

ULTRAFINE PARTICLES

Particles smaller than a tenth of a micron have properties different from those of larger particles of the same materials and are finding use as catalysts, filters, light absorbers, medical tools, magnetic media and new materials.

Chikara Hayashi

Scientists have been dealing with particles with diameters in the range 1–100 nm, albeit in dispersed systems, since the founding of colloid chemistry in the 1860s. However, it is only in the last 25 years that we have been able to study individual particles of this size. The result has been the discovery that these “ultrafine” particles have properties not displayed by larger or smaller collections of atoms or molecules, properties that suggest many scientific and technological applications.

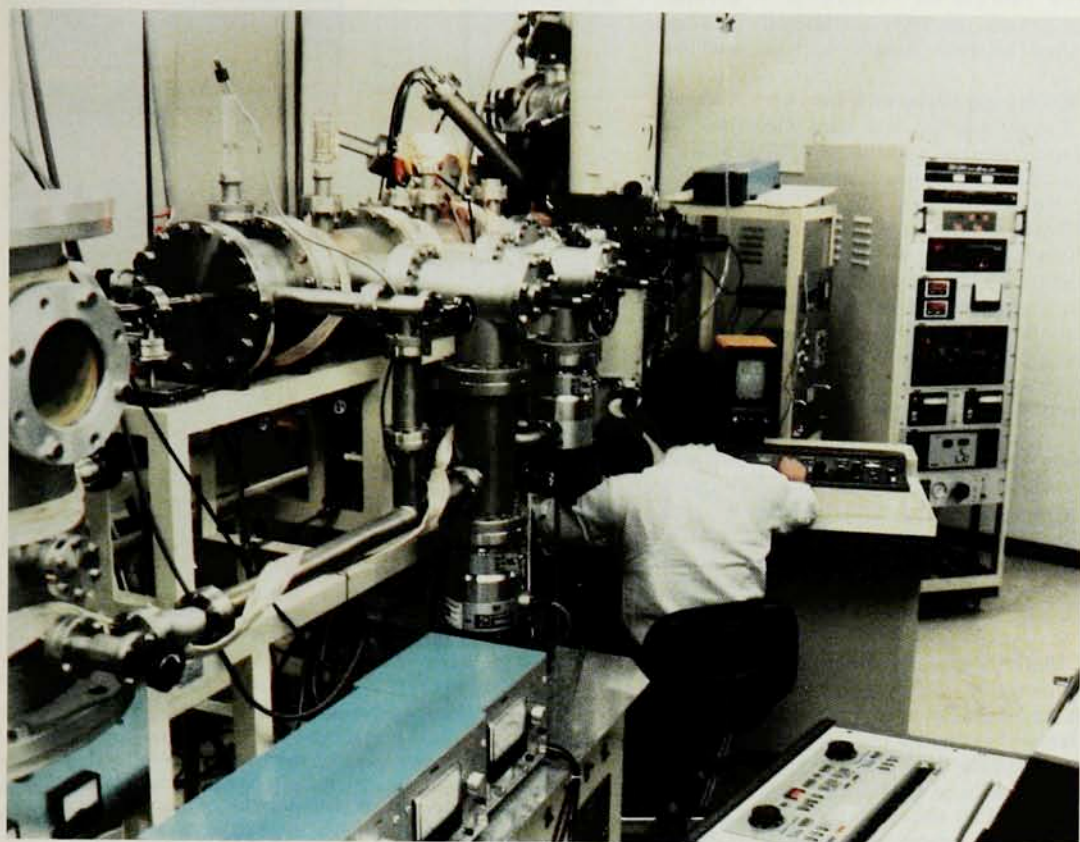
From 1981 to 1986 I headed a special exploratory project, funded by the government of Japan, to clarify the physical properties of particles smaller than those of conventional fine powders and larger than those of so-called clusters of atoms, and to evaluate the possibilities for using these ultrafine particles in industry, medicine and scientific research. We investigated the physical, chemical and biological properties of these particles and measured their electromagnetic, crystallographic, optical, thermal and catalytic characteristics. And we studied the mechanism by which ultrafine particles nucleate and grow, with the aim of developing techniques for controlling their size and composition. Figure 1 shows a laboratory for working with ultrafine particles.

Our project was organized in a nontraditional way and therefore was a social experiment as well as a scientific and technological one. I will explain this aspect of the project in the first part of this article, which describes the ERATO system of about a dozen research projects, one of which was our ultrafine particle project. Then I will summarize the history of research on ultrafine particles and the achievements of our project.¹

The ERATO system

In 1981 the Research Development Corporation of Japan, a corporation wholly owned by the Japanese government, inaugurated a program known as Exploratory Research for Advanced Technology. ERATO initiated a number of five-year projects in an attempt to create new fields and

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Ultrafine particles laboratory at Meijo University. Sumio Iijima, group leader in the ERATO ultrafine particles project, uses an electron microscope to observe ultrafine silicon particles with modified surfaces. Figure 1

radically new technologies in materials science and life science. Each project in the ERATO system is staffed by 15 to 20 researchers and has a five-year budget of 1.5–2.0 billion yen, or 10–13 million dollars. ERATO initiates one or two new projects each year.

