9. C. J. Tsai and K. D. Jordan, *Chem. Phys. Lett.* **213**, 181 (1993).
10. K. Kim, K. D. Jordan, T. S. Zwier, *J. Am. Chem. Soc.* **116**, 11568 (1994).
11. R. J. Saykally and G. A. Blake, *Science* **259**, 1570 (1993).
12. N. Pugliano and R. J. Saykally, *ibid.* **257**, 1937 (1992); K. Liu *et al.*, *J. Am. Chem. Soc.* **116**, 3507 (1994); K. Liu *et al.*, *Faraday Discuss.* **97**, 35 (1994).
13. J. D. Cruzan *et al.*, *Science* **271**, 59 (1996).
14. K. Liu, M. G. Brown, J. D. Cruzan, R. J. Saykally, *Science* **271**, 62 (1996).
15. K. Liu *et al.*, in preparation.
16. R. Fellers *et al.*, in preparation.
17. L. H. Coudert and J. T. Hougen, *J. Mol. Spectrosc.* **139**, 259 (1990).
18. B. J. Smith *et al.*, *J. Chem. Phys.* **92**, 1240 (1990).
19. D. J. Wales, *J. Am. Chem. Soc.* **115**, 11180 (1993).
20. J. N. Gregory and D. C. Clary, *J. Chem. Phys.* **102**, 7817 (1995); *Chem. Phys. Lett.* **228**, 547 (1994).
21. J. E. Fowler and H. F. Schaefer, *J. Am. Chem. Soc.* **117**, 446 (1995).
22. D. Sabo, Z. Bacic, T. Bürgi, S. Leutwyler, *Chem. Phys. Lett.* **244**, 283 (1995); T. Bürgi, S. Graf, S. Leutwyler, W. Klopper, *J. Chem. Phys.* **103**, 1077 (1995); W. Klopper, M. Schütz, H.-P. Lüthi, S. Leutwyler, *ibid.*, p. 1085; W. Klopper and M. Schütz, *Chem. Phys. Lett.* **237**, 536 (1995); M. Schütz, T. Bürgi, S. Leutwyler, H. B. Bürgi, *J. Chem. Phys.* **99**, 5228 (1993); *ibid.* **100**, 1780 (1994).
23. M. Schütz, W. Klopper, H.-P. Lüthi, S. Leutwyler, *J. Chem. Phys.* **103**, 6114 (1995).
24. J. D. Cruzan *et al.*, in preparation.
25. D. J. Wales, unpublished results.
26. D. J. Wales *et al.*, *J. Am. Chem. Soc.*, in preparation.
27. J. N. Gregory and D. C. Clary, unpublished results.
28. F. H. Stillinger, *Science* **209**, 451 (1980); A. C. Belch and S. A. Rice, *J. Chem. Phys.* **86**, 5676 (1987); R. J. Speedy and M. Mezei, *J. Phys. Chem.* **89**, 171 (1985).
29. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983); M. Townsend, S. A. Rice, M. D. Morse, *ibid.*, p. 2496.
30. K. Watanabe and M. L. Klein, *Chem. Phys.* **131**, 157 (1989); P. Cieplak, P. Kollman, T. Lybrand, *J. Chem. Phys.* **92**, 6755 (1990).
31. G. Corongiu, *Int. J. Quantum. Chem.* **42**, 1185 (1992).
32. K. Laasonen, M. Sprik, M. Parrinello, R. Car, *J. Chem. Phys.* **99**, 9081 (1993).
33. G. Corongui and E. Clementi, *Chem. Phys. Lett.* **214**, 367 (1993).
34. P.-O. Astrand, A. Wallqvist, G. Karlstrom, *J. Chem. Phys.* **100**, 1262 (1994).
35. G. Fraser, *Int. Rev. Phys. Chem.* **10**, 189 (1991).
36. N. Pugliano and R. J. Saykally, *J. Chem. Phys.* **96**, 1832 (1992); N. Pugliano *et al.*, *ibid.* **98**, 6617 (1993).
37. C. Leforestier, *ibid.* **101**, 7360 (1994).
38. M. J. Elrod and R. J. Saykally, *Chem. Rev.* **94** (7) 1975 (1994).
39. B. F. King and F. Weinhold, *J. Chem. Phys.* **103**, 333 (1995).
40. S. C. Althorpe and D. C. Clary, *ibid.* **101**, 3603 (1994).
41. J. N. Gregory and D. C. Clary, *ibid.*, in preparation.
42. C. Millot and A. J. Stone, *Mol. Phys.* **77**, 439 (1992).
43. P. M. Holland and A. W. Castleman Jr., *J. Chem. Phys.* **72**, 5984 (1980); S. Wei, Z. Shi, A. W. Castleman Jr., *ibid.* **94**, 3268 (1991); X. Yang and A. W. Castleman Jr., *J. Am. Chem. Soc.* **111**, 6845 (1989).
44. M. M. Teeter, *Proc. Natl. Acad. Sci. U.S.A.* **81**, 6014 (1984).
45. T. Baker, E. Dodson, G. Dodson, D. Hodgkin, R. Hubbard, in *Crystallography in Molecular Biology*, D. Moras, J. Drenth, B. Strandberg, D. Suc, K. Wilson, Eds. (Plenum, New York, 1985), pp. 179–192.
46. S. Neidle, H. Berman, H. S. Shieh, *Nature* **288**, 129 (1980).
47. T. K. Kim and M. S. Jhon, *J. Mol. Liq.* **59**, 179 (1994).
48. T. Head-Gordon, *Proc. Natl. Acad. Sci. U.S.A.* **92**, 8308 (1995).
49. R. N. Pribble and T. S. Zwier, *Science* **265**, 75 (1994).
50. M. F. Vernon *et al.*, *J. Chem. Phys.* **77**, 47 (1982); R. H. Page, J. G. Frey, Y.-R. Shen, Y. T. Lee, *Chem. Phys. Lett.* **106**, 373 (1984).
51. F. Huisken, M. Kaloudis, A. Kulcke, D. Voelkel, *Infrared Phys. Technol.* **36**, 171 (1995).
52. J. J. Scherer *et al.*, *Chem. Phys. Lett.* **245**, 273 (1995).

