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ATOMIC CLUSTERS

Classification and Structure of Silicon Carbide Phases

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Abstract—Molecular-mechanical and semi-empirical quantum-mechanical methods have been applied to model and calculate a geometrically optimized structure of clusters of polymorphic types of silicon carbide, their structural parameters and some properties (densities, sublimation energies) have been determined. A classification of silicon carbide phases has been proposed, which shows the possible existence of twenty one SiC phases whose atoms are at crystallographically equivalent sites. The structure of seventeen proposed silicon carbide phases have been described and studied for silicon carbide for the first time.

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1. INTRODUCTION

Theoretical and experimental studies of silicon carbide (SiC), i.e., wide band-gap semiconductor with dominantly covalent chemical bond, performed to the present time suggest the possibility of the existence of various structures of silicon carbide phases which are conventionally classified as various polytypes. Among such SiC polytype modifications, phases with cubic crystal structure β-SiC (or 3*C*-SiC) stable to 2000°C are distinguished and phases with hexagonal and rhombohedral α-SiC structure (e.g., 2*H*-SiC, 4*H*-SiC, 6*H*-SiC, and *nH*-SiC, 15*R*, 21*R*, and others) stable at higher temperatures [1–3]. The main structural differences of polytypes are controlled only by the alternation order and period of layers along the crystallographic *Z* axis, the primitive unit cell type, and the degree of hexagonality. The properties of various SiC polytype are given in [1–5].

The structure of silicon carbide phases is similar to the structure of phases of a number of compounds with preferentially covalent bond type, i.e., diamond-like, silicon, and others [1–4]. For diamond-like phases, there exist a number of structural modifications other than polytypes [6–11]. Therefore, it is necessary to search for silicon carbide phases of analogues. The urgency of the study of such phases is caused by the fact that their structure can vary in a wider range than that of polytypes; their properties can differ significantly, and silicon carbide materials with such a structure are promising for wide applications as structural materials and in electronic devices.

New silicon carbide phases can be obtained from SiC clusters. The possible structure of such clusters was considered in many studies. For example, in [12], the structure and thermal properties of optimized "heterofullerenes" $C_{54}Si_6$ was theoretically calculated. In [13], the electronic structure and stability of Si_xC_{n-x} clusters were studied. Previously, such silicon carbide clusters were synthesized and studied in [14]. The optimized configuration, electronic structure, and spectral characteristics were calculated in [15] for fullerene-like clusters $Si_{12}C_{12}$ and some other wide band-gap semiconductors of composition $X_{12}Y_{12}$ as the most stable ones.

The most complete set of crystal-forming silicon carbide clusters (fulsicen) Si_nC_n and crystals on their basis (fulsicenites) was theoretically studied in detail in [16]. For clusters with n = 12, 16, 18, 24, 36, 60, energy characteristics were calculated and the dependence of configuration distortions and carbon and silicon carbide cluster stability on the number of carbon and silicon atoms per cluster were determined. For the constructed clusters, the bond lengths and angles between bonds were determined. Furthermore, the crystal structure of phases constructed based on spherical Si_nC_n clusters with n = 12 and 24 was modeled by molecular dynamics methods. According to the results of calculations, five new phases were proposed for the first time, and their X-ray diffraction patterns were theoretically calculated [16].

Thus, a number of new fullerene-like SiC clusters were experimentally synthesized to the present time. Based on some of them, new silicon carbide phases were proposed and theoretically studied. However, the features of the formation of such phases remain poorly studied. There is no classification of such phases; it remains unclear, what number of such phases can exist, what nanostructure precursors (in addition to