The Japanese government envisioned the ERATO system as a complete break from the traditional way of conducting research. A proposal for a new project can come from industry, government or academe, and the project can situate itself in existing laboratories. A project leader may hire researchers from anywhere in the world so long as there are no political barriers. Because each project aims to create fundamental and radically new technologies that will initiate the exploration of new fields in industry and science, researchers in a project maintain close contact with academic scientists while staying aware of subjects that are of interest to industry. ERATO holds an annual symposium, usually in the fall, at which researchers present results from each project.

The Research Development Corporation of Japan retains half of any patent rights that result from a given project, and the other half goes to the inventors. A researcher who is employed by a private corporation, government organization or university can take a leave of absence to join a project if his or her employer agrees. The Research Development Corporation of Japan then pays the researcher at the same rate as the home institution. Otherwise a researcher is guaranteed a salary and benefits equivalent to those of Japanese civil service

employees. The salary and benefits are not less than the average for Japanese companies.

When the ERATO system was inaugurated, a report said it was a mechanism by which Japan could hunt for Western brains for its own benefit. There was no such strategic intent, but participation from overseas is encouraged and stimulus from abroad should foster a creative atmosphere. The contributions arising from the ERATO system were conceived to be international in scope.

In addition to the project on ultrafine particles, ERATO has established projects on amorphous and intercalation compounds, fine polymers, perfect semiconductor crystals, "bioholonics" (biological computing), information flow in biological systems, "superbugs" (strong microorganisms), nanometer-precision engineering, solid surfaces, quantum magneto flux logic, the response of organic molecular assemblies to environmental fluctuations, and biological organisms that transmit or receive light.

History of ultrafine particles

In 1861 the British chemist Thomas Graham coined the term "colloid" as colloid chemistry was beginning to develop. Wolfgang Ostwald classified dispersed systems of particles with sizes of about 1–100 nm as colloids. John Tyndall, Hermann Helmholtz, Lord Rayleigh, James Clerk Maxwell and Albert Einstein were among the physicists who studied the characteristics of colloids around 1900. The main experimental tools of observation were viscometers, potentiometers, permeable membranes

and optical microscopes for the observation of scattering. During the 1930s Arne Tiselius began the study of protein and other biological colloids by developing a precise electrical migration device. In 1934 the so-called Langmuir-Blodgett method became a new tool in surface chemistry.

During the 1960s Ryogo Kubo and his coworkers at the University of Tokyo pointed out that electrons in metallic ultrafine particles are in a unique situation and do not obey Fermi statistics because the number of such electrons is small.² Kubo noted that for particles smaller than 10 nm, it is difficult either to add or to remove a single electron, so such particles have a strong tendency to remain electrically neutral. The ways this affects specific heat, magnetization and superconductivity is now called the Kubo effect. Japanese scientists have been the main experimental investigators of this effect, and French,³ Japanese⁴ and American⁵ scientists have obtained interesting results analyzing ultrafine particles by means of nmr spectra.

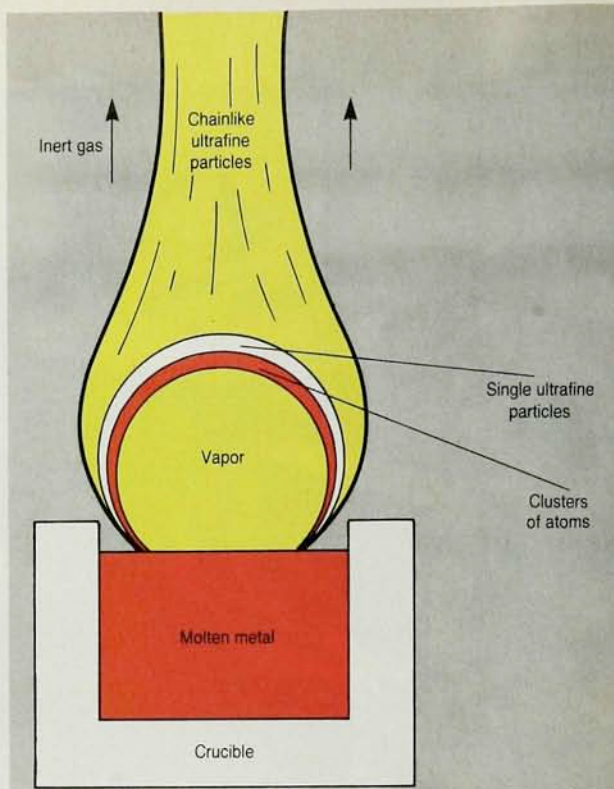
Also in the 1960s, Ryozi Uyeda and his coworkers at Nagoya University used electron microscopy and electron diffraction to determine the morphologies and crystal structures of single particles of metals and metallic compounds.⁶ They also made advances in producing relatively clean ultrafine particles through evaporation and condensation in an inert gas—the gas evaporation method.

In the early 1980s Shun-ichi Kobayashi and his coworkers at the University of Tokyo performed experiments that treated the assembly of ultrafine particles as an example of Anderson localization.⁷ However, samples of ultrafine particles in those days suffered from nonuniformity in size, composition and spatial arrangement.

Particles consisting of up to about 100 atoms or less than 1 nm in size are called clusters. The study⁸ of these particles began around 1980. Thanks to progress in mass analysis, the use of large computers and energy analysis using lasers, we are now able to extract clusters with known numbers of atoms and determine their average energies. However, it is not yet possible to observe directly the atomic arrangement of clusters. One can use electron microscopy to obtain clean images of the crystal structure of metal or metallic compound particles greater than 2 nm in size, but no technique has been developed to analyze the energies of individual particles. Several books have been published reviewing the development of research on clusters and ultrafine particles.⁹

Industry has long used ultrafine particles in dyes, pigments, adhesives and catalysts. The 1960s saw the use of arc furnaces, plasma furnaces and chemical flame furnaces to produce submicron particles of alumina, carbonated tungsten, Si_3N_4 and other heat- and acid-resistant carbonates and nitrides of active metals and rare earth metals. Manufacturers use these ultrafine powders in tools, ceramics and materials that must withstand heat. Alloys and plastics can be made more uniform and harder by a process called dispersion hardening, in which ultrafine particles of an insoluble material are dispersed in a host material and then the mixture is sintered or exposed to a catalyst. Ultrafine particles of latex, which is an organic polymer, are commonly used as a vehicle for biological and chemical manipulation in the pharmaceutical industry and other fields. Aerosols, which are colloidal particles dispersed in a gas, are used in agriculture, forestry, military technologies and medicine.

During the 1970s researchers in Japan developed 30-nm ultrafine particles of magnetic alloys for use in magnetic tape. They found that an ultrafine particle medium made from an iron-nickel-cobalt alloy produced



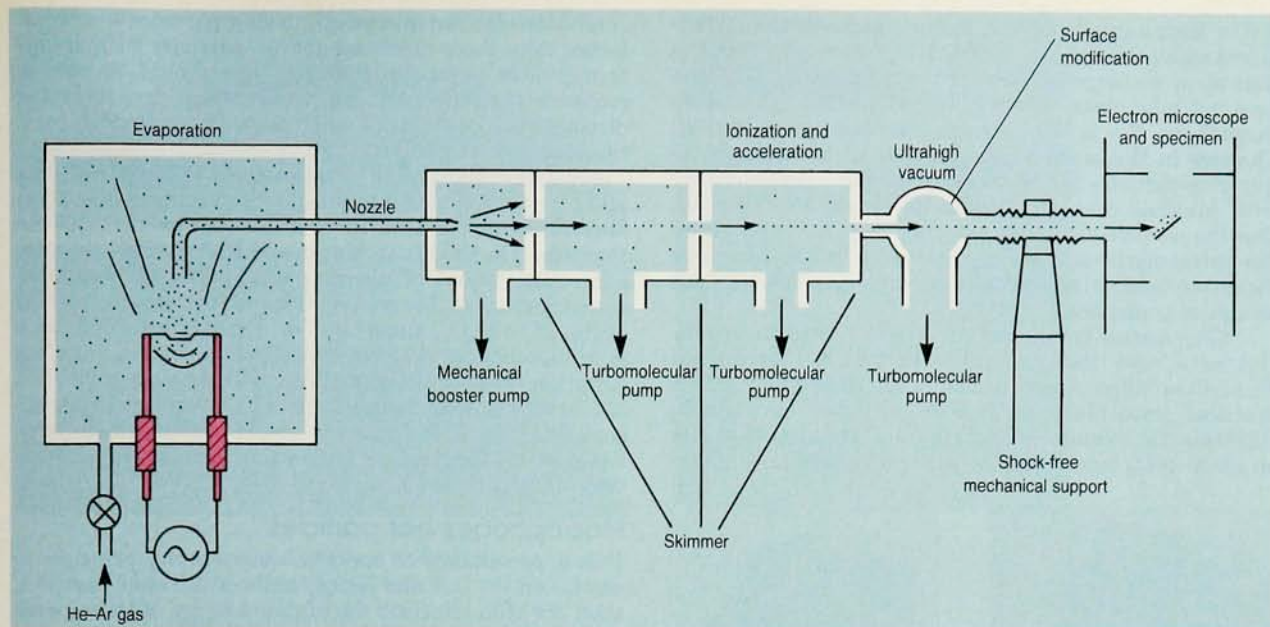
Gas evaporation method for making ultrafine particles. In principle one can use this method to prepare ultrafine particles of any size and of any material, with little contamination except by the inert gas used in the process. Figure 2

in a high-vacuum induction-heated melting furnace exhibited the expected excellent recording characteristics, and the production of metal tape began. After much effort to reduce the cost of production, ultrafine particle recording media are now manufactured by the inexpensive chemical technique of hydrogen reduction and have become commercial products.

Ultrafine particles have yielded important contributions to science. An example is a heat exchanger made of ultrafine silver particles and used in a $\text{He}^3\text{-He}^4$ dilution refrigerator.¹⁰ Ultrafine particles of silver alloy made by the gas evaporation method were compacted and used as the heat exchanger; this reduced from 30 mK to 2 mK the lowest temperature attainable with the dilution refrigerator. Another example is the discovery by our ultrafine particles project team that observations of ultrafine particles with an extremely high-quality electron microscope give direct and very important information on the physics of the "quasisolid" state of ultrafine crystals and on the physical chemistry of surfaces. I will discuss this in more detail below.

(A comment on terminology: When we look at the changing structure of a single ultrafine particle, the term "quasisolid" seems an apt description of the particle. On the other hand, when we see groups of ultrafine particles behaving as gases, liquids or solids, it seems more appropriate to call ultrafine particles "quasimolecules.")

Research in the 1970s found that ultrafine iron particles that are carefully covered with an oxide film less than 1 nm thick are very stable and resistant to weather



Beam generator. The author's research group designed and built the system shown here to generate a beam of ultrafine particles. **Figure 3**

corrosion at normal temperatures. This property assured researchers that ultrafine metal particles could lead to a new generation of industrially useful materials and gave added impetus to the inauguration of the ultrafine particles project.

Around 1900, colloid chemists were asking themselves the question, "Is colloid chemistry a fundamental field of science?" Almost 90 years later, the degree to which we should regard phenomena on the scale of the ultrafine particle as fundamental remains an issue, but there are now some more practical questions as well:

▷ Will ultrafine particles become an important new industrial material?

▷ When assemblies of atoms grow from clusters to ultrafine particles, at what stage of growth and through what processes do they begin to exhibit some of the characteristics of macroscopic materials?

▷ When do assemblies of atoms exhibit biological activity?

▷ What roles do ultrafine particles play in the creation and annihilation of stars?

▷ Is it possible to come up with a simple theory and a large-scale computer program for understanding and designing ultrafine particles and the compound materials made from them?

None of these questions is easy to answer, but they are all worth investigating.

Achievements of the project

Our ultrafine particles project encompassed four groups: basic properties, physical applications, biological and chemical applications, and formation processes. We used the so-called gas evaporation method (figure 2) to prepare most of our ultrafine particles. In principle one can use this method to prepare ultrafine particles of any size and of any material, with little contamination except by the inert gas used in the process.

The basic-properties group observed ultrafine particles with a specially designed high-resolution electron microscope capable of operating in various modes, includ-

ing electron diffraction. This instrument obtained images in an extremely short time—short enough that changes in the samples were not a problem. It was equipped with a fast videotape recording system that operated at 60 frames/sec. The group also designed and built a system, shown schematically in figure 3, capable of transporting ultrafine particles to a sample holder with minimum contamination. Such a high-resolution electron microscope system when combined with good samples of ultrafine particles can produce important scientific and technical information.

An example is the discovery of the quasisolid state, so named by Sumio Iijima, leader of the basic-properties group. A video recording (figure 4) of crystalline particles of gold about 2 nm in diameter shows that these particles are not fixed in shape, but spontaneously take on various forms such as cuboctahedron, single twin, icosahedral multitwin and truncated decahedral multitwin. In addition to these morphological changes, there are changes in the internal arrangement of the gold atoms within the particles. Iijima's group found that the morphological and structural transformations, which occur in fractions of a second, are not due to temperature changes. When they placed the gold particles on ultrafine particles that were much larger—several tens of nanometers in diameter—and that were covered with a thin film of SiO_2 , the gold particles changed shape as they moved over the SiO_2 film and some of them merged to form larger particles. The dynamic behavior of the gold particles as shown by the video recording is quite impressive and resembles the behavior of viruses attacking cells.

A second scientific finding from high-resolution electron microscopy is illustrated by figure 5, which shows two images of the edge of a gold particle obtained by transmission electron microscopy using a tangentially incident electron flux. These are frames from a video recording that shows the (111) surface atomic layer to be constant in time and the (100) surface atomic layer to be continuously changing. The energy given to the gold particle by the electron flux dissipates on the (100) surface.

But on such a small particle, reorganization of the surface atoms along the lines of the 3×3 or 7×7 reconstructions that occur on large surfaces of materials such as silicon does not take place. Instead, reconstruction takes place throughout the entire particle, as mentioned earlier. Changes in the atomic arrangements of the surfaces of ultrafine particles can be observed almost simultaneously with internal changes. One must remember, however, that the particle diameters are often equal to or less than the wavelengths and mean free paths of the electrons inside the solid. In this respect we can regard the particles as almost transparent.

The gaseous environments in which ultrafine particles exist and the substrates to which they attach themselves affect their behavior in ways that are of practical importance. Ultrafine particles on a Fe_3O_4 substrate, for example, behave differently from particles on an Si-SiO_2 substrate. By using a high-quality, high-

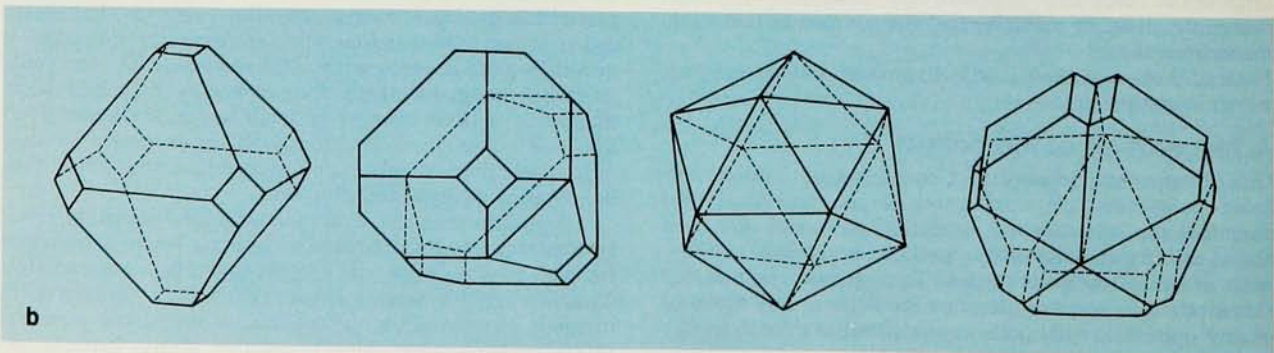
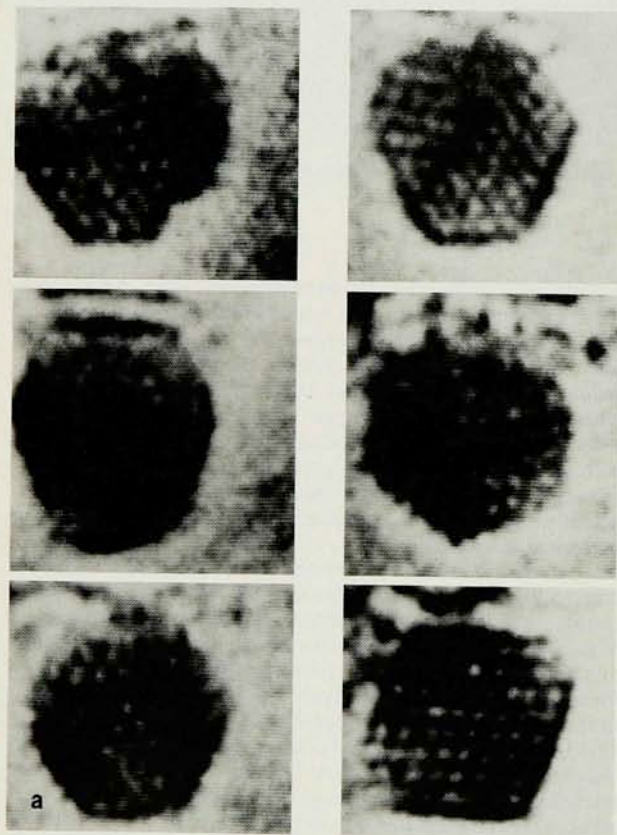
resolution electron microscope to view particles somewhat larger than those discussed above—particles with diameters greater than about 20 nm—one should be able to measure the effect of the environment by observing directly such phenomena as deposition, sputtering, sorption and catalytic action.

We have seen much progress since 1971, when Iijima and others used a high-resolution electron microscope to observe the crystal structures of ultrafine particles for the first time. In 1983 L. D. Marks and D. J. Smith published edge observations of ultrafine gold particles.¹¹ In 1984 Iijima published his observations of the structures and edges of $\gamma\text{-Al}_2\text{O}_3$ alone and of $\gamma\text{-Al}_2\text{O}_3$ attached to a rhodium cluster. And in 1987 Katsumichi Yagi and his coworkers at the Tokyo Institute of Technology published the results of experiments done in a sample chamber cooled by liquid helium and under an extremely high vacuum.¹² This chamber gave valuable information from very clean surfaces.

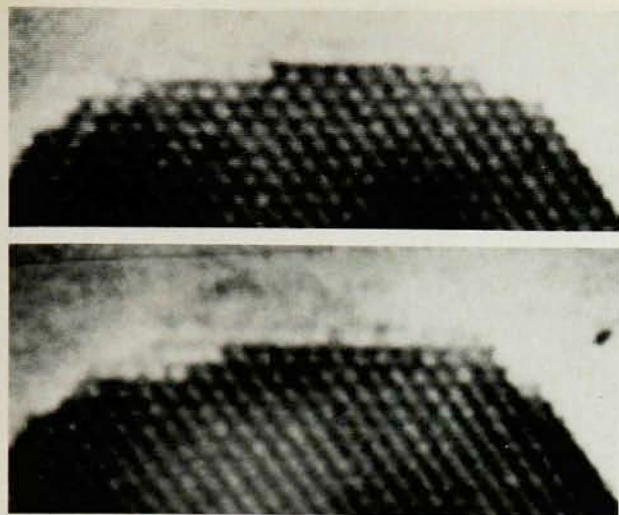
Macrophages eat particles

If it is permissible to apply the uncertainty principle to objects on the size and energy scale of ultrafine particles, then the characteristic fluctuation energy of these particles is 0.01–0.001 eV. This is the energy range of biological phenomena, and, in fact, macrophages—large cells that engulf foreign material—do eat various ultrafine particles. Our biological and chemical group combined the videotaping system with a high-magnification optical microscope to investigate how the macrophages known as J-774 and BHK eat such particles. The table on page 50 shows preliminary results from that work, and figure 6 shows two images. Macrophages tend to avoid “phagocytosis,” or eating, of ultrafine particles of iron, nickel and copper. Macrophages that do eat these particles die relatively quickly. The results shown in the table indicate that the electrokinetic potential, or zeta potential, plays a role in the discrimination of particles. The creation of ions inside the cell may play a further role.

Richard Blakemore and his colleagues proved directly that living organisms make use of the geomagnetic field by means of magnetic ultrafine particles.¹³ Certain freshwater bacteria gain the ability to move along magnetic flux lines by producing internally more than ten ultrafine magnetite particles smaller than 50 nm. We have developed a technique for using the gas evaporation method to produce ultrafine particles of Fe, Fe-Ni-Co and other magnetic alloys with sizes of 20–30 nm linked in straight chains. These ultrafine particles are obviously nonspherical, which enhances their magnetic dipole moments. Through movement controlled with nonuniform magnetic fields, these straight-chain ultrafine parti-



Cluster of about 460 gold atoms. The high-resolution electron microscope images in **a** show various shapes taken on by the cluster, which is about 2 nm in diameter. The model structures in **b** are based on 459 atoms and correspond to some of the shapes that are actually observed. **Figure 4**



Surface action. This pair of electron micrographs, reproduced from a videotape, shows movement of gold atoms on the surface of a gold particle. Each dark blob is a projection of several atoms. Note the change in the atomic steps and corners and the "atom clouds" that hang over the (001) surface. The horizontal section shown here is 8 nm in length. **Figure 5**



Macrophages and eaten particles. Phagocytosed, or eaten, ultrafine gold particles accumulate within the cells. In the phase-contrast image at the top, the particles appear as bright dots. In the bright-field image of the same scene at the bottom, the particles are dark. **Figure 6**

cles may serve as a tool for surgery on microscopic living organisms. For such biological applications it is desirable to prevent chemical reactions by coating the ultrafine particles with a suitable organic polymer film; one can also add a biologically active site to the film.¹⁴ Japanese researchers have managed to use 10–20-nm ultrafine ferrite particles with ligands in a nonuniform magnetic field to separate specific endocytic vesicles.¹⁵ This method may become a powerful tool in microbiology.

Organic polymers can be made into ultrafine particles, and 10-nm particles of organic polymers have been relatively easy to make by the gas evaporation method.¹⁶ Organic polymers that are hydrophobic as a bulk material can become hydrophilic when they are made into ultrafine particles. We have not examined whether this is due to the size effect in water or to chemical modification of the surface during the gas evaporation process, but the fact that ultrafine particles can become hydrophilic is extremely interesting from the point of view of pharmaceutical applications.

Deposition of high-speed particles

Seiichi Kashu and his coworkers at Vacuum Metallurgical Co. developed the so-called gas deposition method, in which a high-speed jet of gas entrains ultrafine particles, which then impinge on metal, glass, ceramic or plastic. Figure 7 shows the process and the result. Simple hydrodynamic calculations show that ultrafine particles with a specific gravity of 8, for example, are completely entrained in under 0.1 msec in a jet of gas at the low pressure of 100 pascals. The time it takes an ultrafine particle to reach the speed of the jet is proportional to the particle's specific gravity. Thus by the time the ultrafine particles with the greatest specific gravities are completely entrained, those with smaller specific gravities have reached the flow velocity, which typically exceeds 100 m/sec.

The gas deposition method was initially developed as a way to evaluate the quality of metallic or ceramic ultrafine particles, because the electrical conductivity of

deposited ultrafine particles is a reproducible characteristic. However, the resulting laminated materials turned out to have special characteristics of interest to physicists. For example, whether the thermal coefficient of electrical conductivity of a 10-nm-thick gas-deposited nickel film is positive or negative depends on how the deposition is done.

Experiments show that nearly 100% of the ultrafine particles impinging on a solid surface adhere if the surface temperature is sufficiently lower than the particles' evaporation temperature. This indicates that the kinetic energy of the ultrafine particles is effectively transformed into adhesion energy at the point of impact, and that shear forces can usually be neglected. With the gas deposition method it is easy to make any kind of compacted mixture of materials with different specific gravities. For example, one can use the gas deposition method to produce superconductors and microelectronic devices, although the requirement that the nozzle diameter be larger than the mean free path of the carrier gas if the gas is to carry ultrafine particles limits practical use of the method. With a little more development work, it should be possible

Particle characteristics and effects on macrophages

Particle	Mobility $\mu\text{m}/(\text{sec V cm})$	Zeta potential mV	Phagocytosis	Viability	Size
Lorex	-6.32	-90.9	+	+	500 nm
NH ₂ -lorex	-2.46	-35.4	+	+	450 nm
COOH-lorex	-6.25	-89.8	+	+	570 nm
$\gamma\text{-Al}_2\text{O}_3$	+1.87	+26.9	-	+	UFP
TiO ₂	-2.23	-32.1	+	+	UFP
SiO ₂	-3.69	-53.1	+	+	UFP
ZnS	-0.46	-6.6	+	+	UFP
$\gamma\text{-Fe}_2\text{O}_3$	-0.34	-4.9	+	+	UFP
$\gamma\text{-Fe}_2\text{O}_3$	-0.90	-12.9	+	+	80 nm
Fe	+2.36	+34.0	-	-	UFP
Ni	+2.94	+42.3	-	-	UFP
Fe ₃ O ₄	+0.81	+11.6	+	+	300 nm
Cu	+3.12	+44.9	-	-	UFP
Ag	-2.95	-42.5	+	+	UFP

Measurements made at 20°C in a pH 7.2 buffer (2 mM imidazole HCl with 2 mM KCl). UFP, ultrafine particle. The 80 nm and 300 nm particles are chemically prepared.

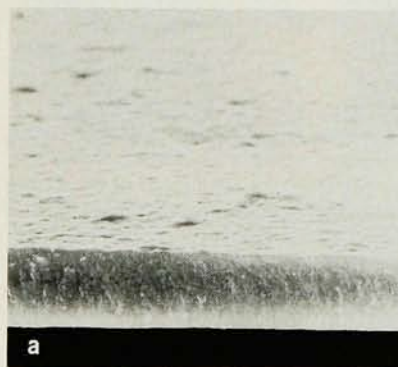
to produce compound materials heretofore unobtainable on Earth because of gravitational segregation, and to do so at low temperatures. This is possible only on the size scale of ultrafine particles.

Shizuo Umemura, the leader of the physical applications group, has attempted to place ultrafine particles on silicon in a very regular array for microelectronics uses such as memories.¹⁹ First he used a narrow electron beam to form a square lattice of carbon on a silicon wafer. Using the lattice elements as containers or barriers, he formed a lattice of ultrafine particle islands made of gold or potassium chloride (figure 8). This method is simpler than the microfabrication method for very-large-scale integration, but its accuracy may be inferior. If such patterns can be made accurately, however, it may be possible to design quantum-well devices based on the size effect, but this will require the development of technology equivalent to or more advanced than that required for the construction of two-dimensional superlattices.

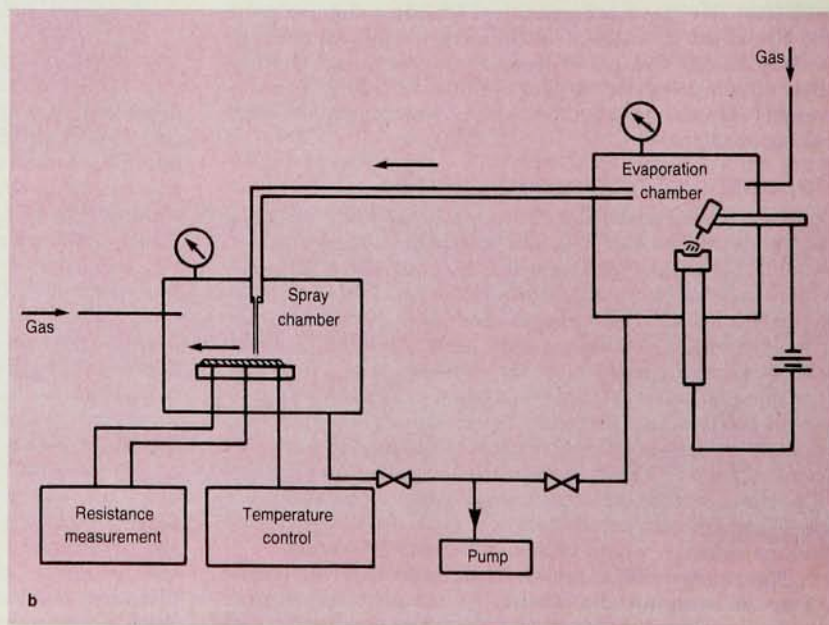
Another subject left for future study is "superatoms"

