Comparison of Quantum Confinement Effects on the Electronic Absorption Spectra of Direct and Indirect Gap Semiconductor Nanocrystals

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The size dependent electronic absorption spectra of CdSe nanocrystals have been measured in a diamond anvil cell. Under pressure, these nanocrystals are reversibly converted from a direct gap wurtzite structure to a rock salt structure which has an indirect gap in the bulk. It is thus possible to compare the influence of quantum confinement on direct and indirect transitions in nanocrystals of the same size. The ratio of oscillator strength between direct and indirect structures does not change with size, indicating that zero-phonon transitions are not occurring in the indirect nanocrystals.

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In semiconductors of finite size, there are pronounced quantum confinement effects on the electronic absorption spectra. Nanocrystals of the prototypical direct gap semiconductor, CdSe, exhibit the following effects: Shifts to higher energy of the onset of absorption on the order 0.5 eV [1], and the concentration of oscillator strength into just a few optical transitions [2], as the size of the nanocrystals is decreased. There is less knowledge of what happens to the optical spectra of indirect gap semiconductors in finite size, which in the bulk require phonon assistance and have much lower oscillator strengths. These issues have been brought to the fore by the observation of intense photoluminescence in porous Si [3] and Si nanocrystals [4]. Much speculation has been made about the exact nature of this luminescence, which is not observed in bulk samples of this indirect gap semiconductor [5]. The relative oscillator strength of direct and indirect gap semiconductor nanocrystals is not experimentally known. Simple confinement models [6], which should apply to both types of transitions, predict comparable shifts in energy levels derived from any highly curved region of the band structure. These same models predict concentration of oscillator strength for both zero-phonon direct gap transitions and phonon assisted (vibronically allowed) indirect gap transitions. However, zero-phonon transitions may become allowed in finite size indirect gap semiconductors due to mixing of momentum states, yielding a further enhancement in the oscillator strength of indirect versus direct gap semiconductors [7,8]. CdSe nanocrystals can be converted under pressure from direct (wurtzite) to indirect gap (rock salt) structures, providing an absolute comparison of the quantum confinement under the different selection rules.

We have chosen to study the effects of quantum confinement on the electronic absorption spectra. While luminescence is frequently used as a measure of oscillator strength in these types of systems, the results are complicated by the fact that luminescence can involve one or more highly localized states. In the case of nanocrystals, these localized states tend to originate in the crystallite surface, which can contain a large fraction of the total number of atoms in the nanocrystal. Extremely fast trapping to the surface has been observed in semiconductor nanocrystals [9], and thus surface dominated luminescence is expected. This is confirmed by the observation that chemical modification of nanocrystal surfaces can change the luminescence. Absorption, in contrast, automatically probes the interior states of the nanocrystal. Support of this conclusion comes from the fact that the relative spacings of the multiple absorption features follow simple confinement rules and the fact that chemical modification of nanocrystal surfaces is not observed to change the absorption.

CdSe nanocrystals in the wurtzite structure were synthesized chemically by a modification of the method of Murray and Bawendi [2,10]. Samples have been characterized by transmission electron microscopy (TEM), x-ray diffraction, small angle x-ray scattering (SAXS), Raman, and x-ray photoelectron spectroscopy and have been shown to be highly crystalline with narrow size distributions ($\sigma = 5\%$). Figure 1(a) (bottom) shows diffraction data obtained on an ensemble of randomly oriented 4 nm diameter wurtzite phase CdSe nanocrystals in a high pressure diamond anvil cell (DAC). The diffraction peaks are broadened only by the finite size of the nanocrystals and are consistent with nanocrystals containing less than one stacking fault per crystallite. The optical absorption spectrum of these same nanocrystals [Fig. 1(b), bottom] consists of a sharp absorption onset with multiple discrete features and is consistent with quantum confined direct gap absorption. For all high pressure diffraction and optical absorption data presented here, nanocrystal samples were homogeneously dissolved in a soft organic solvent (4-ethyl-phridine) which has been shown to be a reasonable quasihydrostatic pressure medium to pressures in excess of 10 GPa. In all cases, pressure was determined using standard ruby fluorescence techniques. Diffraction data were obtained at the Stanford Synchrotron Radiation Laboratory in an angle dispersive geometry using a Merrill-Bassett style diamond anvil cell. High pressure

