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Quasicrystals and approximants in the Ag-In-*M* and Au-Sn-*M*(*M*:Ca or rare earth metals) systems

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Formation of 1/1 Yb-Cd type approximants has been verified in the Ag-In-RE system for RE=Tm, Tb, Er, Dy, Gd, Pr, Ce, Eu. The compositons of the 1/1 approximants determined by wavelength dispersive X-ray analysis (WDX). By employing the empirical rule of $e/a \approx 2.0$, where e/a is valence electron concentration, a number of approximants are newly found in the Au-Sn-RE systems for RE=Sm, Pr, Ce, Dy, Tb, Gd, Eu where the 1/1 approximants are formed in the range of 61≈64 at.% Au, 20≈23 at.% Sn and 14≈15 at.% REs. While the 2/1 approximants only form in $Ag_{43}In_{43}Eu_{14}$ and $Au_{60}Sn_{25}Ca_{15}$ for M=Eu, Yb, Ca, where atomic size for Eu, Yb and Ca is larger than that for other REs and they are all divalent. Quasicrystals are also oberved at $Au_{60}Sn_{25}Ca_{15}$ as a stable phase. Basically, the 2/1 and 1/1 approximants share the same e/a with the quasicrystals found in the In-Ag-*M* and the Cd-*M* groups. It is likely that the phase selection among the quasicrystalline, the 1/1 and the 2/1 approximants phases are dominated by a parameter, $R_{r.e}$, namely *effective atomic size factor*.

Keywords: quasicrystals, rare-earth compounds, valence charge density

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Formation of quasicrystal and approximant phases and their structures in Zn-Mg-(Ti, Zr, Hf) alloys

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Following the study of $Zn_{84}Mg_7Ti_6$ by Ishimasa et al [1], stable quasicrystals (Qc) and an 1/1 approximant in the Zn-Mg-Zr (Hf) system have been identified [2]. The Qcs reveal primitive (P) and face-centered (F) lattices which formed at different compositional regions. In this study, we investigate compositional regions for these two types of Qcs and 1/1 approximants (AP) for Zn-Mg-(Ti, Zr, Hf) systems and perform single-grained X-ray study for the 1/1 approxiamnts in order to get insights into the structure of icosahedral cluster. The compositional region of Qc was around $Zn_{83.5}Mg_{9.5}Zr_7$ for the P-ype Qc and around $Zn_{75}Mg_{18}Zr_6$ for the F type Qc. The 1/1 approximant is around $Zn_{77}Mg_{18}Zr_5$. The formation tendency is similar for the Zn-Mg-Hf system. It is noted that the concentration of Zr is almost the same for the two Qc phases but that of Mg is much higher for the F-type. This is an indication that the chemical order between Zn and Mg generates superlattice reflections which characterize the F-type structure. On the other hand, no Qc but only the 1/1 approximant was observed for the Zn-Mg-Ti system. The structures of the three 1/1 approximants have been analyzed by single crystal X-ray diffraction [3]. It is clear that these approximants contain two different types of clusters, which is different from that of Zn-Mg-Sc system.

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Keywords: quasicrystals, superlattices, clusters

P23.03.04

The role of Mg in the stable Cd-Mg-RE (RE: rare earth metals) quasicrystals

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Since discovery of a stable binary Cd-Yb quasicrystal [1](Qc), the Qc with the same type of structure has been found in a large number of related alloys. Meanwhile, attention has also been drawn to Cd_6RE approximants since phase transitions at low temperatures [2] have been observed for these approximants. Except the Cd-Yb system, no Qc was observed for other Cd-RE systems. However, it was found that replacement of a certain amount of Cd with Mg promotes formation of the Qc [3]. In this study, we investigate formation of the Qc and approximants in relation to the content of Mg for the Cd-Mg-RE systems. Formation of the Qc was confirmed in the Cd-Mg-RE system with RE of Y, Dy, Gd and Tm. Phase transitions from approximants to Qcs facilitated by replacement of Cd with Mg were observed around 20～30 at.% Mg. Further replacement, in contrast, stabilized crystalline phases. The role of Mg will be discussed on the basis of structures analyzed by single crystal X-ray diffraction.

