

論文内容の要旨

First-principles theoretical study of electronic structures and lattice dynamics in C₆₀ polymers

(C₆₀ ポリマーの電子状態と格子力学の第一原理からの理論的研究)

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Since the discovery of C₆₀ fullerene¹ and the finding of a simple method for producing it in macroscopic quantities, a number of investigations have been done both experimentally and theoretically, which revealed physical and chemical properties not only of C₆₀ but also of other members of the fullerene family. They have numerous interesting properties, which significantly stimulated various fields of research, one of which is the exploration of new solid phases of carbon. The pressure-temperature phase diagram of C₆₀ in experiments is shown in Figure 1. Important is inquiry into the interesting properties of C₆₀ polymorphs not only under an atmospheric condition but also under extreme conditions. Various kinds of C₆₀ polymers have been synthesized under high pressures and/or high temperatures, in which C₆₀ molecules comprise 1-3 dimensional networks. Amongst them the three-dimensional C₆₀ polymers have been attracting attention of researchers for their electronic properties and hardness. Although there exist theoretical studies of the three-dimensional orthorhombic (3D-o) polymers³⁻⁵(see left part of Figure 2), the origin of its metallicity has not been satisfactorily elucidated. Furthermore the relative stability between the possible 3D-o structures in connection with the chemical bonding needs to be analyzed in detail. For the three-dimensional rhombohedral polymer¹ (3D-r), which is synthesized from the two-dimensional rhombohedral (2D-r) polymer (see right part of Figure 2) and its experimental geometry is unknown, one should explore possible structures of it and analyze their energetics. These problems are addressed in this thesis.

In this study we provide unified understanding of the electronic and thermodynamic properties of the C₆₀ polymers from a viewpoint of chemical bonding. We employ the density functional theory (DFT) and Kohn-Sham theory for electronic structure calculations, which is summarized in Chapter 2. For understanding how the chemical bonds of the individual atoms affect the energetics of the whole systems, we developed in Chapter 3 a method for calculation of the energy assigned to the individual atoms in an electronic system within the framework of DFT. For analyses of thermodynamic behavior of the atoms in connection with its bonding nature in the C₆₀ polymers, we calculate their phonon dispersions and thermodynamic functions using the direct method⁶, briefly summarized in Chapter 4.

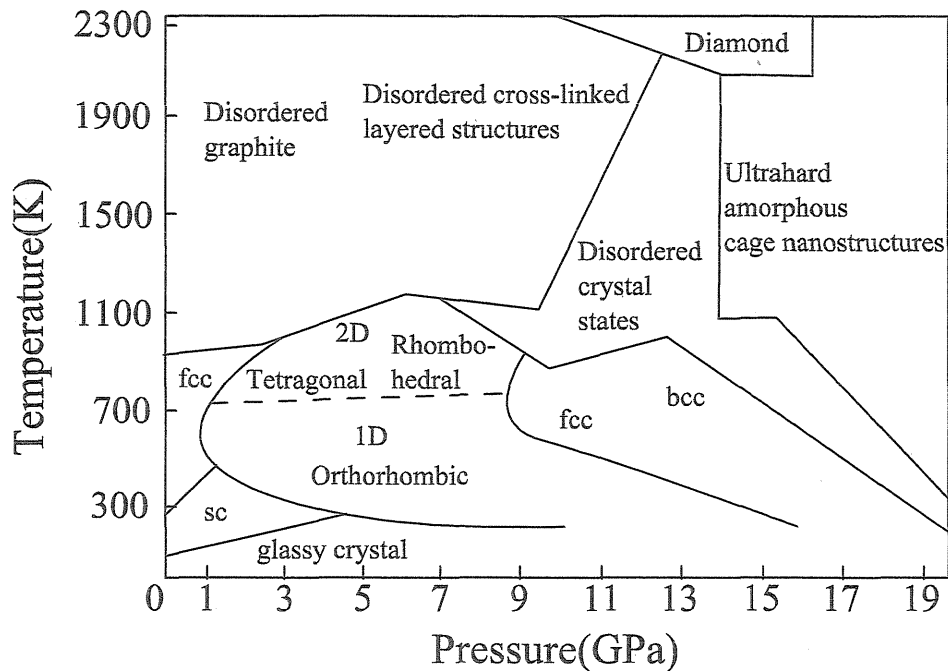


Figure1 The pressure-temperature phase diagram of C₆₀ in experiments, based on that provided by Blank *et al.*²

