Pseudo-crystals of the group 14 elements with both 5-fold central rotation symmetry and divisional translation symmetry

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(Dated: December 2, 2013)

Crystals are the materials which can be described by uniform periodic lattices. Traditionally, only the 1-, 2-, 3-, 4- and 6-fold symmetry are allowed in crystals because other n-fold rotation symmetries are forbidden by the fully periodic translation symmetry. Materials containing rotation symmetries forbidden in crystals can be optionally described as quasicrystals with aperiodicity. The theoretical predictions and experimental discoveries of quasicrystals have enriched our knowledge of crystallography and topology, and expanded the capability of growing novel materials. Mathematically, one can fill the whole space with quasi-uniform lattices through divisional translations and arbitrary n-fold central rotations, including the 5-fold symmetry. However, it is unknown if such pseudo-crystals with 5-fold symmetry exist in reality. Here we propose a generalized crystal-prediction-method which can be used to search for potential pseudo-crystals possessing both arbitrary n-fold rotation symmetry and divisional translation symmetry. Successful examples with 5-fold central rotation symmetry based on the group 14 elements are discussed. We expect timely experimental explorations on such peculiar structures, especially on the very promising clathrate phases of the group 14 elements with only slightly larger binding energies compared with the diamond phases.

PACS numbers: 61.44.Br, 61.50.Ah, 61.05.J-

Crystals are a class of materials which can be described by periodic lattice with translation symmetry. According to the well-know theorems of crystallography derived nearly two centuries ago, only the 1-, 2-, 3-, 4- and 6-fold symmetry are allowed in crystals because other n-fold symmetries, such as 5- and 7-fold ones, are forbidden by the fully periodic translation symmetry. The absence of 5-fold symmetry in periodic lattices had been mysterious in history for scientists. Kepler explored some special arrangements of planar pentagons [1] which can be viewed as preforms of Penrose’s aperiodic tilings [2]. Their endeavors provide important mathematical theory to describe a new type of materials defined as quasicrystals [3] with aperiodicity and the rotation symmetries forbidden in crystals. Since 1984 when Shechtman et al. first discovered [4] the crystal-like diffraction pattern with forbidden icosahedral symmetry from aluminum-manganese alloys, the mathematical topologies of pentagons derived from Kepler [1] and Penrose [2] have became more and more popular [5] in mathematics, crystallography and physics, and the quasi-crystallography has been developed into an elaborate disciplines [5]. The theoretical predictions and experimental discoveries of quasicrystals have significantly enriched our knowledge of crystallography and topology, and the Nobel Prize in Chemistry 2011 was awarded to Shechtman for the discovery of quasicrystals. Today, it is clear that one can only have periodic crystals and aperiodic quasicrystals, and any crystalline phases cannot possess both fully translation symmetry and 5-fold rotation symmetry. Nevertheless, we note that one can mathematically fill the whole space with quasi-uniform lattices through divisional translation operations and arbitrary n-fold central rotation operations. For example, Fibonacci pentilings containing 5-fold symmetry can be described by quasi-uniform parallelogram lattices through divisional translation operations and 5-fold rotation operations [5]. Here, we focus on the important question that “Is there any physically realistic materials containing both divisional translation symmetry and 5-fold rotation symmetry can be theoretically constructed and experimentally touchable?”. We expect such a novel topological manner of materials as new optional understandings [5-7] of the potential experimental discoveries of 5-, 8-, 10- and other higher n-fold diffraction-patterns. We propose a generalized crystal-prediction-method for the purpose of searching for potential crystalline networks containing both divisional translation symmetry and arbitrary n-fold rotation symmetry. With this method, we successfully realized some promising pseudo-crystals possessing both 5-fold central rotation symmetry and divisional translation symmetry, which can be potentially formed by the group 14 elements.

