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News and opinions

Crystallization goes its own way

Cordelia Sealy

The classical model of crystallization – which governs the formation of solid matter from rocks to biological material – holds that nuclei form from a supersaturated medium when the nucleation barrier is overcome through fluctuations in the local concentration of atoms. But new observations made by scientists at the Universities of California, Los Angeles (UCLA), Buffalo, Colorado, Nevada – Reno, and Lawrence Berkeley National Laboratory using atomic electron tomography (AET) reveal some unexpected behavior [Zhou et al., *Nature* **570** (2019) 500, https://doi.org/10.1038/s41586-019-1317-x].

"Nucleation is a ubiquitous phenomenon in many physical, chemical, and biological processes and we wanted to understand nucleation at four-dimensional (4D) atomic resolution (*i.e.* three-dimensional (3D) space plus time)," explains Jianwei Miao of UCLA, who led the study.

Observing the early stages of nucleation represents a particularly tricky scientific conundrum as nuclei forming from a few atoms or molecules are extremely small, scarce, and highly mobile. Any technique with sufficient resolution to resolve the structure of these tiny clusters of atoms can struggle to spot them. Miao and his colleagues hit on a clever way to get around this problem by studying the nucleation of FePt nanoparticles, which form crystals from a chemically disordered alloy in a solid-to-solid transition during annealing. The emerging nuclei rearrange their 3D atomic positions as they transform from the chemically disordered phase into a tetragonal crystalline arrangement. Using AET, the researchers tracked the same nuclei at different annealing points during the process.

"We measured a series of two-dimensional (2D) images from an advanced electron microscope by tilting FePt nanoparticles to many different orientations. The 3D structure of the nanoparticles was then iteratively reconstructed from the images and the 3D atomic coordinates were identified with high precision. We then annealed the nanoparticles for different amounts of time and determined their 3D atomic positions in each case," explains Miao. "This allowed us to capture 4D atomic motion in materials for the first time."

The team observed that the initial nuclei of a few atoms are irregular – varying in size and shape, depending on the time. This flies in the face of classical theory, which assumes that a nucleus is approximately spherical or tetragonal, to minimize energy. Moreover, the interface between the core of the nucleus and the surrounding phase is not sharp but diffuse, depending on the distance from the core. During the crystallization process, the nuclei grow, fluctuate in size and shape, dissolve, merge with other nuclei, or divide (Fig. 1).

"Our experimental observations were further corroborated by molecular dynamics simulations of heterogeneous and homogeneous nucleation in liquid-solid phase transitions of Pt," Miao adds. "Both our experimental and molecular dynamics results differ from classical nucleation theory (CNT), indicating a theory beyond CNT is needed to describe early stage nucleation at the atomic scale."

The observations indicate that crystallization is not the single-step process laid out by theoretical models, but follows a much

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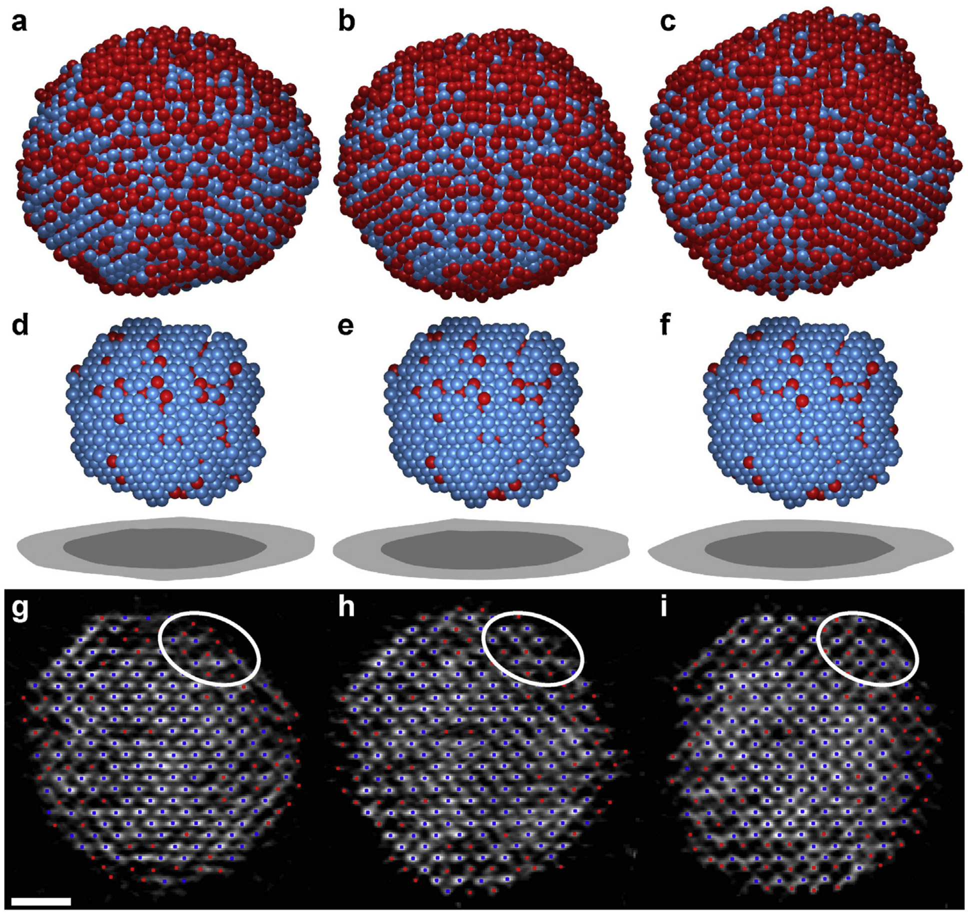

Fig. 1. (a–c) 3D atomic models of an FePt nanoparticle (Fe shown in red, Pt in blue) at annealing times of 9, 16, and 26 min. (d–f) Pt-rich core of the nanoparticle remains the same throughout the annealing process. The light and gray projections below show the whole nanoparticle and core, respectively. (g–i) The internal atomic layer of the nanoparticle along the [010] direction at the same annealing times, where a fraction of the surface atoms rearrange to form a new phase. Scale bar, 1 nm. Reprinted by permission from Springer Nature: Zhou et al., *Nature* **570** (2019) 500. © 2019.

more diverse, idiosyncratic pathway that varies over time as tiny clusters of a few atoms or molecules grow into larger crystals.

"Visualizing the arrangement of atoms plays an important role in the evolution of modern science and technology," points out Miao. "We anticipate that 4D AET will open the door to the study of many fundamental problems in materials science, nanoscience, condensed matter physics and chemistry."