Quasicrystalline Order Revealed in Nanoparticle Superlattices

Quasicrystals are a class of materials that show sharp diffraction peaks despite presenting forbidden symmetry operations in classical crystallography. D.V. Talapin and M.I. Bodnarchuk from the University of Chicago; E.V. Shevchenko from Argonne National Laboratory; and X. Ye, J. Chen, and C.B. Murray from the University of Pennsylvania, have reported in the October 15 issue of Nature (DOI: 10.1038/nature08439; p. 964) that different binary nanoparticle colloidal systems can self-assemble into 12-fold rotational quasicrystalline order. According to the researchers, the compositional flexibility demonstrated that quasicrystalline ordering could be a relatively common phenomenon in nanocrystal solids, with suitable size ratios between particles.

Addendum


The researchers obtained the quasicrystalline nanoparticle assemblies by evaporating relatively concentrated colloidal solutions of 13.4-nm Fe3O4 and 5.0-nm Au monodisperse nanoparticles capped with oleic acid and dodecanethiol molecules, respectively, in tetrachloroethylene at 50°C under reduced pressure (~3.2 kPa) on a carbon-coated transmission electron microscopy grid or a silicon nitride membrane tilted by 60° or 70°. The researchers used the surfactant molecules to introduce short-range steric repulsion that counterbalanced the van der Waals forces and prevented uncontrollable aggregation of nanocrystals in the colloidal solution. They observed that during this process the nanocrystals self-assembled in AlB2- and CaB6-type phases, and on the (32-4.3.4) Archimedean tiling structure, depending on the Fe3O4-to-Au nanoparticle ratio. This structure is formed by five planar polygons (three triangles and two squares) sharing a common vertex in such a way that they fill the plane with no overlaps and no gaps, depending on the Fe. The nomenclature of these structures lists in order the polygons that meet at each vertex using integers that correspond to the numbers of sides of the polygons. So, the (32-4.3.4) structure consists of two triangles sharing a common edge, surrounded by two squares at each side of the triangles, and filling the empty space by another triangle, all of them sharing a common vertex. In proximity to the (32-4.3.4) phase in the binary phase diagram of these nanoparticles, the researchers observed reproducible formation of a type of binary superstructure without translational symmetry. They observed that these structures showed sharp electron diffraction patterns revealing dodecagonal rotational symmetry, a symmetry operation forbidden in periodic structures. The researchers identified these self-assembled nanoparticle superstructures as dodecagonal quasicrystals (DDQC), a phase that formed also from colloidal solutions containing 12.6-nm Fe3O4 and 4.7-nm Au nanocrystals, and 9-nm PbS and 3-nm Pd nanocrystals, with size ratios between particles of ~0.43.

The researchers said that the space-filling factor had a significant effect on the relative stabilities of binary nanoparticle phases, and the quasi-periodicity could be a result of maximizing the entropy of arrangement of square and triangular “tiles.” They consider that the discontinuity in the entropy density corresponding to the DDQC state might provide a mechanism for locking the quasicrystalline state over a range of nanocrystal concentration ratios. The researchers think that these studies will provide insight into the formation of the quasicrystal phase in atomic systems, and can be used as a convenient platform for detailed investigation of quasicrystal properties.