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Solid State Communications 113 (2000) 189–193

solid
state
communications

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Wannier function analysis of InP nanocrystals under pressure

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Received 19 July 1999; received in revised form 1 October 1999; accepted 4 October 1999 by S.G. Louie

Abstract

The effect of quantum confinement upon the pressure induced direct to indirect interband transition in InP nanocrystals is investigated. We examine the behavior of the transition as a function of nanocrystal size. It is computed that smaller nanocrystals require less pressure to become indirect than larger nanocrystals. Our results suggest that the properties of the transition may be sensitive to nanocrystal stoichiometry. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; A. Semiconductors; D. Optical properties

Semiconductor nanocrystals provide an excellent system for exploring the physics of quantum confinement; for a review see Ref. [1]. Samples can be synthesized with well-characterized lattice structures and narrow size distributions. Optical studies of nanocrystals have yielded a wealth of spectroscopic data about nanocrystal electronic structure [2–5]. The data from these photoabsorption, photoluminescence, and photoluminescence excitation experiments have been compared thoroughly with calculations that assume the nanocrystal interior is bulk-like (and treat the surface in a simplified fashion) [6]. The agreement between experiments and these bulk derived theories is relatively satisfying in many cases, although some points of concern do exist [7]. The notion that the interior of a nanocrystal can be treated as bulk-like conveys a lot of intuition about how to manipulate nanocrystals to achieve useful new electronic structures. For example, since the application of pressure to bulk crystals can bring about well-understood changes in electronic structure, it is interesting to contemplate how these changes might be influenced by quantum confinement. A particularly intriguing case concerns the application of pressure to InP nanocrystals to cause a direct to indirect interband transition [8]. Such a transition has been observed in bulk zincblende semiconductors: as pressure is applied the energy of the conduction band state at Γ

increases and the energy of the state at X decreases (both relative to the valence band maximum) until the semiconductor becomes indirect. In the case of bulk InP, the transition from direct to indirect character is obscured since it occurs at around the same pressure as a phase change from the zincblende structure to the rocksalt structure [9]. In nanocrystal form, on the other hand, InP should become indirect at a relatively low pressure because confinement effects shift the state at Γ up in energy significantly even before any pressure is applied. In addition, it has been observed that the nanocrystal undergoes a phase change at somewhat higher pressures than the bulk crystal [10]. This suggests the remarkable possibility of seeing a transition in the nanocrystal that is difficult to see at all in a bulk crystal. In this paper, we explore this confinement-assisted change in the optical properties of InP. Our efficient Wannier function method [11,12] is employed to map out how the direct to indirect transition depends upon nanocrystal size.

In the laboratory, samples of InP nanocrystals are synthesized as colloids with passivated surfaces [13–15]. With selective precipitation, nanocrystals of differing sizes are separated from one another. This process yields nanocrystals with roughly spherical geometry (aspect ratio between 1.0 and 1.15) and size distributions of small standard deviation. Samples can, therefore, be meaningfully described giving only a typical nanocrystal diameter. In our study, we consider InP nanocrystals with a 1:1 stoichiometry of

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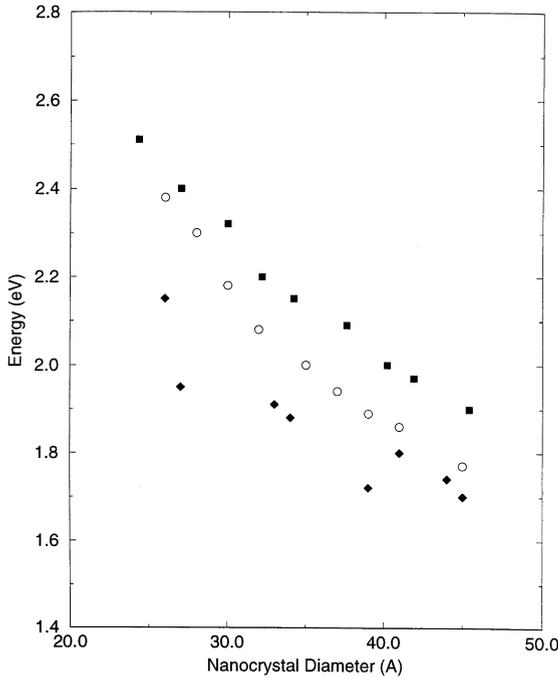


Fig. 1. Comparison between theory and experiment for InP nanocrystals. Nanocrystals are under no applied pressure. Filled diamonds and squares show experimental measurements of Refs. [9,11,12], respectively. Open circles show theoretical calculations.