In traditional crystal prediction methods [8,11], one constructs the initial testing phase of elements or compounds through randomly filling specially defined lattice cell with corresponding symmetry operations from the space group and then fill the whole space with the constructed unit cell through only the translation
operations to form a crystal. In fact, under some special conditions we can fill the whole space with the constructed unit cell through the combination of translation operations and n-fold rotation operation. As shown in Fig.1 for the two-dimensional case, it is mathematically acceptable when the lattice cell is non-triclinic and the third lattice angle is $2\pi/n$. Taking the 5-fold (10-fold) one as example, we can fill the 1/5 area of the whole space with the $72^\circ$ ($36^\circ$) monoclinic cells through translation operation and the rest 4/5 areas with $C_5$, $C_5^2$, $C_5^3$ and $C_5^4$ rotation operations. That is to say, we can mathematically construct crystals with both translation symmetry and arbitrary n-fold central rotation symmetry. For the physically acceptable substantiality, we prefer to use the perfect and simple lattice of graphene as an example for the 3-fold condition. As indicated in Fig.1, we can represent graphene with the $120^\circ$ hexagonal lattice cell (with six carbon atoms) through translation operations and 3-fold rotation operations. We can also describe graphene with the same $120^\circ$ hexagonal lattice cell through only translation operations in a traditional way.

To construct a physically acceptable pseudo-crystal with both divisional translation symmetry and arbitrary n-fold central rotation symmetry, we need a proper arrangement of atoms or molecules in the unit cell, which ensures that neither translation operation nor rotation operation creates unreasonable configuration, especially on the areas of cell boundaries. Such a special physically acceptable arrangements of atoms or molecules can be easily identified by well-developed computer programs for topology analysis (such as TOPOS, Topological Databases and Topological Types Observed, http://www.topos.ssu.samara.ru) and physically optimized by first-principles calculations through a special cell-shape-keeping procedure. In summary, we can predict pseudo crystalline phases of elements or compounds with both divisional translation symmetry and arbitrary n-fold central rotation symmetry through: 1) randomly fill the special unit cell with atoms or molecules, 2) structurally filter reasonable arrangements of atoms or molecules, 3) physically optimize the unit cell and its inner atomic positions by first-principles calculations, and 4) extend the unit cell to crystalline form through divisional translation operation and corresponding n-fold rotation operation. With this method, we are able to predict many new crystalline phases of elements or compounds with both divisional translation symmetry and arbitrary n-fold central rotation symmetry.

Except for the two-dimensional graphene for the 3-fold condition discussed above, we find that the clathrate structure of type II can be considered as an excellent example for filling the three-dimensional space with divisional translation operations and 5-fold central rotation operations. Fig.2 shows the fundamental structural units, cage 20 and cage 28, of the clathrate structure II. Clathrate structure II can be realized in crystalline forms of elements Si and Ge with or without guest atoms in the cage positions [12–16]. It has also been discovered in crystalline forms of Tin [17] and hydrates [18, 19], in which guest atoms are popular. Clathrate structure II containing structural units of cage 20 and cage 28 can be described by a face-center cubic lattice with 136 vertexes (Fcc136), in which only three vertexes are not equivalent due to the high symmetry of its space group of Fd-3m (227). In fact, clathrate structure II can also be optionally described by other forms of lattices, such as the monoclinic I, II and the rectangular III and IV as indicated in Fig.2. The third angles of the monoclinic lattice-I and lattice-II are 35.265$^\circ$ and 75.530$^\circ$, respectively, very close to 36$^\circ$ and 72$^\circ$ (Lattice-II is a $\sqrt{2} \times \sqrt{2}$ supercell of lattice-I). Interestingly, we find that applying the 5-fold rotation operation (10-fold rotation reversion) on lattice-II (lattice-I) creates no any unreasonable interfacial configurations if we impose its third lattice angle to be 72$^\circ$ (36$^\circ$). This suggests that we can theoretically construct a promising crystalline network containing both divisional translation symmetry and 5-fold (10-fold) central rotation symmetry based on
We then performed cell-shape-keeping optimizations of the 36°-lattice-I structures in the situations of elements C, Si and Ge, respectively and then constructed the corresponding crystals of 36°-lattice-II through extending the optimized ones of 36°-lattice-I to \( \sqrt{2} \times \sqrt{2} \) supercells. The optimized lattice constants for crystals of 36°-lattice-II and lattice-I (35.265°) for C, Si and Ge are summarized in Fig.3. Comparing the lattice constants, we can see that the shear deformation from 35.265° to 36° slightly decreases the lattice constants of a and b but increases the lattice constant c. The small deformations in lattice-I for elements C, Si and Ge require very small deformation energies, indicating that the structures of 36°-lattice-I are physically realistic and experimentally touchable. In Fig.3, we also summarize the average energies of lattice-I and 36°-lattice-I for C, Si and Ge, respective to their corresponding ground states in the diamond-lattice. The corresponding deformation energies from lattice-I to 36°-lattice-I for C, Si and Ge are also summarized. For carbon, we can see that lattice-I possesses relatively high energy (\( \sim \)75 meV/atom) respective to diamond-lattice. This may be the reason that carbon-version clathrate structure II has not been experimentally reported. The deformation energy of lattice-I to 36°-lattice-I of 5.8 meV/atom is very small to be realized by temperature or other growth conditions. The average energy of Si-version (Ge-version) lattice-I respective to its corresponding ground state of diamond-lattice is 19 meV/atom (14 meV/atom). Such a small energy difference indicates a high probability of co-existences of Si (Ge) in lattice-I and diamond-lattice, which is in good agreement with the fact that Si and Ge clathrate II structures have been successfully discovered in experiments [12,14]. Moreover, the deformation energy of Si (Ge) lattice-I from 35.265° to 36° is only 2.5 meV/atom (1.4 meV/atom), indicating that Si (Ge) phases in perfect lattice-I and 36°-lattice-I are nearly energy degenerated. From the calculated density of state of these phases as shown in Fig.3, we can see that the slight deformations in these crystalline phases of C, Si and Ge slightly affect their electronic properties. The density of states of crystals of lattice-I and crystals of 36°-lattice-I are nearly degenerate too. Experimentally, Si and Ge phases in the perfect lattice-I (equal to
clathrate structure II) have been successfully discovered [12-16]. We expect their corresponding 36°-lattice-I can be discovered in future experiments, especially in the special topological manner with 5-fold central rotation symmetry as discussed below.