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Semiconductor Clusters, Nanocrystals, and Quantum Dots

A. P. Alivisatos

Current research into semiconductor clusters is focused on the properties of quantum dots—fragments of semiconductor consisting of hundreds to many thousands of atoms—with the bulk bonding geometry and with surface states eliminated by enclosure in a material that has a larger band gap. Quantum dots exhibit strongly size-dependent optical and electrical properties. The ability to join the dots into complex assemblies creates many opportunities for scientific discovery.

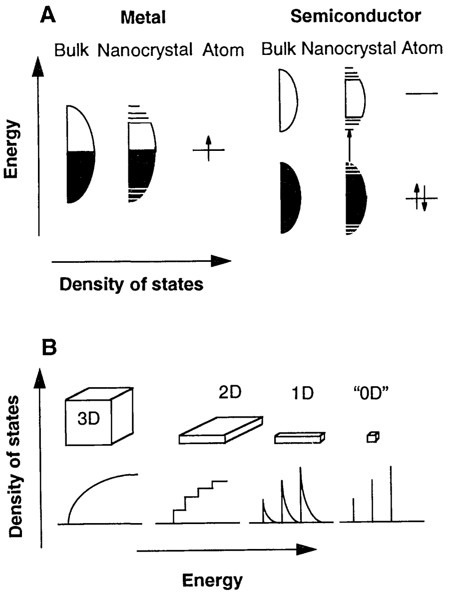

Fig. 1. (**A**) Schematic illustration of the density of states in metal and semiconductor clusters. (**B**) Density of states in one band of a semiconductor as a function of dimension.

Cluster science is devoted to understanding the changes in fundamental properties of materials as a function of the size, evolving from isolated atoms or small molecules to a bulk phase. In the case of semiconductors, this evolution is remarkable (*1*). For example, the band gap in CdS can be tuned between 4.5 and 2.5 eV as the size is varied from the molecular regime to the macroscopic crystal, and the radiative lifetime for the lowest allowed optical excitation ranges from tens of picoseconds to several nanoseconds (*2*). The energy above the band gap required to add an excess charge decreases by 0.5 eV (*3*). The melting temperature increases from 400° to 1600°C (*4*), and the pressure required to induce transformation from a four- to a six-coordinate phase decreases from 9 to 2 GPa (*5*). This enormous range of fundamental properties is realized in a material of a single chemical composition, purely by increasing the size, and can be used to advantage in light-emitting diodes (*6*, *7*) and other optical and electrical devices in the future. Two peculiar characteristics of semiconductors influence the ways in which we think of an ideal semiconductor cluster, which is often called a quantum dot.