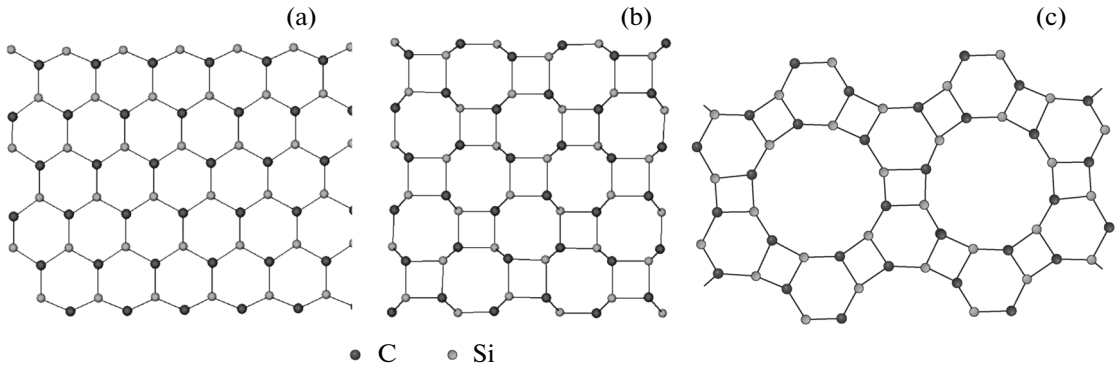

Fig. 1. SiC layers consisting of (a) hexagons; (b tetragons and octagons; (c) tetragons, hexagons, and dodecagons.

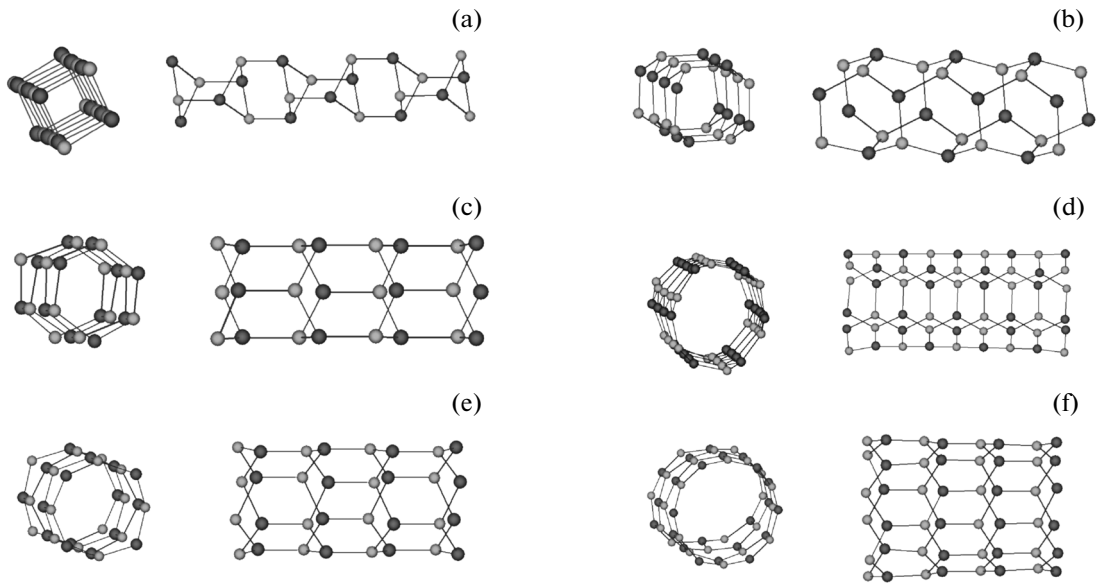

Fig. 2. SiC nanotubes: (a) (2,0); (b) (2,2); (c) (3,0); (d) (3,3); (e) (4,0); (f) (6,0).

fullerene-like clusters) can be a basis for their construction, and what is the final structure of new silicon carbide phases. In this paper, we theoretically analyze the possible structure of silicon carbide phases in which carbon and silicon atoms are at crystallographically equivalent sites and calculate their structure and some properties.

2. STRUCTURAL MODEL AND CALCULATION PROCEDURE FOR SILICON CARBIDE PHASES

SiC phases belong to compounds with preferably covalent chemical bonds; hence, structures similar to those diamond-like phases should be formed. Previously [11], a classification scheme for structural types of diamond-like phases and a model mechanism of their construction were developed. For silicon carbide phases, a similar classification scheme and a model mechanism of their structure construction can be proposed.

Initial structural elements for model construction of silicon carbide phases can be nanostructure precursors; as such, we used layers consisting of silicon and carbon atoms (Fig. 1) and framework silicon carbide nanostructures, i.e., fullerene-like SiC clusters (Fig. 2) and single-wall SiC nanotubes (Fig. 3).