In to P, which is most appropriate for direct comparison with experimental measurements [15]. By studying nanocrystals with equal numbers of In atoms and P atoms, we also complement another theoretical work [8] and provide insight into the dependence of the transition on stoichiometry.

The essentials of the Wannier function method are described in previous papers and will only be summarized here [11,12]. To compute the electronic structure of a nanocrystal, we begin with the assumption that the Hamiltonian in the nanocrystal interior is equal to the Hamiltonian of the bulk. In order to exploit this fact, we will express the nanocrystal Hamiltonian in a basis of spatially localized Wannier functions. The Wannier function $a_n(\vec{r} - \vec{R})$ is defined in terms of the Bloch functions $\psi_{n,\vec{k}}(\vec{r})$ of a bulk system as follows [16]:

$$a_n(\vec{r} - \vec{R}) \equiv \frac{1}{\sqrt{\Omega}} \int_{\text{BZ}} d^3k e^{-i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r}). \quad (1)$$

Here n is a band index, \vec{R} is a lattice vector, Ω is the volume of the first Brillouin zone (BZ), and the integral proceeds over the BZ. The function $a_n(\vec{r} - \vec{R})$ is localized about the site \vec{R} and two Wannier functions characterized by different n or \vec{R} values are orthogonal. Since the Bloch functions are energy eigenstates,

$$H_{\text{bulk}} \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r}), \quad (2)$$

it follows from definition (1) that

$$\begin{aligned} \langle a_{n,\vec{R}_i} | H_{\text{bulk}} | a_{m,\vec{R}_j} \rangle &= \int a_n^*(\vec{r} - \vec{R}_i) H_{\text{bulk}} a_m(\vec{r} - \vec{R}_j) d^3r \\ &= \delta_{m,n} \tilde{E}_n(\vec{R}_i - \vec{R}_j). \end{aligned} \quad (3)$$

In this equation,

$$\tilde{E}_n(\vec{R}) \equiv \frac{1}{\Omega} \int_{\text{BZ}} d^3k e^{i\vec{k}\cdot\vec{R}} E_n(\vec{k}) \quad (4)$$

is a kind of Fourier component of the bulk band structure. Note that the matrix elements (Eq. (3)) are block diagonal in the band index.

To model the eigenstates of a nanocrystal, we diagonalize the matrix $\langle a_{n,\vec{R}_i} | H_{\text{bulk}} | a_{m,\vec{R}_j} \rangle$ for a given band n , where the \vec{R}_i and \vec{R}_j are restricted to the nanocrystal interior. This restriction captures the quantum confinement that results from the finite size of the nanocrystal. The matrix elements are computed numerically using Eq. (4). From a computational standpoint, the Wannier function method permits us to work with a Hamiltonian matrix that is only $N \times N$, where N is the number of unit cells in the nanocrystal. This small matrix size accounts for the efficiency of the method. The method has been applied successfully in the past to both CdS and InAs nanocrystals [11,12]. In Fig. 1, we show the good agreement between our calculated fundamental gaps and experimental photoabsorption measurements for the case of InP [15,17].