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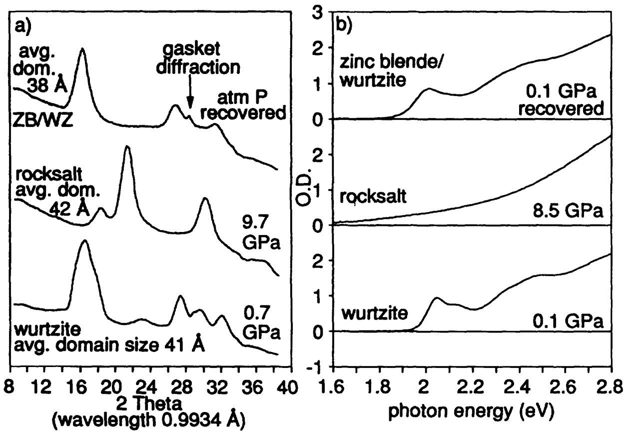

FIG. 1. (a) High pressure x-ray diffraction data obtained on 4 nm diameter CdSe nanocrystals showing forward and reverse pressure induced structural transformations. (b) High pressure optical absorption of the same 4 nm CdSe nanocrystals.

electronic absorption data were collected in a modified Mao-Bell style diamond cell. Visible absorption was obtained using a scanning Cary model 118 spectrometer. Extension of this data to the near IR (Fig. 2) was accomplished using a chopped tungsten lamp, lock-in detection, and either two germanium or two silicon diodes.

The x-ray diffraction data in Fig. 1(a) (middle) shows that under pressure the nanocrystals undergo a solid-solid phase transition. The new diffraction pattern at 9.7 GPa indexes cleanly to rock salt structure CdSe. Furthermore, the diffraction linewidths do not broaden, indicating no introduction of defects into the sample upon phase transition. Electronic absorption data obtained on rock salt phase nanocrystals at 8.5 GPa [Fig. 1(b), middle] show no discrete features in the IR or visible regions and are thus consistent with a vibronically allowed transition. The strength of the absorption near threshold is much weaker in this phase. Upon release of pressure, recovery of a direct gap, tetrahedral structure is observed in diffraction [Fig. 1(a), top]. The recovered diffraction data are consistent with a mixture of the closely related direct gap structures, zinc blende and wurtzite. The electronic spectrum also recovers its full intensity and many of the discrete features, albeit with some broadening. The recovery of discrete features upon release of pressure supports our assumption that lack of structure in the rock salt phase absorption spectrum is intrinsic and not due to inhomogeneity: Shape and surface structure variation resulting from one solid-solid phase transition should only be increased after two such transitions. Additionally, because the rock salt structure has higher symmetry than the wurtzite, the number of possible transition paths, and thus the potential for induced inhomogeneity, in going from wurtzite to rock salt is much lower than that in recovering from rock salt to zinc blende or wurtzite [11]. These effects combine to show that crystalline, homogeneous, rock salt CdSe nanocrystals can be created at high pressure and that the spectra of these nanocrystals do not exhibit discrete states.

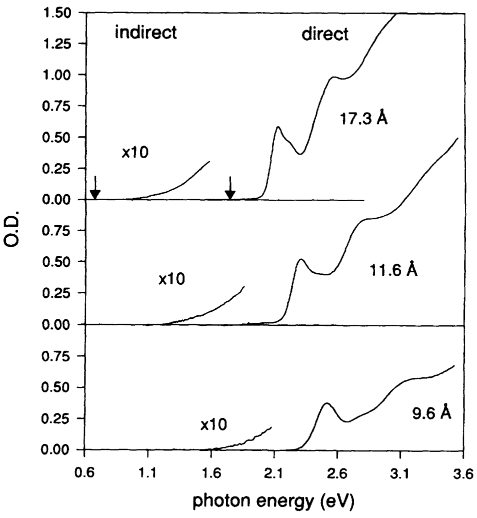

FIG. 2. Electronic absorption of 17.3, 11.6, and 9.6 Å CdSe nanocrystals in the wurtzite (atmospheric pressure) and rock salt phases (9.3 ± 5 GPa). The spectra have been normalized so that the concentration and path length in the direct and indirect gap phases are the same. Additionally, spectra have been scaled so that the integrated area under the first two absorption features in the direct gap phase are the same. Indirect gap spectra have been multiplied by 10 to improve clarity. The bulk CdSe rock salt band gap at 9 GPa and the bulk wurtzite band gap at atmospheric pressure are indicated with arrows.

