

NMR Study of Semiconductor Molecular Clusters

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Three sizes of CdSe molecular clusters were studied by ^{77}Se NMR spectroscopy. The clusters are synthesized via arrested precipitation in a structured medium and are isolated as a molecular solid after modification of their surfaces with covalently attached organic ligands. While one component of the broad ^{77}Se NMR line shape corresponds to the bulk material, increasing proportions appear at shifts upfield as a function of decreasing particle size. The line positions and distribution of chemical shifts can be related to a size dependence of the electronic structure and the local chemical environments.

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In recent years, there has been much interest in the experimental study of small semiconductor particles in order to understand the photochemistry of surface reactions and the dependence of electronic properties on particle size.¹ Such studies explore the realm of quantum size effects, that is, the size-dependent nature of materials in an intermediate regime between a molecular structure and the solid state. Although optical spectroscopies allow one to observe trends with size,¹ the optical excitations are delocalized and chiefly respond to an average electronic environment of the entire particle. Because nuclear magnetic resonance (NMR) spectroscopy is sensitive to the local chemical or electronic environments of the nuclear spins, it complements the optical results as well as providing additional information.

The magnetic-field-dependent Knight-shift and chemical-shift interactions observed in NMR are measures of the local bonding, symmetry, and electronic surroundings of a nuclear species. The Knight shift is dominant in metals, and size effects in small metallic particles² are detected via the magnetic susceptibility of unpaired conduction electrons that perturb local magnetic fields at the nuclear spins, usually through the electron-nuclear contact term. Thus changes in the susceptibility, from size-dependent changes in the electronic nature of a metal particle, are expected to manifest themselves in the NMR spectrum. In nonmetallic materials, the second-order chemical-shift interaction remains and measures the nuclear interaction with local magnetic fields that arise from the influence of an applied magnetic field on the valence electrons. In this case, size effects on chemical bonding and lattice symmetry can be expected to appear in the chemical shifts.

Solutions of semiconductor particles are amenable to study by NMR in part because of the line narrowing caused by Brownian motion and the absence of a metal-support interaction. In this Letter, we discuss the results of a study of semiconductor molecular clusters terminated with organic ligands. CdSe molecular clusters were prepared by arrested precipitation in a structured medium.³ A microemulsion is prepared by our first dissolv-

ing the surfactant di(2-ethylhexyl)sulfosuccinate (AOT) in heptane (0.05M), and subsequently adding small amounts (up to $\approx 1\%$ by volume) of water. The water is dispersed by the formation of heptane-soluble, AOT-stabilized water pools (micelles). Cd^{2+} is delivered to the water pools as aqueous $\text{Cd}(\text{ClO}_4)_2$. Addition of bis(trimethylsilyl)selenium immediately forms AOT-stabilized CdSe crystallites. In order to isolate the clusters as molecular solids, two subsequent steps are included in the synthesis:³ (1) Cd^{2+} is added to produce a cadmium-rich particle surface, and (2) RSeSiMe_3 ($\text{R} = \text{phenyl}$ or butyl) is added. Modification of the particle surfaces, by encapsulation with the covalently bonded Se-R moiety, allows for isolation of the CdSe particles through precipitation, washing, and drying of the solid material. The "capped" CdSe particles can be redissolved in some organic solvents.

Three samples,¹⁻³ of differing sizes (≈ 12 , 15-18, and 30-35 Å in diameter, respectively) were prepared for study by ^{77}Se NMR. These samples were isotopically enriched with ^{77}Se to 61% in order to increase the signal-to-noise ratio of the data and to aid in interpretation of the spectra. The ^{77}Se was incorporated in the internal portion of the cluster, rather than the organoselenide ligand. The highly colored solutions contained approximately 30-50 mg of the particles dissolved in 0.25 ml of pyridine. Bulk cubic CdSe, used as a reference compound, was obtained by pyrolysis of CdSe molecular clusters.

The ^{77}Se NMR spectra were obtained on a Bruker model CXP-200 with a 7.05-T cryomagnet (57.2 MHz). Spectra were obtained by Fourier transformation of accumulated quadrature-detected free-induction decays observed after a 90° pulse. A 180° prepulse was applied prior to the 90° pulse on alternate free-induction decays in order to reduce receiver recovery effects. The ^{77}Se NMR spectra of the three sizes of cluster are shown in Fig. 1. Selenium bonded to the organic ligands appears near -800-900 ppm, outside of the frequency range shown in Fig. 1.

Immediately evident is the fact that the linewidths of

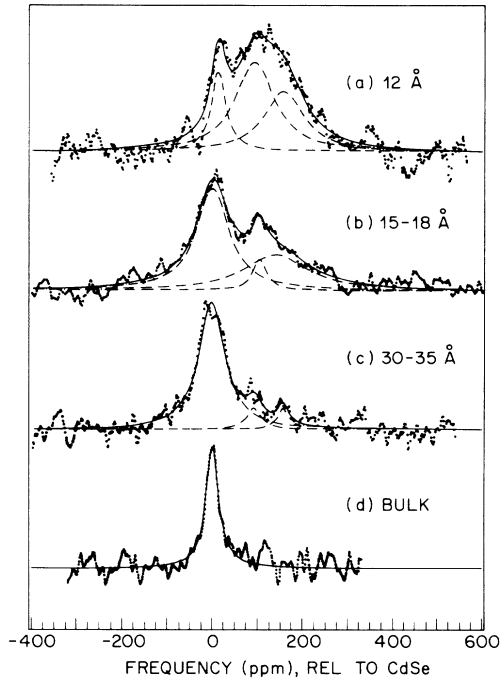


FIG. 1. ^{77}Se NMR spectra of three sizes of CdSe- R (R =phenyl, butyl) clusters in pyridine, and bulk cubic CdSe. The spectra are plotted on the σ scale for chemical shifts with negative shifts corresponding to lower field. With increasing particle size, the relative proportions of the three line-shape components change. For the largest size clusters, the intensity is shifted almost entirely towards the chemical shift of the bulk material, shown at the bottom.

the clusters in solution are even broader than the powder spectrum of the solid material. These broad line shapes can be fitted with a minimum of three Lorentzian components which have fairly consistent chemical shifts and linewidths in the three particle sizes. The chemical-shift center of the most downfield component of the broad line corresponds most nearly to that of the bulk cubic CdSe material. Smaller particles have a greater proportion of the upfield components, as reflected by the first moments of the lines: sample 1, 102 ppm; sample 2, 59 ppm; and sample 3, 16 ppm. Dance⁴ has found that the shift of four interior Cd atoms in [CdS]- R molecules (R =phenyl), containing ten Cd atoms, differs by ≈ 100 ppm from the shift of those Cd atoms on the exterior which are bound only to bridging or terminal organosulfide groups. A similar sensitivity to nearest-neighbor environment has also been observed for Se and Cd nuclei in the particles in this study.

The spectra of the particles contain some resolved features which are attributed to different portions of the particles (*vide infra*). For sample 2 (≈ 15 -18 Å) spin relaxation estimates indicate at least two components to the line shape, the downfield component with a T_1 of ≈ 28 s and the two upfield components with T_1 's of ≈ 12

s. In addition, selective inversion experiments⁵ indicate that on time scales of 0.1-1000 ms, there is no exchange between these portions of the spectrum. The spectrum of this same material taken at a lower field showed that the linewidth is proportional to the applied field. In brief, the salient features of these spectra are a distribution of chemical shifts and a greater upfield fraction of the signal intensity as particle size decreases.