First, it is important to realize that in any material, substantial variation of fundamental electrical and optical properties with reduced size will be observed when the electronic energy level spacing exceeds the temperature. In semiconductors, this transition occurs for a given temperature at a relatively large size compared to metals, insulators, or molecular crystals. This difference can be understood by considering that the bands of a solid are centered about atomic energy levels, with the width of the band related to the strength of the nearest-neighbor interactions. In the case of van der Waals or molecular crystals, the nearest-neighbor interactions are weak, the bands in the solid are very narrow, and consequently, not much size variation in optical or electrical properties is expected or observed in the nanocrystal regime. As cluster size increases, the center of a band develops first and the edges last. Thus, in metals, where the Fermi level lies in the center of a band, the relevant energy level spacing is

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small, and at temperatures above a few kelvin, the electrical and optical properties resemble those of a continuum, even at relatively small sizes (tens or hundreds of atoms) (8). In semiconductors, however, the Fermi level lies between two bands, such that the edges of the bands dominate the low-energy optical and electrical behavior. Therefore, optical excitations across the gap depend strongly on size for clusters as large as 10,000 atoms. (Fig. 1A). Electrical transport also depends strongly on size, mainly because of the large variation in energy required to add or remove charges on a nanocrystal. As a consequence, many useful size-dependent phenomena are observed in clusters so large that they possess an identifiable interior, structurally identical to the corresponding bulk solid, with a substantial fraction of the total number of atoms on the surface. Clusters of this size are often called nanocrystals.

A second important characteristic of semiconductors concerns the influence of the surface on optical and electrical properties, and the need to embed semiconductor clusters in a passivating medium. At first, it might appear as though the most compelling ideal of a semiconductor nanocrystal might be a compositionally pure collection of atoms, mass-selected, isolated in the gas phase, and thermally annealed (9). In this form, the influence of size might be most directly observed, and indeed, many beautiful studies of such clusters followed the discovery of laser vaporization and mass selection. Despite the seeming perfection of a pure cluster in the gas phase, from the point of view of semiconductor physics, it is in many ways a highly defective system. At the surface of a pure tetrahedral inorganic semiconductor, substantial reconstructions in the atomic positions occur, invariably leading to energy levels within the energetically forbidden gap of the bulk solid. These surface states trap electrons or holes and degrade the electrical and optical properties of the material. Passivation is the chemical process by which these surface atoms are bonded to another material of a much larger band gap, eliminating all of the energy levels inside of the gap. The ideal termination naturally removes the structural reconstructions, leaving no strain, and simply produces an atomically abrupt jump in the chemical potential for electrons or holes at the interface. This potential confines electrons or holes inside the cluster, much like the "particle in a box" of elementary quantum mechanics. A great deal of current research into semiconductor clusters is thus focused on the properties of quantum dots with the bulk bonding geometry and with surface states eliminated by enclosure in a material of larger gap.

Scientists have approached the fabrication and investigation of quantum dots from two very different points of view: a top-down approach in which the extent and dimensionality of solid matter has gradually been reduced, and a bottom-up approach in which quantum dots are viewed as extremely large molecules or colloids. Both approaches are yielding exciting samples: Fig. 2 displays a gallery of modern-day quantum dots and assemblies of dots produced by these methods. The quantum dots grown by molecular beam epitaxy and lithographic techniques are in the size regime from 1 μm down to 10 nm (*10*). They are well passivated and immobilized on a substrate where they may be investigated optically and electrically. The colloidal samples vary in diameter from the truly molecular regime of 1 nm to about 20 nm. Their surfaces are derivatized with organic molecules, which prevent them from aggregating and render them soluble. It is an open question whether these organic molecules provide electronic passivation as well. However, these samples may be manipulated chemically in a wide range of ways, yielding entirely new sample configurations, such as the recently reported three-dimensional quantum dot superlattice (*11*).

Quantum Confinement and Optical Properties

The most striking property of semiconductor nanocrystals is the massive change in optical properties as a function of size (Fig. 3A). As size is reduced, the electronic excitations shift to higher energy, and the oscillator strength is concentrated into just

