

consequence of a phenomenon known as quantum confinement — their potential is even greater.

Although the formation of CdSe nanoparticles⁶ and their crystallization into larger three-dimensional superlattices⁷ has been reported before, as well as some suggestion of the formation of stable clusters with well-defined size (magic clusters)^{8,9}, the present study is the first to provide atomically resolved spectroscopic evidence for the extreme selective stability of the (CdSe)₃₃ and (CdSe)₃₄ clusters. Moreover, Kasuya and colleagues conduct first-principles calculations (based on density functional theory), supported by experimental X-ray diffraction and absorption data, to finally pin down the atomic structure of these clusters. In contrast to previous theoretical studies — which considered only structures that were similar to these materials' corresponding bulk crystal structure, and fails to explain the existence of magic clusters — Kasuya and colleagues find that their clusters display a distinct cage-like structure that is entirely different from the bulk (see Fig. 1). Significantly, the surface of this structure is much smoother, with no deleterious 'dangling bonds' present, than could be achieved by the wurtzite structure of bulk CdSe. Typically for clusters, the large surface-to-volume ratio dominates and stabilizes the

reconstruction of this surface. Such surface 'self passivation', which eliminates dangling bonds, results in clusters that are less reactive and prevents them from merging together to form larger clusters, allowing them to maintain their discrete nature — crucial to their utility as building blocks for making three-dimensional cluster arrays.

The use of these clusters as building blocks in the synthesis of cluster-assembled matter could open a new world of materials, taking advantage of the manifold of clusters with tunable properties as a function of their size. A future challenge is to find ways for a controlled production of size-selected clusters with 'passivated' surfaces. The new results on the ultrastable chalcogenide nanoclusters are a promising step in the search for such cluster-based materials.

References

1. Kasuya, A. *et al. Nature Mater.* 3, 99–102 (2004).
2. Sattler, K. *et al. Phys. Rev. Lett.* 45, 821–824 (1980).
3. Palmer, R. E. *et al. Nature Mater.* 2, 443–448 (2003).
4. Khanna, S. N. & Jena, P. *Chem. Phys. Lett.* 219, 479–483 (1994).
5. Krätschmer, W. *et al. Nature* 347, 354–358 (1990).
6. Peng, X. G. *et al. Nature* 404, 59–61 (2000).
7. Talapin, D. V. *et al. Adv. Mater.* 13, 1868–1871 (2001).
8. Murray, C. B. *et al. J. Am. Chem. Soc.* 115, 8706–8715 (1993).
9. Ptatschek, V. *et al. Ber. Bunsenges. Phys. Chem.* 102, 85–95 (1998).

MATERIAL WITNESS

Designing with complexity

When I hear the word 'complexity', I don't exactly reach for my hammer, but I suspect my eyes narrow. It has the dangerous allure of an incantation, threatening to acquire the same blithe explanatory role that 'adaptation' once did in biology.

But whereas there is no denying that certain 'complex systems' of many interacting parts do seem, in the natural world, to have an uncanny ability to self-organize into coherent modes of behaviour, the intersection of complexity with engineering has the potential to generate friction.

For one thing, the notion that complex systems have discrete 'attractors' or stable modes of behaviour could be deemed to constrain the engineer's freedom to design. Not only does it imply that not all designs are possible, but it might imbue small changes with disproportionate consequences.

There seems no question that studies of complexity have a place in materials science and engineering — for example, in the behaviour of granular media, complex fluids and colloidal crystals. Even old-fashioned crystallization is arguably a process of complex pattern formation arising from cooperativity between the components, and it remains a hard thing to predict.

But can engineers and materials designers make rational use of the sorts of phenomena that complex systems produce? Self-assembly, now widely used in materials synthesis, need not be inherently complex, in that the final state of a multicomponent system may be uniquely specified by the design of the components and thus not really an emergent property at all. But some researchers, like George Whitesides at Harvard University, are

interested in developing non-equilibrium self-assembling materials systems that show dynamic, dissipative ordered states, more akin to the traditional structures of 'complexity science'.

Whitesides described such systems at a conference on complex systems last year that explicitly included engineering and industrial perspectives (<http://complexsystems.mccormick.northwestern.edu>).

The idea of 'emergence' is being harnessed by others to solve problems in engineering design. One can argue that even well-established finite-element optimization routines for shape engineering embody the spirit of complexity. Some of these draw inspiration from the growth-and-feedback processes evident in nature, for example in the formation of wood and bone. Biology, like engineering, must address the conflict between emergence and function, or spontaneity and purpose.

The engineering of complex systems has been studied for some time now (S. Wolfram *Physica D* 22, 385–399; 1986). One current example is the European SYNAMEC project for aeronautical engineering, an aspect of which is the use of self-organizing agents for mechanical design (see www.co.umist.ac.uk/~mcaihak2/papers/esao03_5c.pdf). Here a set of components interacts to find the best mechanical design for a job. As yet, there is no theory that can prove the optimality of these emergent solutions, however — indeed, a general 'theory of complexity' remains perhaps the biggest challenge for the field.



Philip Ball