whose edge is twice the original value. Similarly, eight of the cubes shown in Fig. 2, combined to form a new cube, give a structural fragment of the diamond crystal with N=64. In the general case, the similarity transformation indicates simply an m-fold increase in the linear dimension of the unit volume, and in the examples which we have considered it corresponds to the equations $N=2m^3$, $N=4m^3$, and $N=8m^3$, where $m=1, 2, 3, \dots$. Some of the first (smallest) values of N are obviously 2, 4, 8, 16, 32, 54, 64, 108, 128, 216, 250, 256. In this connection, for systems in the above list of stoichiometric compounds, such as B₂O and BeN₂, it is possible in principle to have a diamond-like structure only at the level of a cell containing 54 atoms, or 250 atoms in the case of Be₃F₂ and Li₂O₃. It can also readily be seen that a diamond-like structure can be realized at N=2 for BN, BeO, and LiF, and at N=4 for LiN₃ and B₃F.

We have also tabulated all nonstoichiometric two-component compounds isoelectronic with diamond in the volume of 4-, 8-, 16-, 32-, and 54-atom fragments of the crystal. The complete list is fairly large, so that we introduce an additional restriction. We define for each element of the second (or third) period a covalency index k. Since Li and F form the most ionic bonds, we assign to them the value $k=0$, and we assign the value $k=1$ to the most covalent element carbon. For Be, B, N, and O, linear interpolation gives $k=1/3, 2/3, 2/3$, and $1/3$ respectively. We next define the average covalency index \bar{k} for a two-component system A_xB_y as $(xk_A + yk_B)/-$

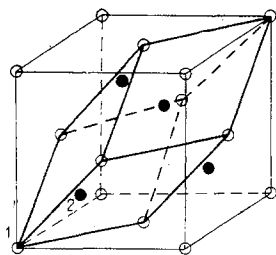


Fig. 1

Fig. 1. Rhombohedral cell with two atoms (1 and 2). The black circles show the atoms of the sublattice situated inside the face-centered cube illustrated.

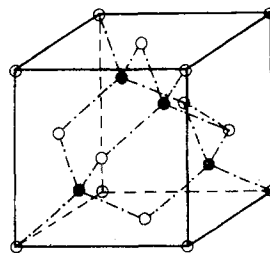


Fig. 2

Fig. 2. Cubic eight-atom cell of the diamond crystal. The dot-dash lines represent the bonds of the atoms of the second sublattice situated inside the face-centered cube.

($x+y$). We shall describe compounds for which $\bar{k} > 1/2$ as predominantly covalent. We are primarily interested in systems of this kind (the limiting covalent bond is realized in diamond). Table 2 gives nonstoichiometric two-component compounds which are isoelectronic with diamond in the volume of 4- and 8-atom fragments of the crystal and which satisfy the conditions: $\bar{k} \geq 1/2$, $|a| \leq 1/2$. It may be noted that this group includes the materials B_4C and Si_3N_4 (C_3N_4) noted above.

Among the two-component systems isoelectronic with diamond in the volume of a 16-atom fragment of the crystal, we shall restrict ourselves to those made up of the atoms of the most covalent elements C, B, and N. These are $B_4C_{13}(+1/16)$, $B_{12}C_7(+3/16)$, $B_{20}C(+5/16)$, $C_{11}N_4(-1/16)$, $CN_{12}(-3/16)$, $B_3N_{11}(-2/16)$, $B_{13}N_5(+2/16)$.

It should be emphasized that in the preceding and subsequent treatment it is not implied that all the compounds given in the tables can exist or are super-hard or hard materials. However, they represent the set of materials promising in this connection, which might be subjected to directed experimental testing and theoretical study by quantum-mechanical methods. The entire scheme of our study is obviously constructed on the treatment of the compounds obtained as defect diamond-like structures (the values of a have significance only with respect to the diamond crystal lattice) with vacancies ($a < 0$) or interstitial atoms ($a > 0$), but this does not mean that this must be the final crystal structure of the materials based on them. Thus the defect diamond-like structure represents the starting material, which, generally speaking, relaxes to an energetically more favorable state, and as a result of the fact that it is isoelectronic with diamond may preserve the qualitative characteristic features of the interatomic chemical bonds characteristic of the latter (with a slight distortion and decrease in their strength) and hence preserve a definite similarity to diamond in its mechanical properties. The high strength (hardness) characteristics of boron carbide B_4C and silicon nitride Si_3N_4 [2], which, as noted above, are compounds isoelectronic with diamond in the volume of fragments with $N=4$ and $N=8$ respectively, indicate that these compounds, which have crystal lattices with rhombohedral and hexagonal symmetry, represent the result of a transformation of this kind.

Two-component systems, although appearing attractive because of their simplicity, naturally open up comparatively few possibilities in the search for new hard materials. The fact is that highly covalent compounds isoelectronic with diamond, such as BN , B_4C , and Si_3N_4 , already exist in practice, and the remaining combinations, with few exceptions (see below) either include too many atoms with a tendency to form ionic bonds or correspond to too great a distortion (too large a number of defects) of the crystal structure relative to diamond, as a result of which stable (or metastable) formation can hardly exist. The more complex ternary systems appear more promising in this connection. The programs discussed above have been used to tabulate three-component compounds formed by the elements of the nontransition periods, isoelectronic with diamond in the volume of 2-, 4-, 8-, and 16-atom fragments of the crystal.

Of the systems obtained in this way (several hundred), the compounds of greatest interest are, firstly, the stoichiometric compounds (with $a=0$) formed by the atoms B, C, N, and O (from the considerations already discussed). It is clear that these compounds, made up of three components, cannot exist for $N=2$. Secondly, nonstoichiometric compounds for which $0 < a \leq 1/2$ and in which the number of defects coincides with the number of lithium or beryllium atoms in the chemical formula are also of interest. The fact is that these atoms are among the most active electron donors (in the second period) and at the same time the Li^+ and Be^{2+} ions are

TABLE 2. Nonstoichiometric Two-Component Compounds Isoelectronic with Diamond in the Volume of 4- and 8-Atom Fragments of the Crystal

System	N	a	\bar{k}	System	N	a	\bar{k}
Be ₂ C ₆	4	+1/4	11/15	B ₄ C ₅	8	+1/8	11/15
B ₄ C	4	+1/4	11/15	C ₃ N ₄	8	-1/8	17/21
LiB ₅	4	+2/4	5/9	BeB ₁₀	8	+3/8	7/11
N ₂ O	4	-1/4	5/9	BeN ₆	8	-1/8	13/21
Li ₄ C ₇	8	+3/8	7/11	B ₉ N	8	+2/8	2/3
Be ₂ C ₇	8	+1/8	23/27	N ₅ F	8	-2/8	5/9

TABLE 3. Two- and Three-Component Systems Isoelectronic with Diamond, Recommended for the Synthesis of New Super-Hard Materials

System	N	a	System	N	a
BeB ₂	2	+1/2	LiBC ₃	4	+1/4
B ₃ F	4	0	LiB ₃ O	4	+1/4
B ₄ C ₅	8	+1/8	BeB ₂ C ₂	4	+1/4
B ₃ N	8	+2/8	BeB ₃ N	4	+1/4
LiBC	2	+1/2	Li ₂ B ₃ N	4	+2/4
BC ₂ N	4	0	LiBC ₇	8	+1/8
B ₂ CO	4	0	BeB ₂ C ₆	8	+1/8
BC ₆ N	8	0	BeB ₅ N ₃	8	+1/8
B ₃ C ₂ N ₃	8	0	BeB ₆ O ₂	8	+1/8
B ₂ C ₅ O	8	0	Li ₂ B ₅ N ₃	8	+2/8
B ₃ C ₄ F	8	0	Li ₃ B ₃ C ₅	8	+3/8
B ₃ NO ₂	8	0	Be ₃ B ₆ C ₂	8	+3/8
B ₅ N ₂ F	8	0	Be ₃ B ₇ N	8	+3/8

small and can readily penetrate into the "cavities" of the open crystal structure of diamond (the ratio of the number of "cavities" to the number of atoms in the crystal is 1:2). Finally, systems containing fluorine also deserve attention, since F atoms, as already noted, for example, in [3], in compounds with graphite act as π -electron charge acceptors and bring about corrugation or destabilization of graphite-like structures. Thus in accordance with the ideas discussed in [3], and also in [4], regarding the mechanisms of the synthesis of diamond, fluorine atoms in systems isoelectronic with diamond may play a dual role, since on the one hand they act as catalysts in the synthesis, and on the other hand they are components of the final product. Three-component compounds satisfying these restrictions are given in Table 3 (for brevity, compounds of this kind corresponding to N=16 are not given). Together with the representatives of the binary systems discussed above, added on the basis of the same considerations, they can be recommended as promising substances for the creation of new super-hard materials. It should be emphasized again that although the chemical formulae include only the symbols of the elements of the second period, the partial or complete replacement of the latter by the corresponding elements of the third period is possible in all cases.