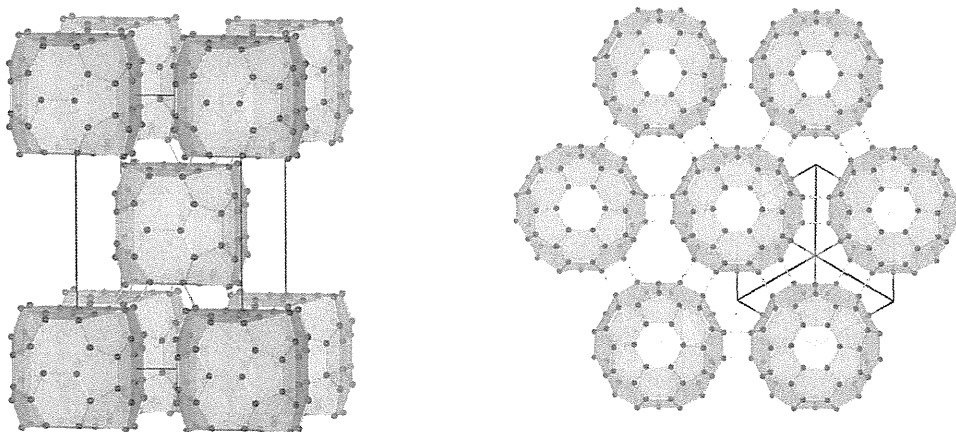


Figure2 3D-o and 2D-r polymers.

In Chapter 5 we developed a scheme for calculating phonon dispersions and thermodynamic functions without using the density-functional perturbation theory (DFPT) for computational efficiency. Our calculation procedure, which consists of the determination of the Hellmann-Feynman forces using the direct method, the Born effective charge tensors and the electronic dielectric tensor, does not require self-consistent calculation other than the ordinary electronic structure calculations. As an application of the scheme we calculated and analyzed the phonon dispersions and

the thermodynamic functions of stishovite, rutile and anatase. We elucidated the thermodynamic behavior of the individual atoms in those systems and how the differences between the bonding nature of the atoms affect the thermal properties of the whole systems.

In Chapter 6 we performed the structure optimizations of the 2D-o and three 3D-o C_{60} polymers and the electronic calculations of them. We found that C_{60} molecules in the 3D-o polymers are strongly deformed and connected to each other, leading to their metallicity due to the presence of the unpaired electrons. It was demonstrated that the energy density analysis associated with the chemical bonding in the compounds clearly elucidates the factors which determine the relative stability of the 3D-o polymers and their electronic properties originating from the bonding nature of the atoms. We further confirmed that the chemical bonding nature of the individual atoms are reflected in their thermodynamic behavior. The new structures of the 3D-r polymers (see Figure 3) were found by considering the chemical bonds which would be realized in periodic crystals. Our successful analyses ensure that even for large molecular solids their electronic and thermodynamic properties can be reasonably predicted from the chemical environment surrounding the individual atoms. The atomic energy analysis introduced in this study is proved to be a powerful tool for understanding energetics of large systems whose geometries partly differ.