Rock salt structure CdS and CdSe are indirect gap semiconductors in the bulk. This conclusion is supported by local density approximation calculations of the bulk CdSe rock salt band structure [12] which predict that this material should be an indirect gap semiconductor with an absorption onset in the near IR. Previous calculations on the related semiconductor, CdS, also show that it is indirect in the rock salt structure [13]. Two possible transitions are suggested by these calculations, from either the L or Σ point in the valence band to the X point in the conduction band. Previous experimental work [14] on bulk CdSe further substantiates the conclusion that rock salt phase CdSe has an indirect gap and places the absorption onset at 0.76 eV at 3 GPa. Finally, the absorption near threshold in rock salt CdS measured by Batlogg *et al.* [15] shows a weak, featureless indirect gap spectrum arising from a far red band gap of 1.7 eV.

"Direct" and "indirect" gap absorption spectra for three sizes of nanocrystals are shown in Fig. 2. While the wurtzite to rock salt structural transformation pressure is observed to vary with nanocrystal size, these size effects are the topic of another paper [16]. For this experiment, all rock salt phase data were collected at pressures well above the highest transition pressure, and all data were collected at approximately the same pressure

(9.3 ± 0.5 GPa). We have previously established that the compressibility of the nanocrystals in both phases is the same as the bulk and does not depend on size within the present range of sizes [11,17]. This ensures that all the rock salt spectra were collected on nanocrystals with the same bond length. We also note that the shift in the bulk indirect gap absorption with pressure is very small, ≈ -15 meV/GPa [14].

The effect of confinement on the energy of the absorption threshold in each phase in Fig. 2 can be clearly seen. More precise indirect absorption onsets were determined by extrapolating O.D.$^{1/2}$ (outer diam) versus energy to the energy intercept. These data, obtained on a wide variety of sizes, are presented in Fig. 3, plotted as confinement energy versus inverse radius squared, with the direct gap absorption data included for comparison. The data are plotted this way because the crudest model of quantum confinement predicts that the shifts will vary in proportion to the increased kinetic energy of the carriers as the "box" size is reduced. In nanocrystals, the translational momentum k is not well defined. Simple confinement theories model the electronic energy levels of a nanocrystal as superpositions of bulk electronic energy levels of differing momentum. For a given size of nanocrystal, the degree of mixing Δk is fixed. One hypothesis is that the intrinsic matrix element for absorption is unchanged in a nanocrystal, but that the density of electronic states is altered by quantum confinement. In that case, the shift in energy ΔE and the concentration of oscillator strength are *both* determined by the curvature of the bulk bands. The fact that ΔE versus size is so similar for the wurtzite and rock salt structure of CdSe (Fig. 3) means that the ratio of oscillator strength should not change as a function of size, provided the oscillator strength dependence on size arises only from this collapse of momentum states. This hypothesis is supported by the observation that the curvature at valence and conduction band extrema is similar in the wurtzite and rock salt structures [12,18]. Any additional oscillator strength changes with size, observed in the ratio of wurtzite and rock salt absorption spectra, can be assigned to changes in the matrix element for absorption, for instance, zero-phonon processes.

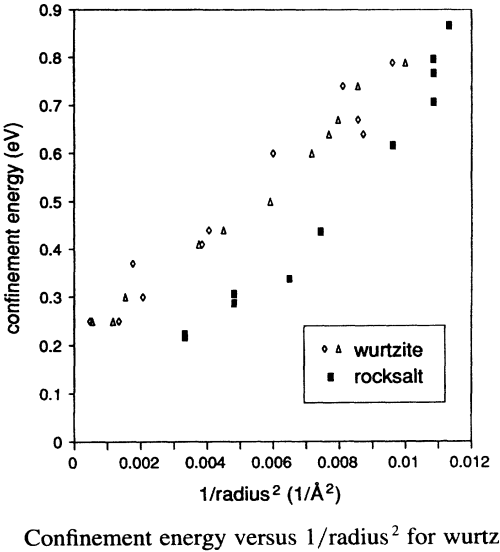

FIG. 3. Confinement energy versus 1/radius^2 for wurtzite and rock salt phase CdSe nanocrystals. Rock salt phase absorption onsets (■) are plotted relative to a bulk value of 0.67 eV at 9 GPa and room temperature [14]. Wurtzite phase nanocrystals are included for comparison. These crystallites were sized by both Tem (◇) and SAXS (△) and are plotted relative to a bulk room temperature absorption onset of 1.74 eV [22]. For the wurtzite phase, the absorption onset is assigned to the peak of the first excited state.