To interpret the effects of particle size on the NMR spectrum, one must consider the possible contributions of the nuclear-spin interactions. Predictions for size effects observable by the NMR Knight shift are suitable only for metallic particles,² and a Knight shift is not expected in wide-gap semiconducting materials such as CdSe. Therefore, attention is focused on the chemical-shift interaction, and size effects presumably result from local changes in the nuclear electronic environment. Frequency shifts reflect the magnetic shielding or deshielding effects of induced circulating electronic charges near the nucleus.

That is, the chemical-shift interaction can be viewed as having diamagnetic, σ_d , and paramagnetic, σ_p , contributions for which the dependence on bond structure and neighboring nuclei can be estimated.⁶ Changes in the diamagnetic term are often ignored since this term is predicted to be insensitive to bonding character.^{6b} The paramagnetic contribution, although frequently viewed as a second-order effect, is expected to be larger.^{6b} Calculation of the second-order perturbation term for σ_p requires a complete knowledge of the energies and wave functions of all the electronic excited states; a closure approximation is often made in which the energy term is factored out, leaving the paramagnetic shift inversely proportional to an "average" inverse energy separation, ΔE^{-1} , of the excited-state energy levels from the ground state and proportional to ground-state matrix elements.⁶ This yields

$$\sigma_p = [-2e^2\hbar^2/3(\Delta E)m^2c^2]\langle 1/r^3 \rangle,$$

in which m is the electron mass and r is the vector from the nucleus of interest to an electron in the ground state.

If we neglect the structure within the spectra, the overall decrease in paramagnetic shift of the first moment with decreasing particle size may be rationalized as the result of the size dependence of the average ΔE and its effect on the average distribution of chemical shifts. In particles of decreasing size the relative separation of excited-state energy levels increases^{1,2} thereby increasing the denominator and decreasing the downfield paramagnetic shift characteristic of the bulk. Figure 2 illustrates this behavior through a plot of the first moment of the NMR lines versus the inverse energy corresponding to the onset of absorption in the uv-visible spectrum. For a bulk semiconductor, this energy would correspond to the band-gap energy. Descriptions of a band edge as related to a band structure may not be appropriate for the small

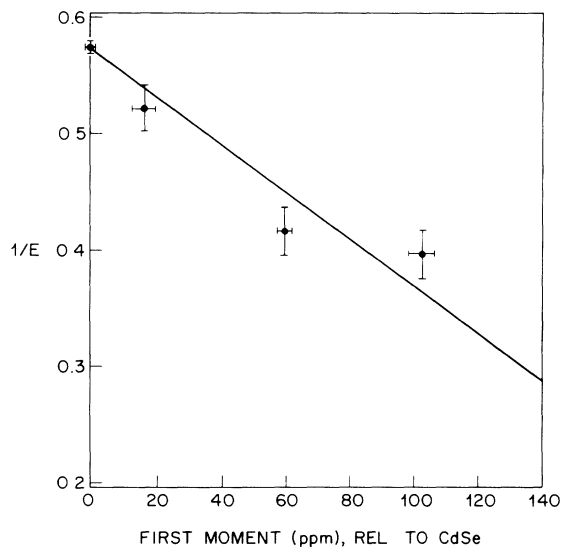


FIG. 2. Plot of the first moment of the ^{77}Se line shapes vs the inverse energy corresponding to the onset of uv-visible absorption. The straight line is a linear regression fit to the data points with an intercept near $1/E_g$ of the bulk material.

particles,^{1,2} although the absorption edge is observed to shift to higher energy and can be related to the overall shift in the energy states of the particle with size.¹ The curvature of the data in Fig. 2 may reflect the expectation that a large part of the change from ΔE of a lattice band gap towards a limiting energy separation corresponding to a particle of molecular size takes place in the range of particles examined.