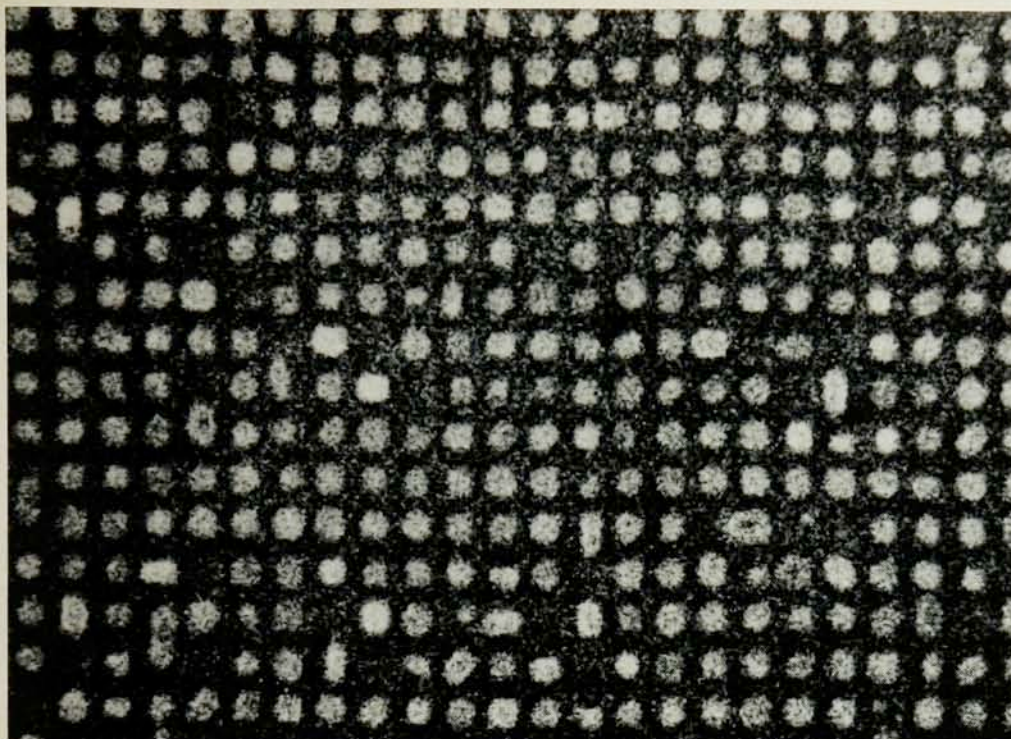
for use in building semiconductor devices. These ultrafine particles, proposed by Hisatsune Watanabe, would be composed of two semiconductor substances, arranged as a core and a shell, which would resemble functionally the nucleus and electron shell of an atom, respectively.²⁰ However, a prerequisite for such developments may be further advances in the technology for producing ultrafine particles of accurate size.

Ultrafine catalysts. Ultrafine nickel particles produced by the gas evaporation method have interesting catalytic properties. For example, unlike the usual Raney nickel catalyst used in the dairy industry, these particles cause the first stage of the hydrogenation of 1,3-cyclooctadiene to occur preferentially, producing cyclooctene and minimizing production of the undesirable second-stage product, cyclooctane.¹⁸ The diameter dependence of the usual catalytic reaction is such that the degree of activation becomes so small as to be useless when the particle diameters exceed 10 nm. However, if a catalyst's selectivity is determined by relatively small energy



Copper film made by the deposition of ultrafine copper particles carried by a fast-moving gas. The three regions in the scanning electron micrograph in **a** are, from bottom to top, the substrate, which appears black in the image; the copper film, 2.2 microns thick, seen in cross section; and the surface of the copper film. The diagram in **b** is a schematic representation of the gas deposition method. **Figure 7**





Lattice of ultrafine potassium chloride particles. The particles, which are 670 nm apart, are in a carbon lattice on a silicon substrate. Figure 8

differences (enzymes, which are biological catalysts, are an example of highly selective catalysts), then relatively large ultrafine particles may have some use as catalysts.

In closing I would like to make a comment relevant to the question of whether ultrafine particles deserve mention in the hierarchy of elementary particles, atomic nuclei, atoms, molecules, bulk material, planets, stars and galaxies. Ultrafine particles do occupy an important region: the transition between the microscopic and macroscopic worlds, a region where much biological activity takes place. Maxwell is said to have benefited from work being carried out at the Bureau of Statistics when he was trying to understand gas motion. Perhaps the study of ultrafine particles will help theoretical physicists understand "biological statistics."

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