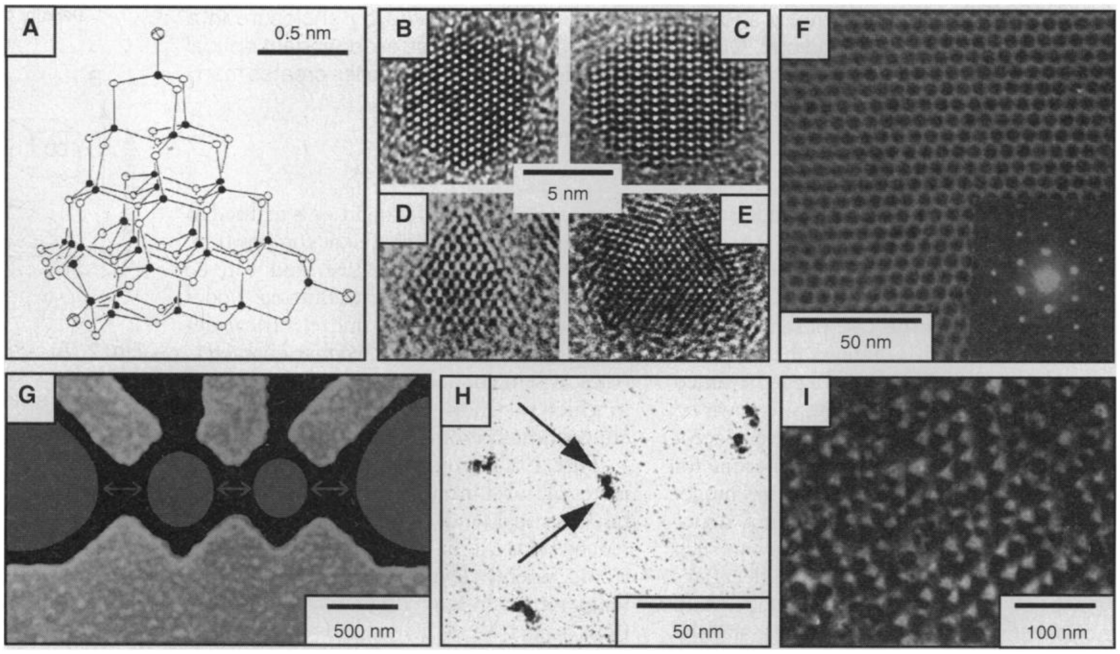

Fig. 2. Gallery of quantum dot structures. (**A**) Positions of Cd and S atoms in the molecular cluster $Cd_{32}S_{55}$, as determined by single-crystal x-ray diffraction. This cluster is a small fragment of the bulk CdS zinc blende lattice. The organic ligands on the surface are omitted for clarity. [Reprinted from (*29*) with permission] (**B** and **C**) Transmission electron micrographs of CdSe nanocrystals with hexagonal structure, as viewed down different crystallographic axes. These nanocrystals were prepared colloidally and exhibit well-defined facets. The surfaces are passivated with organic surfactants. (**D** and **E**) Transmission electron micrographs of CdS/HgS/CdS quantum dot quantum wells, prepared by the method of Weller and coworkers (*18*). The faceted shapes show that epitaxial growth for passivation is possible in colloidally grown nanocrystals (*30*). (**F**) Transmission electron micrograph of a CdSe quantum dot superlattice. [Reprinted from (*11*) with permission] (**G**) Scanning electron micrograph of two coupled GaAs quantum dots about 500 nm in diameter. The strength of the coupling can be adjusted by means of the gate voltage. [Reprinted from (*23*) with permission] (**H**) Transmissionelectron micrograph of coupled CdSe nanocrystal quantum dots 4 nm in diameter. These crystallites are joined by an organic molecule. The coupling can be tuned by changing the linker length. (**I**) Transmission electron micrograph of InAs quantum dots in a GaAs matrix, prepared by molecular beam epitaxy. [Reprinted from (*10*) with permission]

a few transitions. These basic physical phenomena of quantum confinement arise as a result of changes in the density of electronic states and can be understood by considering the relation between position and momentum in free and confined particles. For a free particle, or a particle in the periodic potential of an extended solid, the energy and the crystal momentum can both be precisely defined, whereas the position cannot. For a localized particle, the energy may still be well defined, but the uncertainty in position decreases, so that momentum is no longer well defined. The discrete energy eigenfunctions of the particle may then be viewed as superpositions of bulk momentum states. Given the relation between energy and momentum in the bulk solid, one can see how a series of nearby transitions occurring at slightly different energies in the bulk will be compressed by quantum confinement into a single, intense transition in a quantum dot. The shifts in absorption onset in colloidally prepared II-VI semiconductors, such as CdS and CdSe, and III-V semiconductors like InP can be a large fraction of the bulk band gap and can result in tuning across a major portion of the visible spectrum. For example, the band gap in CdSe can be tuned from deep red (1.7 eV) to green (2.4 eV) by reducing the cluster diameter from 200 to 20 Å (*12*).

Nanocrystal-based light-emitting diodes (LEDs). The luminescence from nanocrystals closely tracks the absorption onset. Narrow-band (15 to 20 nm), size-tunable luminescence with efficiency on the order of 10% is observed from semiconductor nanocrystals at room temperature; these properties are highly desirable for the production of LEDs. Two reports of LEDs made with polymers and CdSe nanocrystals have appeared within the last year (*6*, *7*). The first group (*6*) assembled nanocrystals into thin layers on the surface of poly *p*-phenylene vinylene (PPV), an electroluminescent polymer. The PPV itself was grown on a layer of indium tin oxide, a transparent hole-injecting contact. Finally, the nanocrystal layer was coated with films of Mg and Ag, the electron-injecting contact. This complete assembly electroluminesces when a voltage is applied. The recombination of electrons and holes takes place in either the polymer layer (which emits green light) or the nanocrystal layer (producing red light), depending on the applied voltage. The nanocrystal emission shifts with size. Thus, these LEDs provide a variety of means for tuning the output color, with no change in the fabrication method.

