学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

The physical space model of the icosahedral quasicrystal
(正二十面体準結晶の物理空間モデル)

The scientific interest in the atomic structure of quasicrystals (QCs), has never faded since Dan Shechtman's discovery in 1982. So far, only about twenty QCs were analyzed quantitatively, what signifies how difficult the process of the structure analysis is. A lot of research has been dedicated to icosahedral (i) QCs in a Tsai-type family, since the first binary Cd-Yb QC was discovered. In 2007, a highly-accurate atomic structure model of this QC, based on the cluster-approach, was developed. Since then, the model has served as a structural template for any other QC in this family. Such a template however, does not exist for the Bergman family, which are formed mainly in the Zn-Mg-*R* (*R* = rare earth) systems. The discovery of Zn-Mg-*R* iQCs arose a great interest in their magnetic properties because well-localized magnetic moments are carried by the 4*f* electrons of the *R* ions which arrange quasiperiodically in the structure. Numerous measurements of magnetic moments show spin-glass-like behavior in a low-temperature regime. In order to explain the measured magnetic properties, a detailed atomic structure model of Bergman QC is needed and such a challenge was taken in this thesis.

In chapter one a thorough introduction to the crystallography of QCs is given. It starts with a historical background about the first observation of structures with a translational symmetry being broken. A whole subsection is dedicated to the definition of QCs as there is still a nomenclature confusion, even among scientists working in the field. The chapter ends with the summary about every of four known types of QCs with forbidden symmetries and the motivation of the thesis being explained.

In chapter two the mathematical foundations of the crystallography of QCs are given. Two methods that were developed to represent mathematically the quasiperiodic structures are described in details: The higher-dimensional approach, where the set of quasiperiodic points is lifted to *n*D space, with $n>3$ for 3D structures and the Average Unit Cell approach (AUC). Those two approaches are shown to be complementary as long as the *n*D representation of the structure exists.

Chapter three focuses on the Ammann-Kramer-Neri tiling (AKNT), which was formerly known as three-dimensional Penrose tiling, and its application to the structure solution of iQCs. The AKNT is shown to be built of two prototiles: oblate and prolate rhombohedra, associated with a golden ratio. Their spatial arrangement ensures the icosahedral symmetry. The projection method, involving a higher-dimensional space is presented and a mathematical procedure of obtaining the AKNT from the *n*D space is discussed. The most important part of this chapter is a meticulous derivation of the structure factor of the AKNT. The AKNT serves as a quasilattice for the iQC and the geometric

component of the structure factor is indispensable.

Chapter four is dedicated to the full analysis of the atomic structure of the Zn-Mg-Tm P-type iQC. It starts with the review of the literature on Bergman QCs. The details on the crystal growth method and the diffraction experiment are presented. Next two subsections focus on the *ab initio* structure solution by a charge flipping method and a consecutive structure refinement of the model. After that, a decoration of the asymmetric part of the rhombohedral units with clusters was found. It is shown that all the atoms belong to a triacontahedral cluster, when the *a*-linkage along a 5-fold direction is allowed. In the end, the *n*D representation of the structure was plotted against a simple-decoration model. The refined model was proven to match the experimental results by calculating the crystallographic R factor equal to 9.8% and the residual electron density being less than 4%.

Chapter five is dedicated to the crystal growth and the local structure analysis of the Zn-Mg-Hf F-type iQC. It is also a Bergman QC, but due to the formation of superstructure, the analysis is far more complicated. The 6D unit cell must be two times expanded every direction with respect to the primitive lattice, resulting in having 32 centering translations. The experimental details are presented, including the first in the literature crystal growth, for this system, that ended with a high-quality single crystals useful for X-ray diffraction. Based on the *ab initio* structure solution two types of clusters were identified. Both are Bergman-type, but are differentiated by the preferential occupancy of the high-symmetry nodes of the rhombic triacontahedral shell by Hf elements.

Chapter six proceeds a discussion of the results and a research impact. First, the new model of the iQC, based on Zn-Mg-Tm system, is interpreted to show its significant differences with respect to the existing model of the Tsai-type QCs. First of all, the model is solved in a real space, not in the higher-dimensional space. Second, clusters are no longer building blocks of the structure and they appear as a result of atomic decoration of the rhombohedra of the AKNT with an edge length of 21.7 Å. Atomic clusters are no longer limited to be linked along *b*- and *c*- linkages but the additional *a*-linkage is permitted. It is supported by the analysis of the electron density in the *ab initio* structure solution. The F-type Bergman QC manifests the same linkages even though two types of clusters must be considered. In the future perspective, the new model of Bergman QC will be generalized to all families of iQC, including F-type superstructures.