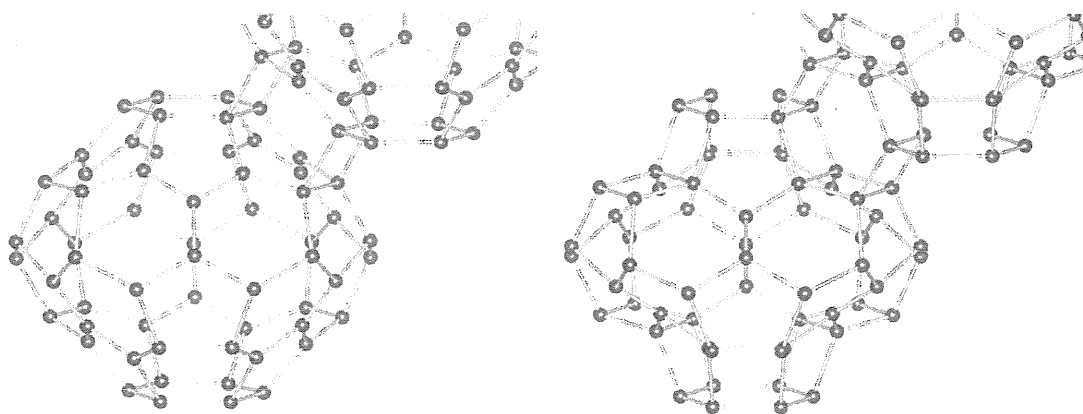


Figure 3. Two 3D-r polymers found in this study.

In Chapter 7 we explored new possible structures of C_{28} solid. Having known from the previous chapter that the shape a cluster in molecular solid is regulated by which atoms of it are chemically bonded to neighboring clusters, we constructed the body-centered tetragonal (bct) lattice of C_{28} molecules by arranging the molecules in the same way as

we did for the 3D-r polymers. The optimization of this geometry resulted in a metastable one (see Figure 4). The bonding nature of the atoms in the bct polymer is different from that in our earliest expectation. We here stress that this result is indicative of the usefulness of our procedure for structure prediction rather than its mistake, since the initial geometry was able to reach the final one with the different bonding nature.

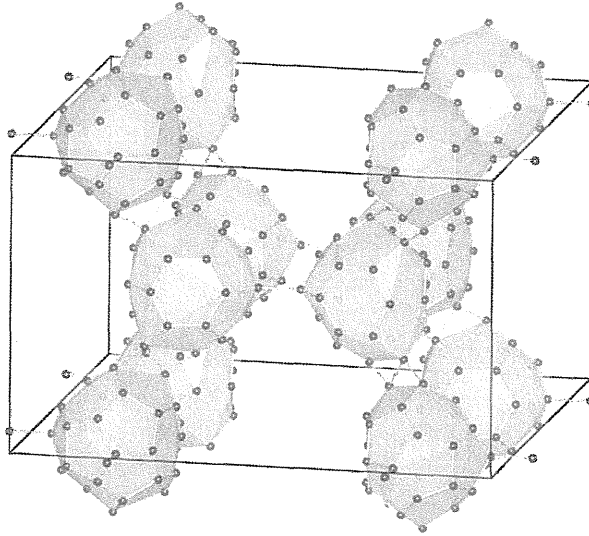


Figure 4. Body-centered tetragonal C_{28} polymer found in this study.

Our studies done in this thesis demonstrated that clear understanding of structural stability, electronic and thermodynamic properties of large systems is possible considering chemical bonding realized inside them and it is helpful for exploration of new structures, which may provide a prescription for design of materials having controllable electronic and thermodynamic properties.

- [1] H. W. Kroto *et al.*, Nature(London) 318, 162(1985)
- [2] V. D. Blank, S. G. Buga, G. A. Dubitsky, N. R. Serebryanaya, M. Yu. Popov, B. Sundqvist, Carbon 36, 319 (1998)
- [3] S. Yamanaka, A. Kubo, K. Inumaru, K. Komaguchi, N. S. Kini, T. Inoue and T. Irifune, Phys. Rev. Lett. 96, 076602(2006)
- [4] J. Yang, J. S. Tse and T. Iitaka, J. Chem. Phys. 127, 134906(2007); J. Yang, J. S. Tse, Y. Yao and T. Iitaka, Angew. Chem., Int. Ed. 46, 6275(2007)
- [5] F. Zipoli and M. Bernasconi, Phys. Rev. B 77, 115432(2008)
- [6] Parlinski K, Li Z Q and Kawazoe Y 1997 Phys. Rev. Lett. 78 4063