To study the pressure dependence of nanocrystal electronic structure, bulk band structures appropriate for various pressures are entered into Eq. (4). These band structures are obtained in three steps. We first perform an ab initio calculation on the bulk material. We employ the local density approximation [18] and use the Ceperley–Alder interpolation formula [19] for the exchange–correlation energy. The scheme of Troullier and Martins [20] is used to generate ab initio pseudopotentials. Irreducible k -points are chosen according to the Monkhorst–Pack method [21]. Convergence is achieved with 10 k -points and a cut-off energy of 50 Ry. Second, the LDA band structure is corrected with a rigid 0.67 eV shift of the conduction band to bring the zero pressure gap into agreement with experiment. Because LDA calculations determine accurately the pressure dependence of band gaps [22], if not their absolute values, this same 0.67 eV shift can be used for all pressures.

Finally, local form factors are derived to arrive at an empirical pseudopotential method (EPM) [23] band structure that reproduces the corrected LDA conduction band structure. It is computationally undemanding to compute the integral in Eq. (4) using this EPM result. To compute the EPM band structure, six local pseudopotential form factors are required. The form factors are determined by a short range search in a six dimensional space that proceeds until an EPM band structure is found that possesses specified conduction band extremum energies. Our bulk EPM band structures are plotted in Fig. 2 along with corrected LDA