Whereas the previous argument accounts for the overall shift of the center of mass of the line, it does not account for the broad line shape or any dependence on r of the electronic wave functions. Relaxation and selective inversion data seem to suggest that the components of the cluster line shape correspond to distinct sites in the particle because of different behavior with respect to exchange and relaxation phenomena, as has been seen in small metal particles.² Further support for the conclusion that the line is inhomogeneously broadened, i.e., consists of a distribution of chemical shifts, comes from the field-proportional nature of the linewidth. Additional couplings of the nuclei, such as J couplings, are expected to be small relative to the linewidth observed,^{4,7} although overlapping subpeaks might add to the breadth and/or a lack of resolution of distinct peaks in the spectra. Since x-ray and electron microscopy data indicate that the clusters have a well-defined lattice structure, one can assign the most CdSe-like chemical shift to the "bulk" of the cluster. The proportion of this material, as indicated by the integrated intensity of the corresponding chemical-shift component in the NMR spectrum, increases with increasing particle size, as would be expected.

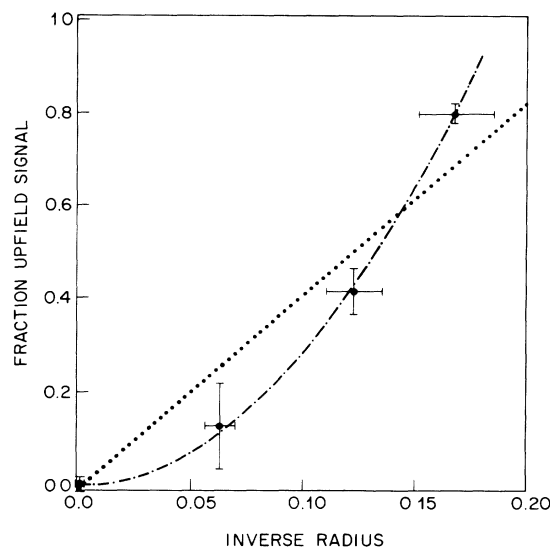


FIG. 3. Plot of $1/r$ vs the percentage of the line shape corresponding to the two upfield components. The data are fitted most closely by a $1/r^2$ dependence as given by the dashed line. The straight dotted line is a least-squares fit of the data by $1/r$.

The other components of the spectra must be attributed to another portion of the cluster with the most likely assignment being a layer near the particle surface, separate from that of the Se atoms bonded to the ligands. Other studies have suggested that the surface of a small particle may be somewhat amorphous relative to the bulk of the lattice fragment,⁸ and that there is a rearrangement of the molecular bonding to reduce the number of dangling bonds.⁹ X-ray data suggest a change in the lattice structure near the particle surface for the semiconductor particles studied.¹⁰ One can readily imagine a variety of sites, with different nearest-neighbor configurations and hybridizations, that might lead to different bonding environments and a distribution in chemical shifts.

In the case of very small particles ($\approx 10 \text{ \AA}$ or ≈ 50 atoms), almost all the atoms reside near the surface and thus there is little or no bulklike lattice.⁹ If the upfield components of the line result from a surfacelike layer, the percentage of this component would be expected to scale as the surface-to-volume ratio or $1/r$. As seen in Fig. 3, the data do not fit this functional form well. However, the data do scale with $1/r^2$. This dependence, which more nearly corresponds to a line-to-volume ratio, might be hypothesized to result from sites occurring at "edges" of the cluster at which many "faces" of the lattice intersect. Such a structure may depend on the growth characteristics of the particle, if in fact certain crystallographic faces or directions of growth are favored. From electron micrographs, the particles appear to be nearly spherical, although subtle changes in particle shape might produce an effect on chemical sites

and shifts. Because of the relatively narrow size distribution of particles indicated by electron microscopy, the spectral features observed are believed to result from changes within particles rather than the distribution of particle sizes.

These results are based upon the sensitivity of NMR to the presence of a distribution of nuclear environments. Although a definitive interpretation of the interesting appearance of the spectra as a function of particle size is not possible, the spectra most probably reflect changes in the surface morphology and possibly dependences on the overall electronic character of the particles. Peak assignments of the chemical shifts are consistent with relevant reference compounds. Further assignments of specific features of the cluster line shape will only be possible with additional experiments on model compounds.

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