As mechanisms for constructing polymorphic SiC types, we used linking of nanostructure precursors or combination of nanostructure precursor atoms. In this case, all atoms of these precursors should be in equiv-

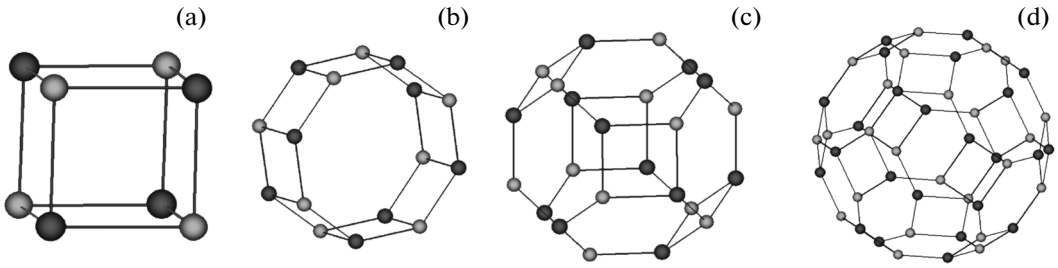

Fig. 3. Fullerene-like SiC clusters: (a) Si_4C_4, (b) Si_8C_8, (c) $Si_{12}C_{12}$, and (d) $Si_{24}C_{24}$.

alent crystallographic states. It seems that the method of model construction of silicon carbide phases from model nanostructures of precursors cannot be experimentally implemented; however, it makes it possible to obtain and describe all possible structures of polymorphic SiC types.

In the case where the nanostructure precursor is the SiC layer, as such precursors, we consider three types of model SiC layers consisting of hexagons; tetragons and octagons; tetragons, hexagons, and dodecagons.

In the case where the nanostructure precursor is a single-wall SiC nanotube, silicon carbide phases with atoms at crystallographically equivalent sites can be obtained only using the following six nanotubes: (2,2), (3,3), (2,0), (3,0), (4,0), and (6,0) (Fig. 2). The limitedness of some nanotubes is due to the fact that some atoms of nanotubes with large indices or some chiral nanotubes remain bound only with three neighbors during linking or combining. This results in the structures with atoms at various crystallographically inequivalent sites, which are not considered in this study.

As the third of possible types nanostructure precursors of silicon carbide phases, we consider a number of fullerene-like clusters, i.e., SiC clusters such as Si_4C_4, Si_8C_8, $Si_{12}C_{12}$, and $Si_{24}C_{24}$ (Fig. 3). The existence of model cluster precursors with the number of atoms less than eight (Si_2C_2, Si_3C_3) is impossible, since the arrangement of silicon and carbon atoms in the lattice is violated in this case (bonds between atoms of the same type are necessary). At the same time, the small number of clusters in this series is caused by a number of limiting factors. First, as in the case of large-diameter nanotubes, linking or combining of fullerene-like clusters containing a larger number of atoms can yield only phases with atoms at various crystallographically inequivalent sites. The second factor rejecting some fullerene-like clusters with a number of atoms less than 48, is the requirement of carbon and silicon atom arrangement at equivalent sites; therefore, framework molecules for which this requirement is not satisfied are outside this series. Finally, the third limiting factor is the necessity of constructing the periodic crystal structures from cluster precursors; the periodic structures can be constructed from clusters with only 2-, 3-, 4-, 6-, or 8-fold symmetry axes. Among the above fullerene-like nanostructure precursors, only one cluster Si_6C_6 is absent, which is not rejected according to three above criteria. This fullerene-like cluster did not enter the series because the SiC phase obtained by linking such clusters can also result from linking the framework molecule $Si_{24}C_{24}$.

The first mechanism of model construction of silicon carbide phases is linking of nanostructure precursors. This operation results in Si–C bond formation between structure precursor atoms. Figure 4 shows the illustrative example of the formation of the silicon carbide structure by linking fullerene-like SiC clusters.

The second mechanism of model construction of silicon carbide phases is the combination of atoms of their structure precursors. In this case, identical faces of nanoparticle precursors are combined followed by removal of atoms of one of coincided faces and linking of dangling bonds. The illustrative example of the formation of the silicon carbide phase structure from fullerene-like SiC clusters is shown in Fig. 5.

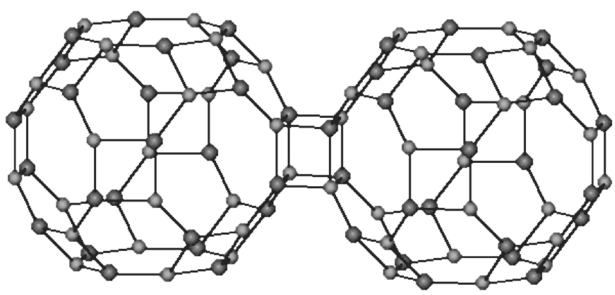

Fig. 4. Model construction of the *CA*4 structure by linking square faces of fullerene-like $Si_{24}C_{24}$ clusters.