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Keywords: quasicrystals, rare-earth compounds, transformation

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Surface studies on quasicrystals

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We have studied structure of quasiperiodic surfaces of various quasicrystals and epitaxial growth on quasicrystal surfaces. STM study on the clean fivefold surface of icosahedral Al-Cu-Fe reveals that the stable surface shows bulk termination at Al-rich planes without detectable reconstruction. A rule for the formation of stable surface is deduced from detailed analyses of the step-terrace morphology. By applying this rule to the refined structure model, the atomic arrangement observed in STM images is successfully explained (Figure 1). The motivation of the epitaxy study on quasicrystals is to evoke unknown phenomena by inducing quasiperiodic structure into various materials. In the case of Bi deposition on the fivefold surface of icosahedral Al-Cu-Fe, a wetting

layer is formed first, followed by the growth of Bi islands for larger coverage. An astonishing feature of this system is that, for multi-layer coverage, Bi deposition yields islands with specific heights (magic height) corresponding to the stacking of a specific number of atomic layers. This unusual growth morphology is interpreted as quantum size effects and explained by confinement of electrons within the film.
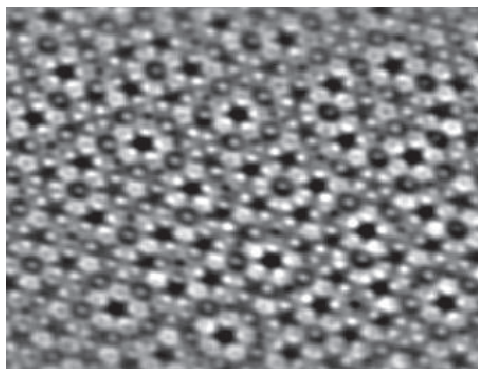
Keywords: quasicrystal, surface, STM

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Influence of the additional ligands dimmensionality on the topology of Zn MOFs

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The use of flexible ligands in the synthesis of MOFs makes possible the obtaining of compounds with not very habitual topologies. Hexafl uoroisopropilidenbisbenzoic (hfipbb) acid has a central atom with sp^3 hybridization, conferring it the possibility of coordinate in a flexible way. On the other hand, the use of auxiliary ligands is relatively usual in the construction of this type of materials, being more or less determinant in the conformation of the final network, either for their geometry, or because they contribute with new interactions. Here is presented the topological study of Zn compounds, synthesized under hydrothermal conditions in presence of the hfipbb dianion, alone or with different auxiliary ligands, all them pyridine derivatives. With hfipbb, a 3D structure has been obtained without any additional ligand; when these are incorporated into the network, the dimensionality of the final structures depends on their coordination mode. If chelating ligands are used, one-dimensional structures are obtained; however, thanks to π-π stacking or H-bonds interactions, 2D nets can be considered. Lineal bitopic, rigid or flexible, ligands give rise to biperiodic nets. In one of these cases, the biperiodic interpenetrated network formed by covalent bonds can be viewed as 3D self-catenated 6-connected net when the π-π stacking interactions are considered.

Keywords: supramolecular interactions, metal-organic frameworks, main-group compounds

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The periodic average structure of 7-, 8-, 10-, and 12-fold quasiperiodic tilings

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The motivation for the present work stems from the study of geometrical aspects of quasicrystal-to-crystal phase transformations, growth of quasicrystal-crystal interfaces, as well as the intrinsic band-gap behavior of phononic quasicrystals [1]. Average structures provide furthermore a tool for the classification of quasiperiodic tilings regarding their degree of quasiperiodicity. In the higher-dimensional approach, a d-fold 2-dimensional (2D) quasiperiodic structure can be described as an irrational cut of a nD hyperlattice decorated with hypersurfaces, with the 2D physical space. If a proper oblique projection of the hyperlattice upon physical space is performed, the vertices project onto the lattice nodes of a periodic average structure (PAS) [2], and the related 2D reciprocal space section contains a subset of reflections of the quasiperiodic tiling. The deviation of the tiling vertices from the PAS nodes is always within the boundaries of the projected hypersurfaces, and the overall intensity represented in the 2D reciprocal space section is a direct measure for the interconnection between PAS and quasiperiodic lattice. By using only strong Bragg reflections as reciprocal basis of the PAS, we can obtain the most representative PASs and compare them for each tiling, comparing thus their degree of quasiperiodicity. The diffraction pattern for each tiling is calculated analytically, by Fourier transformation of the hypersurfaces (which are 2-dimensional for the 8-, 10- and 12-fold tilings, and 4-dimensional for the 7-fold tiling).

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Keywords: quasiperiodic tiling, periodic average structure, higher dimensional crystallography

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The breaking of duality symmetry, melting, and glass transition

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Extending the Sethna-Sachdev-Nelson formula. we will introduce a theoretical formula based on the gauge-invariant Lagrangian density with spontaneous breaking for three-dimensional metallic glasses. We discuss a generalized view of the physical origin of the Boson peak in the gauge-invariant formula. The localized modes(massive gauge modes), which correspond to the Boson peak, are required naturally through the Higgs mechanism in the present theory. It is proposed that the duality symmetry between the new order parameter and the new disorder parameter might be related to the melting. In addtion, we will discuss the relation between the glass transition and the breaking of duality symmetry .

Keywords: duality symmetry, melting, glass transition

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