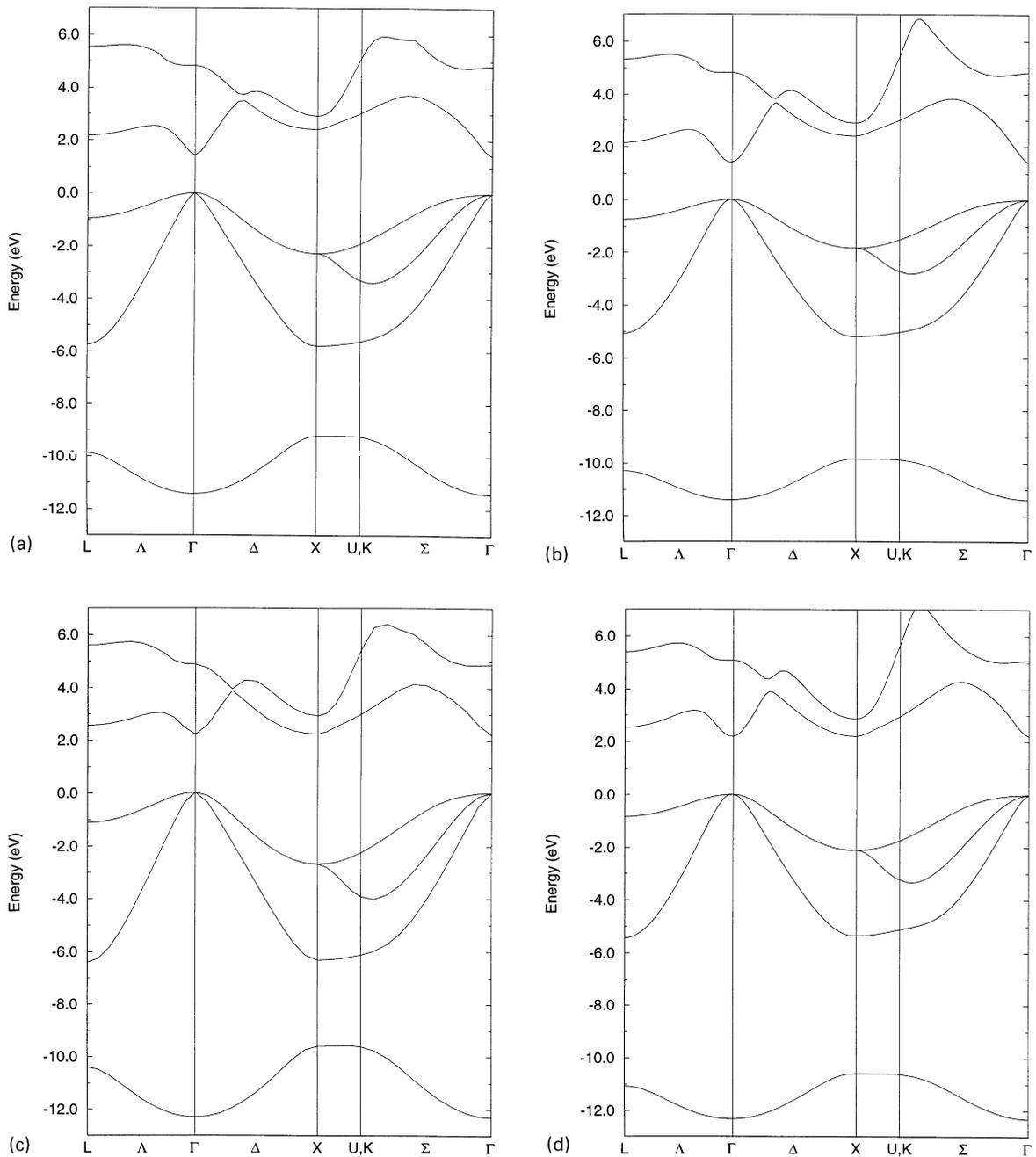


Fig. 2. (a) the corrected LDA band structure; (b) the EPM band structure at experimental lattice constant ($-\Delta a/a = 0.000$); (c) the corrected LDA band structure; and (d) the EPM band structure at computed lattice constant of direct to indirect transition ($-\Delta a/a = 0.042$). LDA band structures are corrected by rigidly shifting the conduction band upwards. EPM band structures are designed to reproduce the corrected LDA conduction bands.

band structures. Calculations are shown for zero lattice contraction and for a lattice contraction given by $-\Delta a/a = 0.04200$, at which bulk InP is computed to undergo a direct to indirect transition. This corresponds to a pressure of approximately 12.8 GPa, while one

recent experimental measurement finds the transition to occur at 11.2 GPa [9].

Once a nanocrystal eigenvector $\psi(\vec{r})$, with eigenvalue E , has been computed in a basis of Wannier functions, it is instructive to express ψ as a superposition of bulk states.

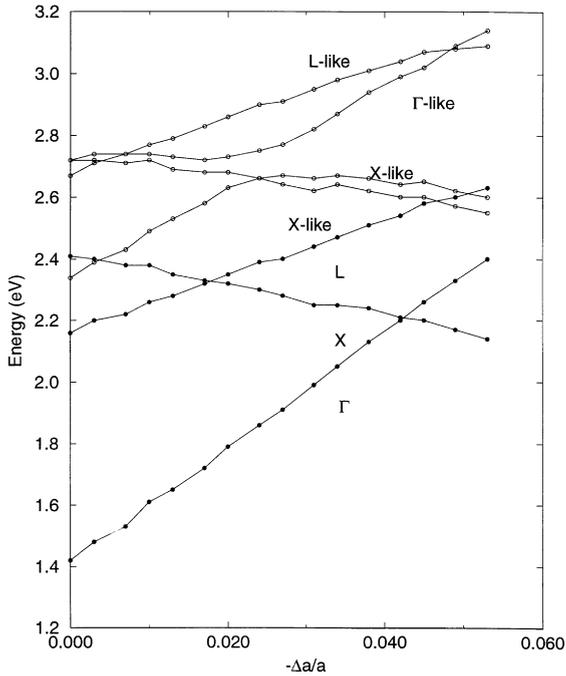


Fig. 3. Pressure dependence of unoccupied states for 27 Å diameter InP nanocrystal. Bulk state energies denoted with filled circles, nanocrystal state energies with empty circles. With the exception of some state anticrossing, confinement energy is largely independent of pressure.