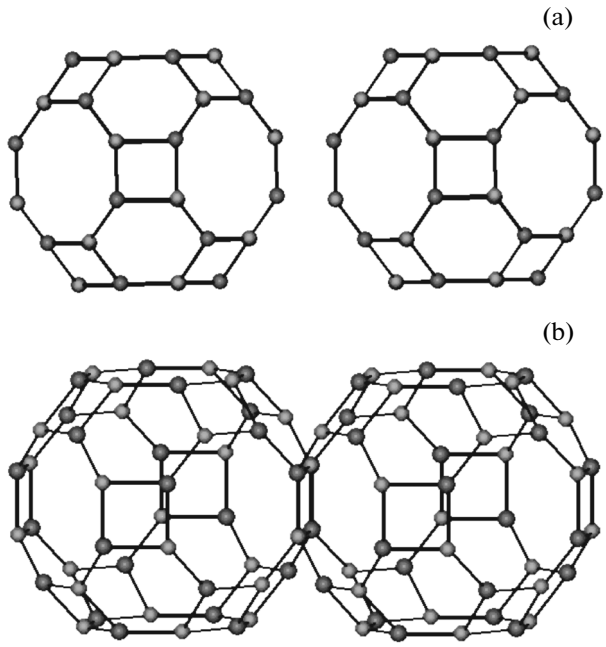

Fig. 5. Mechanism for constructing the *CA*4 structure, based on combination of SiC clusters $Si_{12}C_{12}$: (a) cluster approaching by square faces; (b) combination of cluster walls.

3. RESULTS

As a result of modeling of new polymorphic types of silicon carbide, three structural families to which all silicon carbide phases can belong were selected: (i) *L*-phases obtained from SiC layers; (ii) *T*-phases constructed based on single-wall SiC nanotubes; (iii) *C*-phases obtained from fullerene-like SiC clusters.

In the notations of SiC phases, symbols denoting the method of their construction from nanostructure precursors (*A* means linking and *B* is combination and the structure precursor (e.g., nanotube (3,0)) were used. Furthermore, different conditional serial numbers (e.g., *TA*1 and *TA*2) were attributed to different phases of the same family, obtained by the same method.

A theoretical analysis of the SiC phases obtained by model calculation showed the possible existence of twenty one silicon carbide phases (Table 1), eight, seven, and six of which belong to *L*-, *T*-, and *C*-phase families (Figs. 6a, 6b, and 6c), respectively. The number of all possible methods for constructing silicon carbide phases varies from one to four (Table 1). As the main method for constructing phases, the most probable among possible ones were chosen. Among nanostructure precursors, the series of the most probable construction (in the order of decreasing probability is as follows: layers, nanotubes, fullerene-like clusters. This series corresponds to the experimentally observed degree of stability of corresponding nanostructures. Among various types of silicon carbide layer structures, the series (in order of decreasing probability) was as follows: 6, 4–8, 4–6–12. Among the mechanisms of phase construction, linking is the most probable one, since combination is not experimentally implementable. For example, if the *CA*3 phase can be obtained by four different methods (from the $C^{A}_{Si_4C_4}$ cluster, by linking; from the T^{A}_{4-8} nanotube formed by rolling the 4–8 silicon carbide layer, by linking; from the T^{B}_{4-8} nanotube, by combination; from the L^{A}_{4-8} layer, by linking), then the most stable precursor for obtaining this phase is the Si_4C_4 cluster. Therefore, this phase got the corresponding notation. The notation of cluster phases begins from the *CA*3 phase, since such silicon carbide phases have diamond-like structural analogues described previously in [11]. For silicon carbide, the existence of phases with *CA*1 and *CA*2 structures is impossible.

The structure of model-constructed SiC phases was compared with the previously known and experimentally synthesized silicon carbide modifications.