Concentration of oscillator strength and nonlinear optical properties. Ignoring the effects of the size distribution, it is important to understand how much oscillator strength can be compressed into a narrow region of the spectrum by quantum confinement. In typical semiconductor nanocrystals, the energy level spacing is on the order of 0.15 to 0.3 eV. If the integrated oscillator strength over 0.15 eV of the bulk spectrum could be compressed into lines with widths on the order of 0.1 to 0.5 meV, nanocrystals would fulfill an important limit in nonlinear optical materials (*13*). Polarizability scales with volume, so that the sharp, intense (radiative lifetime on the order of picoseconds) transitions of the nanocrystals could be readily manipulated by off-resonant electric fields. A prototype optical switch with gain, for instance, would be one in which the transmission of a high-power laser beam near the absorption threshold of the nanocrystals is modulated by a weaker, off-resonant pulse by the ac Stark effect.

The homogeneous linewidths, however, are extremely broad (*14*), corresponding to dephasing times on the order of 100 fs, with faster decays observed in smaller crystallites (*15*). As a consequence, the spacings between nanocrystal electronic transitions exceed the linewidths only slightly, so that despite the large shifts to higher energy observed in the spectra, the idealized discrete spectra of Fig. 1B are not fully realized in practice in colloidal samples. The organic molecules used to provide chemical passivation (providing solubility without aggregation) may not provide good electronic passivation.

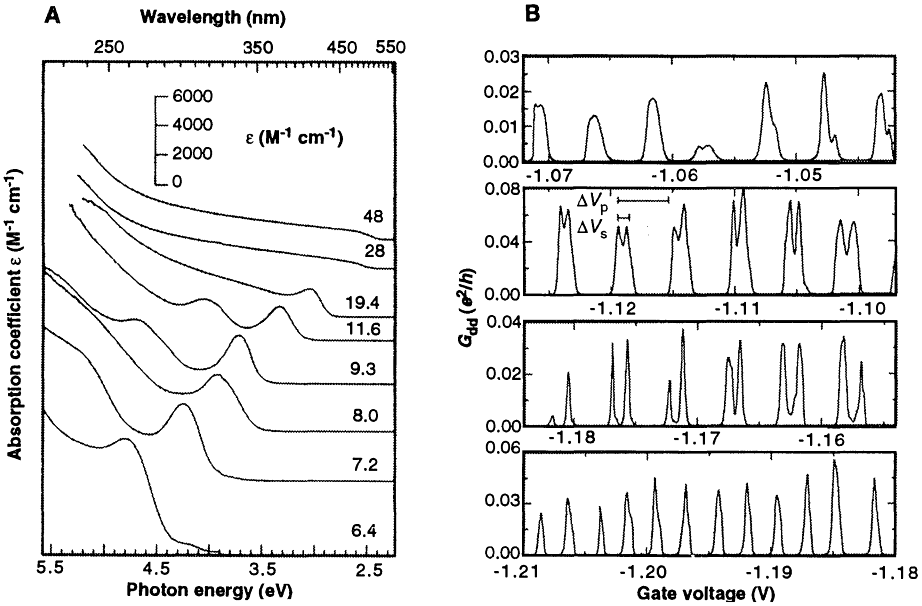

Fig. 3. (**A**) Quantum confinement effects on the absorption spectra of CdS nanocrystal quantum dots. With reduced size, the spectra shift to higher energy and the oscillator strength is concentrated into a small number of transitions. [Reprinted from (*2*) with permission] (**B**) Variations in the conductance G_{dd} versus gate voltage for two coupled GaAs quantum dots, as a function of the interdot coupling. V_d, drain voltage; V_s, source voltage. [Reprinted from (*23*) with permission]

Passivation

The importance of electronic passivation is illustrated by recent results obtained on cathodoluminescence from single InAs quantum dots fabricated by molecular beam epitaxy and embedded inside GaAs (Fig. 2E), which has a larger gap (*10*). These crystallites show exceptionally narrow emission linewidths, but absorption or luminescence excitation spectra, which may be broader, have not yet been reported. These experiments suggest that the nonlinear optical properties of quantum dots deserve serious attention and that further work on inorganic passivation of colloidal nanocrystal surfaces is needed. Given the multiple sources of inhomogeneous broadening (including size, shape, local fields, and defects), single-molecule spectroscopy (*16*) and near-field scanning probe microscopy (*17*) show great promise as tools to aid in deciphering the nature of the intrinsic absorption spectra of nanocrystals.

As the foregoing discussion illustrates, a method of preparing well-passivated quantum dots colloidally is needed. Toward this goal, Weller and co-workers (*18*) recently synthesized a remarkable nanocrystal heterostructure. These particles consist of a tetrahedral CdS core, about 50 Å in size, with (111) facets. When exposed to Hg^{2+} ions, the Hg^{2+} displaces precisely one monolayer of Cd^{2+} from the surface. Subsequently, the HgS layer may be capped with a final layer of CdS. The resulting sample can be described as a CdS/HgS/CdS quantum dot quantum well. Transmission electron microscopy shows that the HgS and the CdS capping layer grow epitaxially on the core (Fig. 2, D and E). Because HgS has a much smaller band gap than CdS, electronic excitations are largely confined in this well, which is embedded inside of a nanocrystal. This experiment suggests that the tremendous successes in passivation achieved by molecular beam epitaxy may soon be replicated in colloidal nanocrystals.

Absorption and Emission of Light in Indirect Gap Semiconductor Nanocrystals

A great deal of interest has been focused on the size evolution of a selection rule that derives from translational symmetry. In Si and several other semiconductors, the transition from the bottom of the conduction band to the top of the valence band violates conservation of momentum and is electronically forbidden. The transition does occur, but only with phonon assistance, and the radiative rate is very slow. For this reason, Si is not used in the generation of optical signals.

The observation of intense photoluminescence from porous Si, a material that consists of fused nanometer-diameter, undulating Si wires, at first suggested that this selection rule might be altered in nanocrystals, which do not possess translational symmetry (*19*). In fact, the observation of luminescence in Si nanocrystals derives partly from small quantum confinement-induced enhancements in the radiative rate, but mainly from confinement-induced reductions in the nonradiative rate, which in bulk Si arise from the three-body Auger effect (*20*). The radiative rates for absorption and emission of light in Si, as in other indirect gap semiconductors, remain well below those of direct gap semiconductors, even in nanocrystals (*21*). The transitions still require phonon assistance, even in crystallites as small as 20 Å in diameter.

Electrical Transport and Quantum Dots

The energy required to add multiple excess charges to a small metal or semiconductor particle varies inversely with the size of the particle. This dependence has its origin in the electrostatic repulsion of charges confined in the dot. At this point, the character of charge transport is altered. As a function of applied voltage, single-electron transport events are seen as discrete steps in the current (*22*). Variations in the current-voltage characteristics with gate voltage, external magnetic field, and dot size are leading to increased understanding of the electronic structure of very large (500 nm) lithographically prepared quantum dots.

These quantum dot structures are the most sensitive instruments known for the measurement of current and local fields and may be used for that purpose or possibly as switches in the future, because the electrons and holes are necessarily delocalized over the entire structure. Analogous structures, in which colloidal nanocrystals of metals and semiconductors are deposited between electrodes, will undoubtedly be investigated extensively in the near future. These structures will be particularly interesting because the energy level spacing attributable to quantum confinement is comparable to or even greater than the charging energy in crystallites that are substantially smaller than the Bohr radius of the bulk semiconductor exciton. In this regime, tunneling and transport occur through single quantum levels of the dot.

Coupled quantum dots: molecules with tunable bonds. Because quantum dots exhibit discrete structure in their optical and electrical characteristics, they are sometimes referred to as artificial atoms, even though to a chemist, they appear to be very large and complex molecules. This analogy is particularly useful when these artificial atoms are being connected into "quantum dot molecules." Much current research has moved beyond the investigation of the properties of isolated dots to the investigation of the properties of such coupled systems. For example, the coupling constant between two quantum dots about 500 nm across (Fig. 2G) was investigated by means of changes in the current-voltage characteristics (*23*). The strength of the coupling (bond) could be varied at will by changes in the gate voltage, such that the structure could be made to act as two dots in series or as a single, strongly coupled system (Fig. 3B). Analogous dimers, on a much smaller length scale and in a different confinement regime, can be prepared colloidally. For example, two CdSe nanocrystals 4 nm in diameter were linked by an organic molecule (Fig. 2H), whose length determines the coupling strength (*24*). This work is a further example of the close intellectual relation between quantum dot structures fabricated by the top-down and bottom-up approaches. "Homo" (same size) and "hetero" dimers are under intensive study. There may be several other analogies between bonding phenomena in molecules and the electronic properties of quantum dot molecules, such as resonance, localization, covalency, and ionicity.