We then construct physically realistic and experimentally touchable pseudo crystalline phases of C, Si and Ge with 5-fold central rotation (10-fold rotation-reversion) symmetry based on the optimized 72°-lattice-I (36°-lattice-II). As shown in Fig 4, we extend the 72°-lattice-I (36°-lattice-II) through divisional translation symmetry operations and 5-fold rotation symmetry operations (10-fold rotation reversion) to form a 5-pointed (10-pointed) star with finite size. Although 36°-lattice-I and 72°-lattice-II form different shapes and edge shapes, they are topologically same pseudo-crystals when they topologically fill fully the infinite three-dimensional space. For example, both can be cut to a uniform shape of pentagon as shown in Fig 4. The electron-diffraction-patterns of Ge in the shapes of 5-pointed star, 10-pointed star and pentagon were simulated and are shown in Fig 4. The corresponding diffraction-patterns for C and Si are very similar to those for Ge (not shown in this letter). From Fig 4, we can see that the diffraction-patterns based on the 5-pointed star, 10-pointed star and pentagon are some different to each other in view of their finite sizes and different edge shapes. However, all of them contain clear 5-fold symmetry and 10-fold symmetry. These diffraction-patterns can be used to identify this novel type of crystals of C, Si and Ge in future experiments. We expect timely experimental explorations on such peculiar structures.

In summary, we have proposed a generalized crystal-predication-method to predict potential pseudo-crystals possessing both arbitrary n-fold central rotation symmetry and divisional translation symmetry through the combination of the traditional space-groups and the point-groups of regular polygons. With this method, we can predict many pseudo crystalline phases of elements or compounds with both divisional translation symmetry and arbitrary n-fold central rotation symmetry, which are significant for extending our the knowledge of crystallography and topology and can be considered as new options for understanding potential discoveries of 5-, 7- and higher n-fold diffraction patterns in future experiments. Based on the experimentally touchable Si and Ge phases in clathrate structure II, pseudo crystalline forms of C, Si and Ge with 5-fold and 10-fold symmetry are predicted.

This work is supported by the National Natural Science Foundation of China (Grant Nos. 11074211 and 51172191), the National Basic Research Program of China (2012CB921303), and the Hunan Provincial Innovation Foundation for Postgraduate (Grant No. CX2013A010).

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