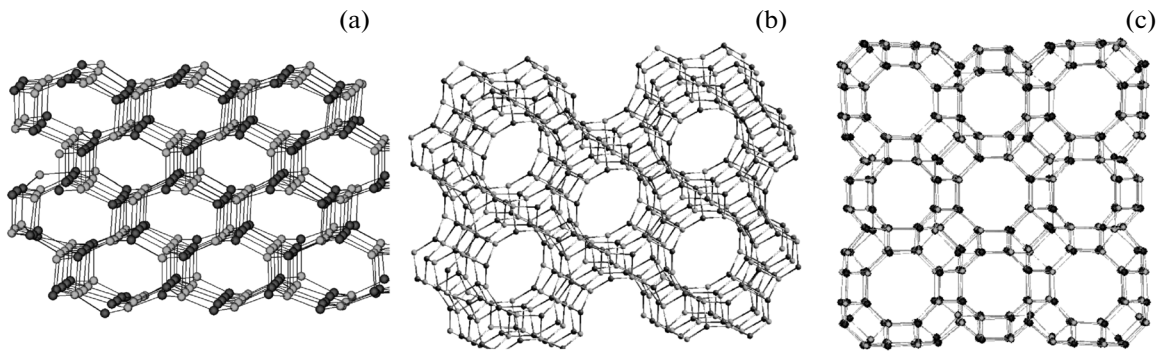

Fig. 6. Structure fragments of phases constructed from nanostructure precursors: (a) *LA*6, (b) *TA*7, and (c) *CA*8.

Table 1. Polymorphic types of silicon carbide

Phase	*Rng*	Def, °	*n*	Precursors	Another notation
*LA*1	6^6	0.419	3	L_6, $T^A_{(3,0)}$, $T^B_{(3,0)}$	β-SiC, 3*C*-SiC [1–4]
*LA*2	6^6	2.135	1	L^A_6	2*H*-SiC [1–4]
*LA*3	4^16^5	51.65	4	L^A_6, $T^A_{(2,2)}$, $T^B_{(2,2)}$, L^A_{4-8}	*
*LA*4	6^6	60.75	1	L^A_6	*
*LA*5	4^16^5	50.40	1	L^A_6	*
*LA*6	$4^26^38^1$	41.32	1	L^A_6	*
*LA*7	$4^26^38^1$	38.45	1	L^A_6	*
*LA*8	4^38^3	64.89	1	L^A_{4-8}	*
*TA*1	$4^26^38^1$	75.33	2	$T^A_{(2,2)}$, L^A_{4-8}	*
*TA*2	4^26^4	70.85	2	$T^A_{(3,3)}$, L^A_{4-6-12}	*
*TA*3	$4^26^28^2$	89.63	3	$T^A_{(2,0)}$, T^B_{4-8}, L^A_{4-8}	*
*TA*4	$4^26^38^1$	52.82	3	$T^A_{(3,0)}$, T^A_{4-8}, L^A_{4-6-12}	*
*TA*5	$4^26^38^1$	57.61	3	$T^A_{(4,0)}$, T^A_{4-8}, L^A_{4-8}	*
*TA*6	4^16^5	48.10	4	$T^A_{(4,0)}$, $T^A_{(2,0)}$, $T^B_{(4,0)}$, L^A_{4-8}	*
*TA*7	4^16^5	48.50	4	$T^A_{(6,0)}$, $T^A_{(3,0)}$, $T^A_{(2,0)}$, L^A_{4-6-12}	*
*CA*3	4^38^3	105.6	4	$C^A_{Si_4C_4}$, T^A_{4-8}, T^B_{4-8}, L^A_{4-8}	*
*CA*4	$4^36^28^1$	104.2	4	$C^A_{Si_4C_4}$, $C^A_{Si_{12}C_{12}}$, $C^A_{Si_{24}C_{24}}$, $C^B_{Si_{24}C_{24}}$	Fulsicenite KSF-$Si_{12}C_{12}$ [15]
*CA*5	4^38^3	107.1	3	$C^A_{Si_8C_8}$, T^A_{4-8}, L^A_{4-8}	*
*CA*6	4^26^4	88.61	2	$C^A_{Si_{12}C_{12}}$, $C^B_{Si_{12}C_{12}}$	*
*CA*7	$4^36^18^2$	118.7	4	$C^A_{Si_{24}C_{24}}$, $C^B_{Si_{24}C_{24}}$, $C^A_{Si_8C_8}$, $C^B_{Si_8C_8}$	Fulsicenite GTsKF-$Si_{24}C_{24}$ [15]
*CA*8	$4^36^18^2$	112.9	2	$C^A_{Si_{24}C_{24}}$, $C^A_{Si_6C_6}$	*

Note: *n* is the number of methods for constructing the phase; notations of nanostructure precursors: *L* is the layered structure, *T* is the tubular structure, *C* is the fullerene-like cluster, the subscript denotes the nanostructure precursor type, the superscript denotes the method for constructing the phase from precursors: *A* and *B* mean linking and combination, respectively; * is the phase described and studied in this work for the first time.

