

and is comparable to the Aurignacian plaques from Blanchard and Lartet already studied by Marshack⁴ and thought by him to carry lunar notation. More importantly, it links the earliest art of south-west France with the similar and contemporary ivory statuettes from Vogelherd in Germany, and is further evidence for the complexity and sophistication of artistic expression in its earliest manifestations.

Armand Viré undertook massive excavations at four sites near Lacave, France, at the start of this century. These excavations, at the sites of Crozo Bastido⁵, Crozo Gentillo^{6,7}, the Grotte de Lacave and the Rivière de Tulle shelter⁶ yielded a series of spectacular assemblages dating to the Solutrean (22,000–18,000 years ago) and the Magdalenian (18,000–12,000 years ago). These assemblages, long considered to have been lost, were also purchased by Pond and are now at the Logan Museum. They include many examples of art and ornamentation, including pierced shells and a shark's tooth that could only have come from the Atlantic coast 200 km away. Apart from abundant Magdalenian

and Solutrean stone tools, there are hundreds of bone and antler artefacts, including several harpoons, dozens of bone needles, a decorated pierced baton and a huge number and range of carefully worked antler objects, some of them nearly two feet long.

The careful reanalysis now in progress will improve our present understanding of the Upper Palaeolithic in the Perigord and Haut-Quercy⁸, although there will always be limitations imposed by some rather poor stratigraphic work. □

1. Collie, G. *Bull. Logan Museum* 1, (Beloit, Wisconsin, 1928).
2. Capitan, L. & Bouyssonie, J. *Limeuil: son Gisement à Gravures sur Pierres de l'Age du Renne* (Nourry, Paris, 1924).
3. Didon, L. *Congrès International d'Anthropologie et Archéologie Préhistorique* 6, 337 (1912).
4. Marshack, A. *The Roots of Civilization*. (Weidenfeld & Nicolson, London, 1972).
5. Viré, A. & Teulière, C. *L'Anthropologie* 37, 449 (1927).
6. Viré, A. *L'Anthropologie* 16, 411 (1905).
7. Viré, A. & Niedertander, A. *Bulletin de la Société Préhistorique Française* 18, 269 (1921).
8. Lorblanchet, M. in *La Préhistoire Française* (ed. De Lumley, H.) 1189 (CNRS, Paris, 1976).

Randall White is in the Department of Anthropology, New York University, New York 10003, USA.

Electron microscopy

Coulomb explosions in metals?

from A. Howie

IN comparison with bulk material, small particles containing less than a few hundred atoms have several anomalous properties, including low melting point, modified lattice parameters, multiple twinning and other structural defects or variations. These effects are of great interest in basic science as well as in crystal growth and catalysis. So far most quantitative studies of them have relied on mass spectrometry or diffraction observations, but direct imaging by high-resolution electron microscopy should in principle provide much more detailed information about individual particles. Recent use of direct imaging with real-time video recording reveal some intriguing and unexpected phenomena related to the high current density of the electron beams used.

The most striking results have been obtained on 2-nm diameter gold particles by Iijima and Ichihashi using a specially constructed, clean vacuum system at the Research Development Corporation of Japan. Preliminary images appeared last summer (*Nature News and Views* 315, 628; 1985) and a more detailed account has now been published (Iijima, S. & Ichihashi, T. *Phys. Rev. Lett.* 56, 616; 1986). Iijima and Ichihashi use a 120-keV electron beam at a current density of 200 A cm⁻² (1.3 × 10⁶ electrons per A² per second) to obtain a recording speed of 60 frames per second. The most noticeable feature of their results is that a given particle

can be seen to jump intermittently between several different states — single crystal, decahedron, icosahedron and complex multiple twin. Sometimes these states seem to be quasi-stable, persisting for a few tenths of a second and exhibiting, for example, local details of surface facets that minimize the energy. At other times, the particle is clearly highly excited and appears to be molten or spinning on the silicon dioxide-covered silicon support.

Although these abrupt changes of overall structure seem to be suppressed in larger (10-nm diameter) gold particles, equally startling and sudden convulsions of surface structure have been observed for particles of this size by J.O. Bovin *et al.* (*Nature* 317, 47; 1985) using a 300-keV electron microscope and a beam intensity of 20–30 A cm⁻². Their images show what appear to be atomic clouds of gold atoms outside the particle that interact with individual atomic columns viewed in projection at the particle surface and were immediately recognized as both interesting and puzzling (see *Nature News and Views* 317, 16; 1985).

The generation and dissipation mechanisms for electron-beam excitations in small particles are reasonably clear in principle, although not perhaps at the level of quantitative detail to answer unequivocally all the questions raised by these observations. The most probable process, the excitation of valence electron-

density oscillations (plasmons) has a characteristic energy-loss quantum of typically 20 eV and would involve one or two per cent of the fast electrons passing through or near the particle. These excitations can decay radiatively, or more probably by emission of a secondary electron, although the latter process can in some cases be inhibited if the particle is not sufficiently well-grounded through its support and becomes positively charged. Charging effects do indeed appear to be relevant because Iijima and Ichihashi find that the small particle motion becomes more sluggish when conducting supports of amorphous carbon are used. Plasmons, however, are generated at such a high rate (10⁵ per second on each particle) that, on the timescale of video recording, one might expect an effective equilibrium with an associated temperature rise of roughly 100°C for the atoms.

The abrupt, kaleidoscopic image changes observed in these experiments are probably caused by some relatively much rarer event such as inner-shell excitation. Such collisions can involve not only the transfer of considerably larger amounts of energy and momentum to the particle but also substantial charging effects via the Auger cascade process. This process occurs when the energy released by filling of the inner-shell vacancy causes injection of two or more less strongly bound electrons from the atom. The resulting Coulomb explosion, a long-established concept in the theory of particle track formation, has recently been identified in various electron-beam desorption effects (Knotteck, M.L. *Nature* 291, 452; 1981 and *Rep. Prog. Phys.* 47, 1499; 1984). It may also play a key role in electron-beam ionization damage in aromatic organic crystals, where K shell ionization rather than valence excitation (Howie, A. *et al. Phil. Mag.* B52, 751; 1985) is the crucial event.

At the other extreme of scanning transmission electron microscopy, where beam-current densities in excess of 10⁵ A cm⁻² can lead to dramatic nanometre-scale hole-drilling in normally stable inorganic materials (Salisbury, I.G. *et al. Appl. Phys. Lett.* 45, 1289; 1984), the Coulomb explosion has also been implicated. Hitherto it has been generally assumed that such effects would be very rapidly screened-out in metals, but the special features of small particles may make them more susceptible to this rather dramatic type of excitation. By looking for coincidences between the sudden changes of particle structure and characteristic energy losses associated with inner-shell excitation, it may be possible to examine this hypothesis more closely. □

A. Howie is Reader in Physics at the Department of Physics, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK.