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Special Report:
Biology Goes
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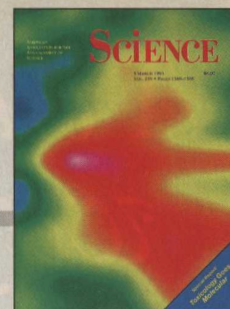
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COVER

Zonally averaged latitudinal spreading of the increase (yellow, orange, and red) in reflected shortwave radiation measured by the Earth Radiation Budget Experiment after the eruption of Mount Pinatubo in June 1991. The vertical scale is latitude from 40° S to 40° N, and the

horizontal scale is time from May to November 1991. Volcanic aerosols reflect some of the sun's energy back to space; as a result, Earth's climate is cooled. See page 1411. [Image: P. Minnis *et al.*, Atmospheric Sciences Division, NASA Langley Research Center]



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1426
A chip of a semiconductor

Indicates accompanying feature

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Crystal Structure and Optical Properties of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$, a Cluster with a 15 Angstrom CdS Core

N. Herron,* J. C. Calabrese, W. E. Farneth, Y. Wang

Recrystallization of the solid $\text{Cd}_{10}\text{S}_4(\text{SC}_6\text{H}_5)_{12}$ from a solution of pyridine and *N,N*-dimethylformamide (DMF) results in the formation of the cluster $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ as pale yellow cubes. The structure consists of an 82-atom CdS core that is a roughly spherical piece of the cubic sphalerite lattice ~ 12 angstroms in diameter. The four corners of the lattice are capped by hexagonal wurtzite-like CdS units, which results in an overall tetrahedral cluster ~ 15 angstroms in diameter. This cluster dissolves intact in tetrahydrofuran where its absorption spectrum reveals a sharp peak at 358 nanometers at room temperature and its emission spectra show a strong broad band at 500 nanometers.

The use of very small molecular clusters as synthetic precursors to bulk, extended solids interests both the physics (1) and chemistry (2) communities. In the particular case of semiconductor materials, the small clusters themselves are of interest, given that the transport and optical behaviors vary as a function of crystallite size. These phenomena have led to a whole area of research into so-called nanoclusters or quantum dots (3). In this size regime (ten to a few hundred angstroms in particle diameter), quantum effects lead to severe perturbations in electronic properties. The clusters act as examples of the quantum mechanical particle in a box (4). Although research in this area has been intense, almost all efforts have suffered from the same problem: attempts are made to relate properties to cluster size, but cluster size is crudely defined. In most cases, only a distribution of sizes is accessible because of the synthetic routes that are used to prepare such clusters (4). Although a few well-defined molecular clusters of this type do exist (5, 6), these tend to be on the small end of the size spectrum where the properties are more like those of the molecules than like those of the bulk.

We report the single-crystal structure and optical properties of a large, well-characterized semiconductor molecular cluster. It is a 15 Å diameter crystalline fragment of bulk cubic CdS with an 82-atom core. This cluster contains all of the structural features of the bulk extended solid, yet it remains soluble in organic solvents and so retains many of the attractive properties (from a characterization and processing viewpoint) of a discrete molecule.

We reported previously (7) that when the discrete molecular species $(\text{NMe}_4)_4\text{Cd}_{10}\text{S}_4(\text{SC}_6\text{H}_5)_{16}$ (5) (Me, methyl) is heated un-

der carefully controlled conditions, the material converts to bulk crystalline CdS. It does so in two distinct steps. First, at 250°C, it loses the tetramethylammonium cations and four of the thiophenolate "caps," which generates a solid, $\text{Cd}_{10}\text{S}_4(\text{SC}_6\text{H}_5)_{12}$. This step is followed by the loss, at 500°C, of the remaining phenyl groups in the form of diphenyl sulfide which leaves behind crystalline CdS. The intermediate composition, $\text{Cd}_{10}\text{S}_4(\text{SC}_6\text{H}_5)_{12}$, is a pale-yellow solid with a broad x-ray diffraction pattern that indicates very small (< 25 Å) sphalerite-phase (cubic) crystallites of CdS. However, this solid is very soluble in pyridine, and such solutions can be recrystallized by the addition of DMF to the point of incipient precipitation. Large, clear-yellow, cubic crystals formed (along with a small amount of yellow powder) during a period of several days at room temperature. The larger crystals appear to fracture when exposed to strong visible or ultraviolet (UV) light. The crystals are, therefore, routinely grown and handled under subdued lighting conditions. One such crystal was suitable for x-ray diffraction analysis.

The solution of its structure (Fig. 1A) reveals that recrystallization has led to the nucleation of a cluster with a stoichiometry of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ (8). This molecule is much larger than the original Cd_{10} cluster from which it was prepared. It appears that this cluster assembled itself from CdS/ SC_6H_5 species of various nuclearities that are in rapid exchange in the pyridine solution [^{113}Cd nuclear magnetic resonance shows broad resonances in pyridine at all of the temperatures that we measured (7)]. This cluster was apparently the least soluble species and therefore the one that preferentially crystallized. The structural details reveal that the 82-atom core is constructed from a large (~ 12 Å diameter), roughly spherical chunk of the sphalerite form of bulk CdS whose requisite "dangling" surface bonds have been terminated by wurtzite-like (hexagonal) CdS units at four tetra-

hedral corners. Thus, the cluster looks like a large tetrahedron whose points have been capped by DMF solvent molecules and is neutral in charge. The cluster core is ~ 15 Å across (from the Cd atom at the vertex of the tetrahedron to the center of the opposite tetrahedral face). All of the edges of the core are covered with phenyl rings of bridging and capping thiophenolate ligands. The structure is, in fact, a larger homolog of the large CdS cluster, $\text{Cd}_{17}\text{S}_4(\text{SC}_6\text{H}_5)_{28}^{2-}$, which was prepared by Dance and co-workers (6). It has all of the same structural features that are noted for that material (including the open clefts that run along each of the tetrahedral edges) except for (i) the capping of the Cd atoms that are at the vertices of the tetrahedron, which, in our case, is performed by DMF solvent but, in the structure of Dance and co-workers, is done by SC_6H_5^- units and (ii) the appearance of four triply bridging sulfide ions in the centers of the tetrahedral faces. At the very center of the cluster is a ten-atom fragment with the same connectivity as bulk sphalerite-phase CdS with four tetracoordinated cadmium and six tetracoordinated sulfide ions in an adamantyl arrangement.

The Cd-S bond length in this core is 2.503(4) Å (where the number in parenthesis is the error in the last digit), which is significantly less than that found for bulk CdS (2.519 Å). The individual clusters of the crystal structure interact only by means of nonbonded contact of the phenyl groups of the capping thiophenolate ligands, as depicted in the packing diagram (Fig. 1B). One fascinating aspect of the packing structure is the presence of very large intercluster voids, which is similar to what is found in zeolites. Channels ~ 8 Å in diameter provide access to large spherical cavities ~ 16 Å in diameter between the individual clusters. These spaces appear to be essentially free of adsorbed solvent molecules.

With such a well-defined molecular cluster, we examined the intrinsic optical properties of a single-sized, 15 Å quantum dot without ambiguities from size dispersion or poorly defined surfaces. On photoexcitation, the crystals emit green light at ~ 520 nm (Fig. 2A). The excitation spectrum shows absorption bands at 325 and 384 nm with a weak shoulder at 435 nm (Fig. 2A).

In pyridine solution, the optical spectra and emission properties are quite different from those of the solid and revert to the behavior of the precursor material, $\text{Cd}_{10}\text{S}_4(\text{SC}_6\text{H}_5)_{12}$, in pyridine (7); this result is consistent with the view that pyridine causes the rapid fracture of the cluster core into a dynamic mixture of species with lower nuclearities. The instability of clusters of this type in coordinating solvents such as pyridine and DMF has been well documented (5). We propose that this is a

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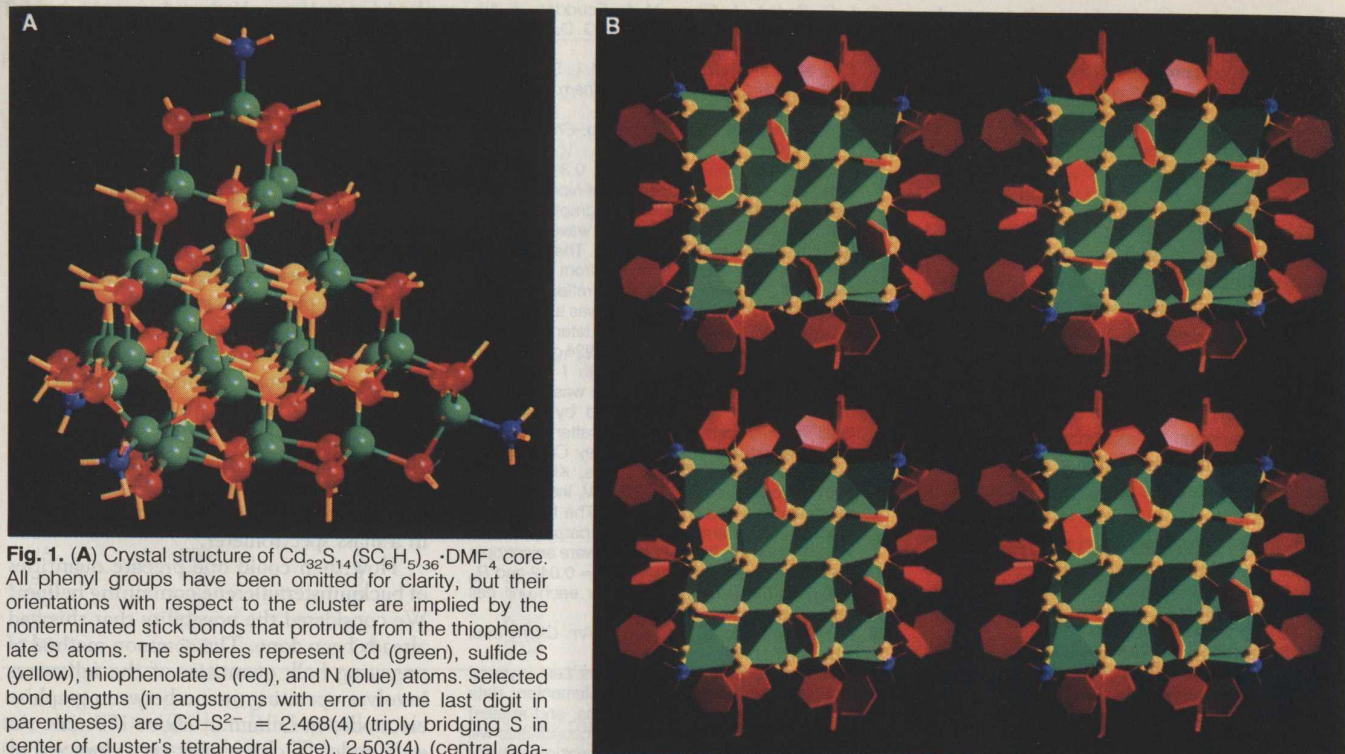


Fig. 1. (A) Crystal structure of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ core. All phenyl groups have been omitted for clarity, but their orientations with respect to the cluster are implied by the nonterminated stick bonds that protrude from the thiophenolate S atoms. The spheres represent Cd (green), sulfide S (yellow), thiophenolate S (red), and N (blue) atoms. Selected bond lengths (in angstroms with error in the last digit in parentheses) are $\text{Cd}-\text{S}^{2-} = 2.468(4)$ (triple bridging S in center of cluster's tetrahedral face), $2.503(4)$ (central adamantyl core), $2.538(8)$, $2.532(4)$, and $2.537(5)$ Å (second shell out from central core); $\text{Cd}-\text{SC}_6\text{H}_5 = 2.495(5)$, $2.569(5)$, $2.546(5)$, $2.503(5)$, $2.554(5)$, and $2.560(5)$ Å; $\text{Cd}-\text{N} = 2.33(4)$ Å. (B) Crystal packing diagram of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ that shows four molecules at the corners of a face of the unit cell. The phenyl rings have been reduced to red hexagons, and the cores of the clusters are represented by green tetrahedra that are centered on the Cd atoms and defined by the attached S (yellow) and N (blue) atoms.

result of the ability of the coordinating solvent to both compete with the surface-capping thiophenolate ligands for the metal sites and to immediately passivate dangling bonds, which arise as individual cluster bonds break and fragments detach from the cluster surface.

When the crystals are dissolved in tetrahydrofuran (THF), however (they are sparingly soluble in this, as well as DMF and acetonitrile solvents), the solution emits at ~ 500 nm (Fig. 2B). The excitation spectrum shows sharp absorption bands at 313 and 366 nm, the same as those observed in the solid crystal except that they are shifted to higher energy by ~ 18 nm. The similarity between the THF-solution and the solid-state spectra indicates that the cluster dissolves intact into this solvent and, furthermore, in the crystal there exist only weak cluster-cluster interactions, which is consistent with the cluster packing that is revealed in Fig. 1B. The $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ solid should therefore be regarded as a molecular crystal, similar to what has been found in the case of C_{60} fullerene crystals.

The lowest absorption band of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ dissolved in THF is located at 358 nm (Fig. 2C). This transition has a large absorption cross section (the extinction coefficient is $\sim 84,500 \text{ M}^{-1} \text{ cm}^{-1}$).

the effect of solvent polarity (from THF to acetonitrile), which indicates that the ground state or the corresponding excited state has a vanishingly small dipole moment. Both the large absorption cross section and the vanishing dipole moment are signatures of an ideal quantum-confined "exciton state" (4), to use a bulk semiconductor term. The possibility that this band is a result of charge transfer from cadmium to thiophenolate, which would yield a large excited-state dipole moment, can be eliminated on the basis of these data.

In spite of the large oscillator strength of the 358-nm state, the luminescence spectrum is dominated by a low-lying excited state that emits in the green (Fig. 2B). There is a very efficient relaxation process that leads to the formation of this second, lower lying excited state. Previous research on small CdS particles (9) has often revealed such an emission band that is at a much lower energy than the absorption edge. This band has usually been loosely associated with defects largely because the samples have not been sufficiently defined to permit a more definitive description. This defect concept is no longer valid for our well-defined cluster, and such an emission band must be attributable to an intrinsic excited state of the cluster. This excited state has a very low oscillator strength (be-

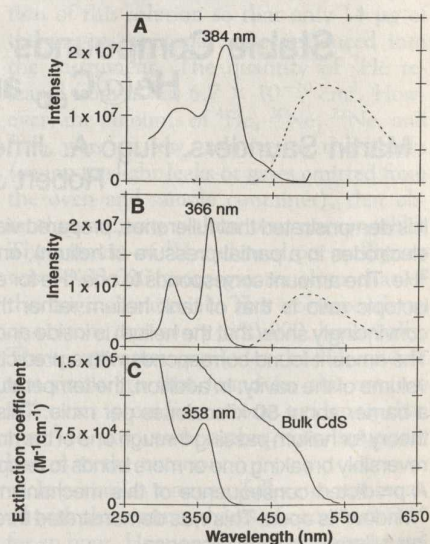


Fig. 2. (A and B) Excitation (solid line) and luminescence (dotted line) spectra of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ cluster (A) as polycrystalline solids at 6.5 K and (B) in THF at 77 K. The spectra were taken with a reflection geometry. The excitation wavelength for the emission spectra was 320 nm, and the monitoring wavelength for the excitation spectra was 520 nm. (C) Absorption spectrum of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\cdot\text{DMF}_4$ in THF at room temperature compared with the bulk CdS absorption spectrum. All three graphs were

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