The structure of the *LA*1 phase corresponds to that of the cubic modification of silicon carbide β-SiC (3*C*), the structure of the *LA*2 phase corresponds to the structure of the hexagonal modification (2*H*), the structures of the *CA*4 and *CA*7 phases obtained based on fullerene-like cluster precursors correspond to the KSF-$Si_{12}C_{12}$ and GTsKF-$Si_{24}C_{24}$ fulsicenite phases experimentally observed in [16]. Sixteen of the phases

Table 2. Structural parameters and properties of silicon carbide phases

Phase	Structural parameters				Phase properties	
	Unit cell parameters					
	Crystal system	a, Å	c, Å	N, at.	ρ, g/cm^3	E_{sub}, kcal/mol
*LA*1	*C*	4.354	–	8	3.227	153.972
*LA*2	*H*	3.091	5.021	4	3.206	153.439
*LA*3	*T*	5.261	3.151	8	3.055	150.854
*TA*1	*T*	7.579	3.150	16	2.944	142.965
*TA*2	*H*	7.274	3.219	12	2.708	146.681
*TA*3	*T*	4.385	5.112	8	2.711	128.733
*TA*4	*H*	8.572	4.971	24	2.527	146.415
*TA*5	*T*	8.400	5.519	32	2.737	139.856
*TA*6	*T*	8.544	5.182	32	2.817	147.455
*TA*7	*H*	8.457	5.192	24	2.486	146.495
*CA*3	*C*	5.955	–	16	2.523	139.824
*CA*4	*C*	7.219	–	24	2.124	143.091
*CA*5	*T*	8.728	5.573	32	2.510	136.639
*CA*6	*C*	5.423	–	12	2.506	138.657
*CA*7	*C*	8.988	–	48	2.202	126.520
*CA*8	*C*	11.388	–	96	2.165	140.341

Note: Results of calculations by molecular mechanics methods *MM*+ and semi-empirical quantum-mechanical method PM3; crystal systems: *C* cubic, *T* tetragonal, and *H* hexagonal ones; *N* is the number of atoms per unit cell, ρ is the density, and E_{sub} is the sublimation energy.

constructed in the study are characterized by the structure similar to the structure of diamond-like phases described previously in [11]. Five layered phases *LA*4–*LA*8 are constructed and studied in this work for the first time; the structure of these phases should have diamond-like analogues not studied previously.

Thus, among twenty one model-calculated structures of SiC polymorphic types, 17 new silicon carbide phases were described and studied in the present work for the first time.

As a result of the comparative analysis of all obtained SiC phases consisting of sp^3-hybridized atoms, it was found that they differ by structure states of atoms which can be characterized by a relative orientation of carbon–silicon σ-bonds formed by each atom. The structure state of atoms in SiC phases (the relative orientation of bonds formed by them) can be described by six angles β_{ij} ($i \neq j$; $i, j = 1, 2, 3, 4$, where i and j are bond numbers) between each pair of four bonds and lengths of four bonds L_i formed by each atom.

Angles between bonds β_{ij} and bond lengths L_i were measured in all structure fragments of polymorphic types of silicon carbide, geometrically optimized by molecular mechanics *MM*+ methods [17]. A comparative analysis of angles β_{ij} of phases showed that their values vary in the range from 82.079 to 136.371°. In this case, the angles between bonds in calculated SiC phases are smaller or larger than 109.5°. The bond lengths are from 1.820 to 2.023 Å. Almost equal bond lengths are observed for the *LA*1 phase (cubic modification of silicon carbide) and the *CA*2 phase. In other phases, σ-bonds are different.