If quantum dots are viewed as artificial atoms, how big is the analogous periodic table? Certainly all of the materials included in the family of inorganic semiconductors may in principle be used to make quantum dot building blocks. The only requirements are the ability to control the size and achieve surface passivation. To date, these prerequisites have been achieved in a variety of systems. Among the colloidal materials, the II-VI nanocrystals stand out as the prototypical systems in which chemical control is well established (*2*, *12*). However, research into the production of III-V (InP, GaAs) (*25*), group IV (Si, Ge) (*26*), and I-VII (AgBr) (*27*) nanocrystals is advancing rapidly. In the epitaxially grown structures, InAs on GaAs (*10*) and GaAs embedded in $Al_{1-x}Ga_xAs$ are the preeminent structures. However, the range of semiconductor nanocrystals that can be synthesized appears to extend well beyond these materials, which are stable semiconductors in extended solid form. By definition, nanocrystals are in a size regime where the number of surface atoms is a large fraction of the whole, and therefore, the surface energy is a large fraction of the total free energy of the system. By manipulating the surface appropriately, one can force the interior of the nanocrystal to occupy bonding geometries that are unstable in a bulk solid. An example is the stabilization of the rock-salt structure of CdS, which in bulk is only stable at high pressure (*28*). The massive changes in the phase diagrams of nanocrystals that occur because of the surface suggest that a wide range of new quantum dots will be synthesized in the future (*5*).

One of the most exciting and novel structures to emerge in quantum dot research in recent years is the quantum dot superlattice (*11*). Colloidal CdSe nanocrystals, passivated with organic surfactants and size-selected to a very high degree, spontaneously precipitated out from solution and formed three-dimensional arrays of quantum dots. In this configuration, the artificial atoms form a quantum dot crystal. The strength of the electronic coupling between adjacent dots was again able to be tuned by variation of the organic passivating molecule, so that bands of states could be formed. Doped or mixed crystals will soon be investigated. This material is ordered on two entirely different length scales: it has a regular bonding geometry within each crystallite and between entire crystallites.

Future Directions

Advances in the science of quantum dots and semiconductor nanocrystals show no sign of abating. On the contrary, goals that 10 years ago seemed unreachable, today appear well within reach. In the next few years, one can expect steady improvements in the range of materials that can be prepared as quantum dots and in the quality of the available samples. At the same time, the current samples are of sufficient quality to enable a new generation of experiments. Quantum dots will be integrated into electrical devices, a process that has only just begun. More complex assemblies of quantum dots are now being investigated, including crystals of nanocrystals, in which the spacing between crystallites can be altered at will, and quantum dot molecules, in which dots of several different materials and sizes are linked together. New physics and chemistry are sure to be discovered as these complex assemblies are investigated.

REFERENCES AND NOTES

1. L. E. Brus, *Appl. Phys. A* **53**, 465 (1991).
2. T. Vossmeyer, L. Katsikas, M. Giersig, I. G. Popovic, H. Weller, *J. Phys. Chem.* **98**, 7665 (1994).
3. V. L. Colvin, A. P. Alivisatos, J. G. Tobin, *Phys. Rev. Lett.* **66**, 2786 (1991).
4. A. N. Goldstein, C. M. Echer, A. P. Alivisatos, *Science* **256**, 1425 (1992).
5. S. H. Tolbert, and A. P. Alivisatos, *Annu. Rev. Phys. Chem.* **46**, 595 (1995).
6. V. L. Colvin, M. C. Schlamp, A. P. Alivisatos, *Nature* **370**, 354 (1994).
7. B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, M. F. Rubner, *Appl. Phys. Lett.* **66**, 1316 (1995).
8. M. L. Cohen, M. Y. Chou, W. D. Knight, W. A. de Heer, *J. Phys. Chem.* **91**, 3141 (1987); C. Ellert, M. Schmidt, C. Schmitt, T. Reiners, H. Haberland, *Phys. Rev. Lett.* **75**, 1731 (1995).
9. A. Liu, Q.-L. Zhang, F. K. Tittel, R. F. Curl, R. E. Smalley, *J. Chem. Phys.* **85**, 7434 (1986).
10. M. Grundemann *et al.*, *Phys. Rev. Lett.* **74**, 4043 (1995).
11. C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **270**, 1335 (1995).
12. C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).
13. S. Schmitt-Rink, D. A. B. Miller, D. S. Chemla, *Phys. Rev. B* **35**, 8113 (1987).
14. A. P. Alivisatos *et al.*, *J. Chem. Phys* **89**, 4001 (1988).
15. R. W. Schoenlein, D. M. Mittleman, J. J. Shiang, A. P. Alivisatos, C. V. Shank, *Phys. Rev. Lett.* **70**, 1014 (1993).
16. W. E. Moerner, *Science* **265**, 46 (1994).
17. J. K. Trautman, J. J. Macklin, L. E. Brus, E. Betzig, *Nature* **369**, 40 (1994).
18. A. Mews, A. Eychmüller, M. Giersig, D. Schooss, H. Weller, *J. Phys. Chem.* **98**, 934 (1994).
19. L. T. Canham, *Appl. Phys. Lett.* **57**, 1064 (1990).
20. L. E. Brus *et al.*, *J. Am. Chem. Soc.* **117**, 2915 (1995).
21. S. H. Tolbert, A. B. Herhold, C. S. Johnson, A. P. Alivisatos, *Phys. Rev. Lett.* **73**, 3266 (1994).
22. M. A. Kastner, *Rev. Mod. Phys.* **64**, 489 (1992).
23. F. R. Waugh *et al.*, *Phys. Rev. Lett.* **75**, 705 (1995).
24. X. Peng, T. Wilson, P. G. Schultz, A. P. Alivisatos, in preparation.
25. O. I. Micic *et al.*, *J. Phys. Chem.* **99**, 7754 (1995).
26. J. R. Heath, J. J. Shiang. A. P. Alivisatos, *J. Chem. Phys.* **101**, 1067 (1994).
27. W. Chen, J. M. Rehm, C. Meyers, M. I. Freedhof, G. McLendon, *Mol. Cryst. Liq. Cryst.* **252**, 79 (1994).
28. J. Lin, E. Cates, P. A. Bianconi, *J. Am. Chem. Soc.* **116**, 4738 (1994).
29. N. Herron, J. C. Calabrese, W. E. Farneth, Y. Wang, *Science* **259**, 1426 (1993).
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Magnetic Clusters in Molecular Beams, Metals, and Semiconductors