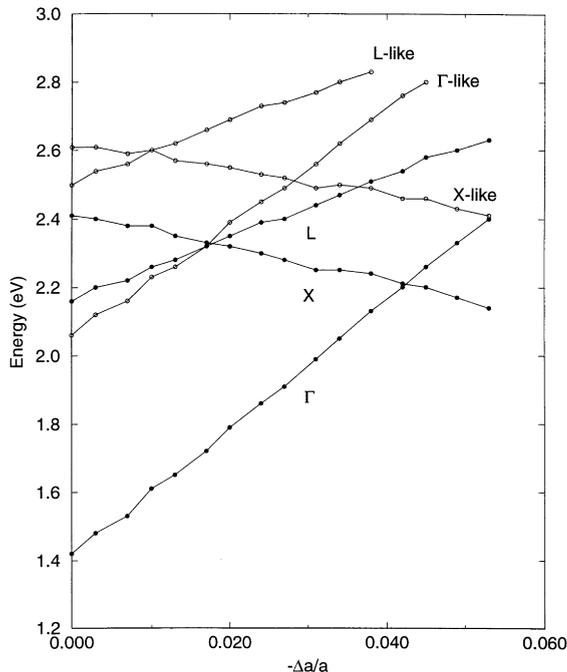


Fig. 4. Pressure dependence of unoccupied states for 37 Å diameter InP nanocrystal. Confinement energy is generally independent of pressure.

Table 1

Lattice contraction needed for direct to indirect transition in InP nanocrystals of increasing size

(InP) _n	Diameter (Å)	-Δa/a
79	20.4	0.017
135	24.3	0.020
177	27.0	0.024
225	30.0	0.025
321	32.2	0.026
369	34.2	0.027
459	37.6	0.028
603	40.2	0.029
675	41.9	0.030
887	45.4	0.031

If we desire a decomposition into Bloch states that is only valid for \vec{r} in the nanocrystal interior then $\psi(\vec{r})$ can be expressed using Bloch functions of energy E only. This is achieved by writing the eigenfunction as follows:

$$\psi(\vec{r}) = \int_{\text{BZ}} d^3k \delta(E - E_n(\vec{k})) f_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r}) \quad (5)$$

Here, $f_n(\vec{k})$ describes the amount of each Bloch wave in the function $\psi_{n,\vec{k}}$. Knowing $\psi(\vec{r})$, we compute a decomposition of the function f into spherical harmonics centered about each extremum in the band structure.

Conduction band eigenvectors, and their bulk association, are displayed for two nanocrystals in Figs. 3 and 4. The same figures show the pressure dependence of the bulk conduction band extrema at Γ , X and L. It is clear from the figures that the nanocrystal states follow bulk states as a function of pressure. In other words, the confinement energies of the nanocrystal states seem to be relatively pressure independent. The only exception to this pattern occurs when two nanocrystal states mix together in an avoided crossing. In the smaller nanocrystal, for instance, the Γ -like LUMO state mixes with an X-like state at around $\Delta a/a = -0.022$. This mixing very slightly smears and broadens the direct to indirect LUMO transition. Other calculations have found strong mixing in small nanocrystals for certain stoichiometries and no mixing for other stoichiometries [8]. It seems that the breadth of the transition depends sensitively on the details of the nanocrystal.

In Table 1, we plot the lattice contraction at which a direct to indirect transition occurs for several nanocrystal sizes. The behavior is monotonic: we find that our smaller nanocrystals have smaller Γ -X separation at zero pressure than our bigger nanocrystals and, therefore, require less lattice contraction to go indirect. Again, given the results of Ref. [8], we develop the impression that variations in stoichiometry can influence this pattern significantly.

In conclusion, we find that the confinement energies of electronic states are relatively pressure independent in InP nanocrystals. Since confinement reduces the Γ -X separation, less pressure should be required to cause a Γ -X

transition in an InP nanocrystal than in the bulk. This fact may make the direct–indirect transition more easily observable in the nanocrystal system than in the bulk case. Our calculations indicate that, for nanocrystals with equal numbers of In and P atoms, the transition pressure decreases monotonically as size decreases. Variations in nanocrystal stoichiometry may have an important impact upon these results. We note finally that this investigation of a direct to indirect transition has afforded an opportunity to test the Wannier function method in the case of an indirect semiconductor; the method has produced reasonable results with relatively little computational effort.

Acknowledgements

We thank C.J. Lee, U. Banin, A.P. Alivisatos for helpful discussions. This work was supported by National Science Foundation grant No. DMR-9520554, and the Director, Office of Energy Research, Office of Basic Energy Services, Materials Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098. A.M. acknowledges the support of a National Science Foundation Graduate Fellowship.

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