For the obtained silicon carbide phases, we also determined the parameter *Rng* describing (in the symbolical form) the structure of rings with a minimum number of covalent bonds, including one atom (similarly to diamond-like structures [11], the number of such rings passing through one atom is six) and the parameter Def which is the sum of magnitudes of the

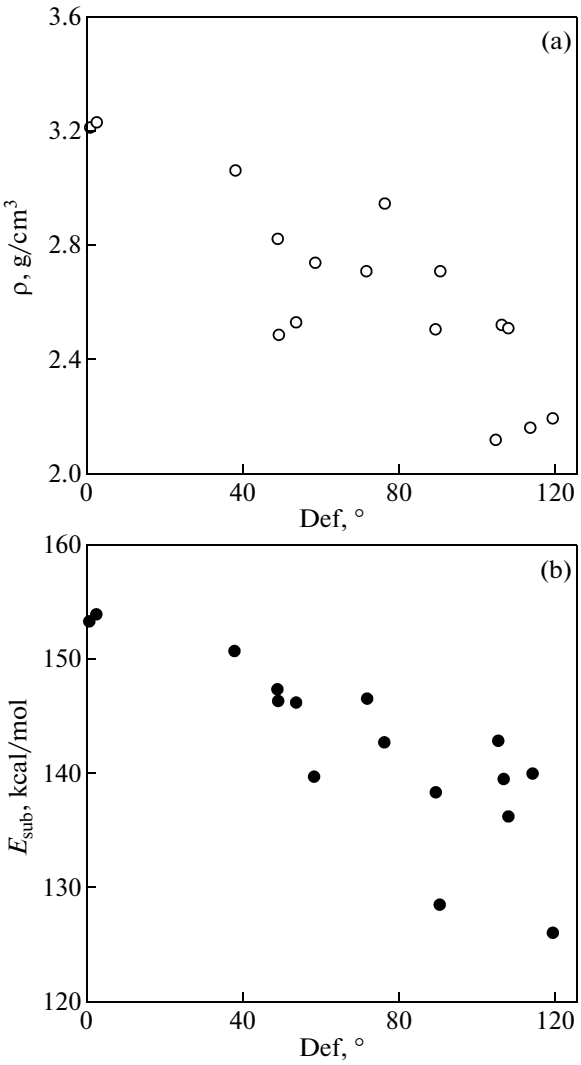

Fig. 7. Dependences of the density and sublimation energy of the silicon carbide phase on the deformation parameter, obtained by the PM3 method.

difference of angles β_{ij} and the angle of the cubic SiC polytype (Table 1),

$$\mathrm{Def} = \sum_{i=1}^{3}\sum_{j>i}^{4}|\beta_{ij} - \beta_{3C}|, \quad \beta_{3C} = 109.5°.$$

The parameter Def makes it possible to characterize deformation of the structures of polymorphic types of silicon carbide.

Calculations of the parameter Def showed that its values are in the range from 0.419 to 118.662°. For the *L*-phase, the deformation parameter vary in the range from 0.419 to 64.887°; for *T*-phases, they are from 48.062 to 89.629°; for the structures, constructed based on fullerene-like clusters, the values of the parameter Def are maximum and vary from 88.607 to 118.662°.

Unit cells of silicon carbide phases correspond to various crystal systems, cubic, tetragonal, or hexagonal ones whose parameters are given in Table 2. The calculated densities of SiC phases vary from 2.124 g/cm^3 for the *CA*4 phase to 3.227 g/cm^3 for *LA*1. The small disagreement between the experimental density of the cubic modification of silicon carbide (3.217 g/cm^3) [4] and the density calculated for the *LA*1 phase shows the correctness of the calculations of the structural parameters of SiC phases. An analysis of the data made it possible to determine the dependence of the density of SiC phases on the deformation parameter Def: the phase density decreases with increasing Def (Fig. 7a).

The sublimation energy of silicon carbide phases was calculated by the quantum-mechanical semi-empirical method PM3 [18, 19] (Table 2). The calculated energies are in the range from 126.520 kcal/mol for the *CA*7 phase to 153.972 kcal/mol for the *LA*1 phase. High-density phases are characterized by the highest energies. Furthermore, the dependence between the energy and deformation parameter is traced: the phase sublimation energy decreases with increasing Def (Fig. 7b).

4. CONCLUSIONS

Thus, as a result of this study, a classification scheme was proposed for silicon carbide phases consisting of carbon and silicon atoms which are in crystallographically equivalent states. Model calculations showed the existence of twenty one silicon carbide phases; the structure of seventeen was described for silicon carbide for the first time. Geometrically optimized structures of SiC-phase clusters were calculated, structural parameters, density, and sublimation energies of phases were determined using molecular mechanics methods MM+ and quantum-mechanical semi-empirical method PM3. The classified and studied phases differ significantly by their lattice structures; therefore, their properties should vary much stronger than properties of silicon carbide polytypes.

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SPELL: 1. fulsicen