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The evolution of magnetic order from the microscopic to the macroscopic regime may be studied with the use of nanometer-scale clusters. A variety of new techniques can be employed to control the size of the magnetic clusters from the atomic level. Molecular beams are used to construct and measure the magnetic properties of isolated metallic clusters. Superparamagnetic metallic particles embedded in a metal exhibit dramatic field-dependent changes in electrical conduction, providing a measure of spin-dependent scattering. Related efforts in semiconductor hosts with the use of ion implantation have generated room-temperature ferromagnetic clusters that can be directly imaged by magnetic force microscopy.

The magnetic properties of isolated atoms are well understood, but the development of magnetic order on a macroscopic scale in a crystal is a more formidable problem. Long-range magnetic order is not simply a superposition of the effects of individual atoms; it is a collective effect of atoms communicating through the Coulomb interaction and the Pauli exclusion principle. These exchange interactions may lead to an alignment (ferromagnetism), an alternation (antiferromagnetism), or more complicated arrangements of the magnetic moments. Magnetic clusters provide a link between magnetism on the microscopic atomic level and the macroscopic state; and by allowing us to observe magnetic order as it develops from individual magnetic atoms to large crystals, such clusters can contribute to our understanding of magnetism in both regimes. Like the study of mesoscopic electronics (*1*), which may lead to more highly integrated circuits, mesoscopic magnetism is not only of academic interest but also of technological importance as magnetic recording densities continue to increase, requiring smaller bits to store information (*2*). In addition to information storage, magnetic clusters are being examined for diverse applications ranging from enhanced magnetic resonance images (*3*) to magnetic refrigeration (*4*).

A great deal of work on small magnetic particles and molecules exists (*5*). Here we describe a select set of recent developments aimed at construction and measurement of such systems in a wide variety of environments. The ideal experiment for the study of clusters would control their size with atomic precision and probe the properties of an isolated individual cluster instead of averaging over an ensemble. A close realization of this ideal is the work on clusters formed in molecular beams, which are also advantageous because there is no interaction between clusters or with a surrounding medium. However, practical applications of magnetic clusters typically require a host. Magnetic clusters may be used to affect electron conduction or optical properties of their host, and in turn the host may have an effect on the magnetic properties of the clusters. In metals, magnetic clusters can produce an unusually large dependence of the resistance on magnetic field, an effect known as "giant magnetoresistance" (GMR) and originally observed in magnetic multilayers (*6*). The change in resistance upon application of a magnetic field is as high as ~20% for Co clusters in Ag and ~50% in the Fe/Cr multilayers, which is a large change when compared with the ~1% effect that is typical in bulk magnetic metals such as iron or nickel. Magnetoresistive materials are being pursued as a promising technology for the next generation of magnetic sensors and recording read heads. The incorporation of magnetic clusters in semiconductors would allow for the integration of microelectronics with recording and storage technologies, as well as enabling spin-dependent switching. Epitaxial growth techniques using semiconductors have been remarkably successful in providing layers of near-atomic thickness for electronic and optoelectronic devices (*1*), and have included recent success in interleaving of semiconductor and magnetic multilayers (*7*). Moreover, the dilution of magnetic atoms into a semiconductor heterostructure gives rise to a variety of new phenomena that are strongly sensitive to magnetic fields (*8*). However, there are a number of technological obstacles preventing the fabrication of practical devices; most suitable magnetic ions tend to order antiferromagnetically and only at low temperatures, generating no net magnetic moment (*8*).

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