Figure 4 shows rock salt absorption data for five sizes of CdSe nanocrystals. The ratios of these data to the integrated area of their recovered direct gap absorption spectra have been determined. Normalization in this way allows for determination of changes in indirect gap absorption intensity relative to the direct gap intensity and accounts for gasket deformation with increasing pressure which can change the optical path length. Gasket deformation upon release of pressure is found to be small. The results show clearly that, within the precision of this experiment (±5%), no change in relative absorption intensity between the two phases is observed for nanocrystals ranging from 9.6 to 17.3 Å in radius. To the degree that quantum confinement influences oscillator strength, it has the same effect on both wurtzite and rock salt electronic transitions.

The featureless nature of the absorption spectrum and its weak intensity relative to the direct gap phase allow us to conclude that in rock salt phase CdSe nanocrystals

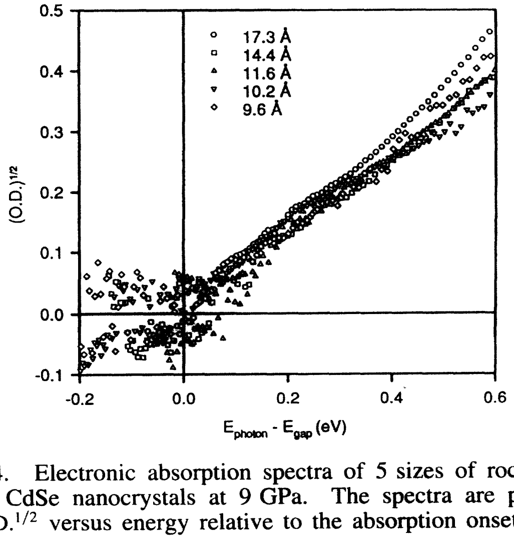

FIG. 4. Electronic absorption spectra of 5 sizes of rock salt phase CdSe nanocrystals at 9 GPa. The spectra are plotted as O.D.$^{1/2}$ versus energy relative to the absorption onset. All spectra have been scaled such that the integrated area under the first two absorption peaks in the recovered direct gap absorption is the same. Within the experimental error, no variation in the ratio of direct to indirect gap absorption intensity can be observed in sizes ranging from 17.3 to 9.6 Å in radius.

down to 9.6 Å in radius, the material is still fundamentally an indirect gap semiconductor. Further, despite the finite size, the terms direct and indirect appear to still apply, in the sense that vibrational assistance is still required in the indirect case. Increases in absorption intensity with size in the indirect gap phase due to concentration of oscillator strength can be accounted for by normalization against the direct gap phase. The possibility of a further increase in oscillator strength in these small nanocrystals of rock salt CdSe due to zero-phonon processes can be ruled out by our observations.

These experimental results are readily generalizable to nanocrystals of other indirect gap semiconductors. In most indirect materials, for example, Si, GaP, and AgBr, as well as rock salt CdSe and rock salt CdS, the change in crystal momentum required for the lowest energy transition is nearly the length of the Brillouin zone. For nanocrystals containing more than about 100 atoms, the crystal momentum mixing induced by finite size is relatively small in comparison to the change in crystal momentum required for the indirect transition and thus does not give rise to significant absorption from zero-phonon processes, as is observed in our rock salt CdSe nanocrystals. Since the amount of crystal momentum mixing depends only on the crystallite size and not the material, this result should also be true for other indirect gap nanocrystals with valence and conduction band extrema that are well separated in k space. This conclusion is shared by Wilson *et al.* [4] who used radiative rate measurements to show that zero-phonon processes do not significantly affect oscillator strength in Si nanocrystals. Experiments by Chen *et al.* [19] on AgBr nanocrystals and calculations by Hybertsen [7] and Wang and Zunger [20] on Si nanocrystals also find slow radiative rates, indicating that phonon assisted processes dominate. Further, these results show that despite the increased oscillator strength in indirect gap nanocrystals compared to the bulk, direct gap nanocrystals retain their advantage over indirect ones for optical applications where fast radiative rates are important [21].

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