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Local atomic structure of icosahedral quasicrystals by X-ray fluorescence holography

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1 Introduction

Quasicrystals are intermetallic compounds having a long-range ordered, but aperiodic, atomic arrangement. In particular, Tsai-type icosahedral quasicrystals (iQCs) exhibit an icosahedral point symmetry and typically consist of rare earth (RE) elements along with Cd or a mix of other two metallic species. Their complex structure is generally investigated experimentally by X-ray and/or electron diffraction experiments in combination with high-dimensional modeling in a (six-dimensional) hyperspace. However, owing to the high complexity of the atomic arrangements in these systems, techniques targeted at the local atomic structures can provide valuable complementary information, which can be used to understand the crystal chemistry, in particular the relationship between the aperiodic order and the physical properties.

Tsai-type iQC consist of a series of atomic clusters: a Cd tetrahedron as the cluster center, surrounded (successively) by a Cd dodecahedron, an Yb icosahedron and a Cd icosidodecahedron.[1] Here, notably, the local view can support the understanding of the connection between neighboring clusters.[2]

Quasicrystals and their (periodically crystalline) approximants (APs) are studied in particular with respect to their peculiar magnetic properties.[3] Most of the magnetic APs show spin-glass-like behavior at low temperatures, which be related to geometrical frustration expected for the icosahedral symmetry clusters. However, there is a lack of knowledge about the local atomic environment in these systems, which could serve as a guiding principle for tuning the magnetic properties.

In this project, we performed X-ray fluorescence holography (XFH) experiments on a series of samples of the icosahedral Ag-In-Yb family.[4] In the series from the 1/1 AP to the 2/1 AP and the iQC, the structural complexity is increasing, presenting a suitable reference to study the local view of XFH on the structures. Furthermore, the Ag-In-Yb system represents a prototype of Tsai-type iQCs, and has been studied extensively. This is because Ag-In-Yb is essentially isostructural to the binary Cd-Yb (basically, Cd is replaced by its neighboring elements Ag & In), the parent quasicrystal of the Tsai-type family and the only iQC whose atomic structures are completely understood.[2]

2 Experiment

The samples of the Ag-In-Yb system (large single crystals) will be placed on a biaxial (θ, φ) goniometer, with angular ranges of $0° < \theta < 75°$ and $0° < \varphi < 360°$. The measured fluorescence is the Lα line of Yb (7.4 keV). The energy of the incident X-ray was measured with 14 energies in 0.25 keV steps using the region of 9.0 – 13.0 keV above the L3 absorption edge of Yb (8.9 keV). The incident X-ray intensity is monitored by an ion chamber. The fluorescent X-rays are focused using a toroidal analyzer crystal and the holograms are recorded using an APD detector. A nitrogen spray type cryo-cooler is used for cooling to LN2 temperature. The single crystal samples of a $Ag_{41}In_{44}Yb_{15}$ quasicrystal and corresponding approximant phases ($Ag_{40}In_{50}Yb_{10}$ and $Ag_{40}In_{46}Yb_{14}$) were prepared at Tohoku University.

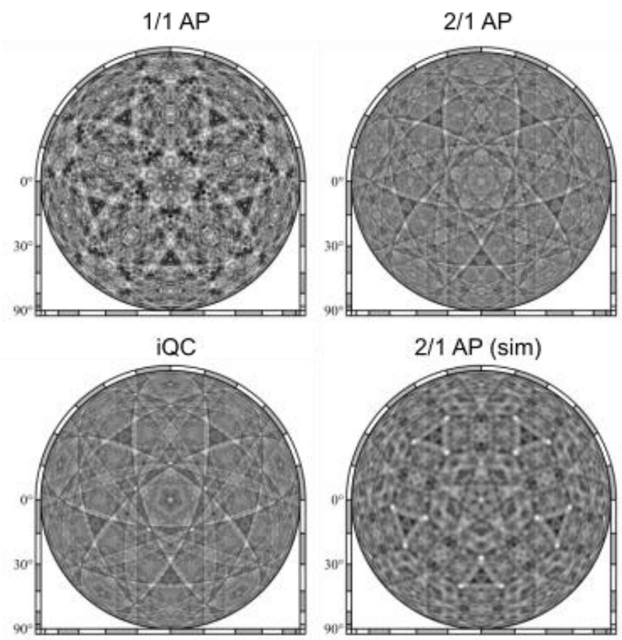

Fig. 1: Orthographic projections of the Yb holograms at 9.5 keV

3 Results and Discussion

Exemplary holograms measured at 9.5 keV are displayed in Fig. 1 for the experimental data and a comparison with a simulation from the unit cell of the 2/1 AP.[2] All holograms are projected along one of the (pseudo-) 5-fold axes.

Reconstructions of the average structure around the Yb atoms can be calculated from these datasets using the Barton algorithm.[5,6] XFH reconstructs the average environment around each atom, which can be difficult to disentangle for complex structures.[7] For Ag-In-Yb, they are shown in Fig. 2, illustrating planes perpendicular to the 5-fold axis. The signals marked by the dashed lines (and circles) can be identified with Yb-Yb connections related to the icosahedral Yb clusters (i.e. the 3rd shell of the Tsai-type clusters). They correspond to the Yb-Yb edge connections and the 1st and 2nd diagonals of these clusters, respectively (from small to large distances). The signals can be found with very good agreement also on the model structure, which is also shown in Fig. 2 (and illustrates the position of the different elements as color code).

In a similar manner, the Yb-Yb connections between these clusters (inter-cluster connections) can also be identified and their relative portion can be estimated. By comparison with the model, we can also identify further specific positions, like the Yb atoms which are not part of the icosahedral shell. The detailed analysis is now in progress.

In summary, the local structures of the APs and of the iQC can be accurately determined by XFH. By comparison with a model system, we can identify signals at certain positions with specific structural features, and quantify their occurrences. The resulting view into the structure will constitute a crucial step towards understanding the complex structure of icosahedral phases from the local perspective. These information will then be useful to study other iQC systems, and to investigate the relationship between the magnetic properties and the aperiodic structure in this complex class of materials.

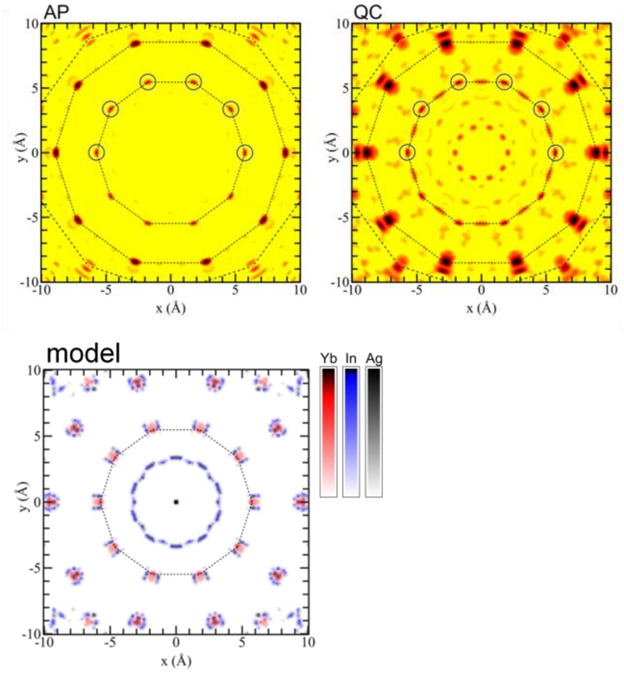

Fig. 2: 2D reconstructions for the 2/1 AP and the iQC, in comparison with the average structure of the model system.

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