In spite of the fact that the compounds given in Table 3 have been obtained "by machine," the similarity between their electronic structures and those of diamond and boron nitride BN is obvious. We can discuss this in more detail, for example, for LiBC, which is isoelectronic with diamond and also BN in the volume of the unit cell of the crystal. This contains two atoms (see Fig. 1), so that the crystal lattice of diamond consists of two face-centered cubic sublattices. In accordance with what was said at the start of the present work, boron nitride BN can be regarded as resulting from the replacement of all the carbon atoms of one of the sublattices in diamond by boron atoms, and the replacement of all the atoms of the other sublattice by nitrogen atoms. If however instead of replacing the C atoms of the second sublattice by N atoms we introduce Li atoms into the "cavities" of the diamond lattice, the electron deficit produced by the replacement of the C atoms of the first sublattice by B atoms will again be eliminated, and the resulting product is LiBC.

The next stage of the work involved a quantum-chemical calculation for model fragments of the LiBC system. The results obtained will be published in a separate paper. The aim of the calculations was to compare the electronic characteristics of the lithium and boron atoms in a hypothetical diamond-like crystal LiBC and in the isolated state and to investigate the degree of correspondence (similarity) between the electronic struc-

ture of this crystal and the crystal of diamond. The desired picture of the redistribution of electronic charge in LiBC corresponds in the limiting case to the reduction of the electronic configuration of all the boron atoms, situated in the diamond lattice sites, to the carbon-like state B^- , and the oxidation of all the lithium atoms, situated in the interstices, to the state Li^+ .

The extended Hückel method was used to carry out calculations for the clusters C_5 , C_4B , C_4BLi , C_{17} , $C_{16}B$, and $C_{16}BLi$ with geometric parameters corresponding to the crystal structure of diamond. The clusters C_5 and C_{17} correspond to one and two coordination spheres of the crystal, C_4B and $C_{16}B$ correspond to the replacement of the central C atom by a boron atom, and C_4BLi and $C_{16}BLi$ correspond to the introduction of a lithium atom at the center of one of the "cavities" in the diamond crystal, closest to the boron atom. Possible distortions of the interatomic distances as a result of the replacement $C \rightarrow B$ or the introduction of the Li atom were ignored. An attempt was made to decrease the influence of surface effects in the clusters by unpairing the spins of all the "surface" electrons (that is the electrons involved in chemical bonds outside the cluster in the crystal).

The results of the calculations are interpreted as follows. The cluster C_5 is assigned four doubly occupied levels, corresponding to bonds between the central carbon atom and the atoms of the first coordination sphere, and 12 singly occupied levels, which correspond to unsaturated bonds formed by separating the cluster from the crystal. The set of these levels forms the "valence zone," and the remaining four unoccupied levels are interpreted as the "conductivity zone." The replacement of the central C atom in C_5 by boron creates in the valence zone a hole state, which disappears when the Li atom is introduced into the cluster, with the formation of, firstly, an additional unoccupied level between the zones and three additional levels in the conductivity zone. Since in the tight binding approximation this hole state is close to one of the valence states of the boron atom, and the additional unoccupied levels correspond to valence states of the Li atom, we should expect a displacement of the center of the region in which the 2s electron of lithium is localized in the direction of the boron atom. The same conclusion may be reached on the basis of a comparison of the values of the Mülliken populations of the boron atom Q_B in the clusters C_4B and C_4BLi . In the first of these, $Q_B = 1.97$, and in the second, $Q_B = 2.48$. The low absolute values of the populations can be attributed to surface effects: According to the calculations, the carbon atoms, which are "surface" atoms in the clusters C_4B and C_4BLi , act as electron charge acceptors (approximately 0.2-0.3 electron for every C atom). An attempt to decrease the influence of the surface by the addition of a second coordination sphere did not give the desired results: In the clusters C_{17} , $C_{16}B$, and $C_{16}BLi$, all the carbon atoms are charge acceptors, and because of their large number, the overall effect is greater than that for the clusters with one coordination sphere. In particular, the populations of the boron atoms in $C_{16}B$ and $C_{16}BLi$ were found to be 1.69 and 2.19 respectively. In both cases, however, there is a clearly defined qualitative tendency for the electron population of the boron atom to increase considerably when the Li atom is introduced into the cluster. In our view, this is in good agreement with the ideal picture outlined above for the distribution of the electronic charge in the hypothetical three-component super-hard material LiBC.

In conclusion, mention may be made of the possibilities for the practical production of the compounds recommended. One such possibility can be seen in the fixation of crystalline structures, isoelectronic with diamond, in a metastable phase by the application of high pressure. Another route involves the dissolution of fractions isoelectronic with diamond in metals and the production of solid solutions isoelectronic with metal carbides (as for example in the case of the material $TiC_{0.5}N_{0.4}$, already used in practice). Finally, it is worth considering the possibility of using the above chemical formulae for a combination of compounds, isoelectronic with diamond, from atoms of the second and third periods (diamond-like structures formed by the atoms of the third period are more stable and hence may "withstand" greater structural distortions; compare diamond, SiC, Si or C_3N_4 , Si_3N_4).

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