PHYSICAL REVIEW B VOLUME 60, NUMBER 3 15 JULY 1999-I

Evolution from individual to collective electron states in a dense quantum dot ensemble

M. V. Artemyev
Institute for Physico-Chemical Problems, Belarusian State University, Minsk 220080, Belarus

A. I. Bibik, L. I. Gurinovich, and S. V. Gaponenko*
Institute of Molecular and Atomic Physics, National Academy of Sciences, Minsk 220072, Belarus

U. Woggon
Physics Department, University of Dortmund, Otto-Hahn-Strasse 4, 44221 Dortmund, Germany

(Received 4 November 1998; revised manuscript received 8 February 1999)

Absorption spectrum of a quantum dot ensemble was found to exhibit a systematic modification with dot concentration from a set of discrete subbands inherent in isolated nanocrystals to a smooth band-edge absorption similar to that of bulk semiconductors. The results are interpreted in terms of an evolution from individual (localized) to collective electron states delocalized within at least a finite number of nanocrystals. The observed behavior is considered as a possible precursor of the Anderson transition in a quantum dot ensemble, i.e., a transition from localized electron states to states that are delocalized over a macroscopically large number of nanocrystals. [S0163-1829(99)01327-2]

Physics of semiconductor nanocrystals that to a large extent possess the properties of zero-dimensional solid-state objects, the so-called quantum dots, is one of the most extensively developing fields of modern condensed matter and material science. Great progress has been achieved in understanding of basic electron and optical properties of isolated, non-interacting nanocrystals.[1–6] Recent advances in the synthesis of spatially organized ensembles of nanocrystals[7–9] pose the problem of an evolution of optical and electronic properties of matter from a single quantum dot toward quantum dot solids. The latter concept proposed by Murray *et al.*[8] implies a kind of a condensed matter with spatial organization on a length scale comparable to the electron de Broglie wavelength. The basic features of dense quantum dot ensembles might be the reproduction of the features inherent in conventional solids, i.e., the formation of energy bands in a perfect lattice and coexistence of localized and delocalized electron states in disordered quantum dot structures. Although the charge transfer in quantum dot structures is being thoroughly examined in the context of novel electronic,[10] light-emitting,[11–15] and lasing devices,[16] the systematic analysis of quantum dot assemblies and superlattices in terms of an evolution from isolated nanocrystals to a quantum dot solid has not been performed to date to our knowledge. In the present paper, we report on an experimental evidence for a systematic evolution of the absorption spectrum of a quantum dot ensemble toward collective electronic states when increasing quantum dot concentration.

In the experiment, cadmium selenide nanoparticles were used whose electronic states and optical properties have been extensively examined in previous studies by various groups.[4–6,8,9] CdSe clusters were synthesized by the reaction between 10^{-2} M cadmium perchlorate and selenourea in dry pyridine at 100 °C under nitrogen flow. The reaction produces a yellow colloidal solution. The absorption spectrum of the resultant colloidal solution in pyridine consists of a number of well-resolved bands in the blue and near-UV region, which indicate the presence of highly monodisperse small-atomic CdSe clusters. Previously, similar CdSe clusters of 1.6 nm in size were synthesized by Ptatchsek *et al.*[17] The good coincidence of the number of bands and their position in the absorption spectrum of our CdSe clusters and those of Ref. 17 suggest that the structure and the size of the CdSe core is the same. The colloidal solution of CdSe clusters in pyridine is stable over weeks in the dark at room temperature. The thin films of CdSe clusters were produced by placing a drop of colloidal solution onto the quartz glass and dried at room temperature. The resultant films are flat, transparent, and crack free. If none nonvolatile components like polymers were added to the colloidal solution of CdSe clusters, the dried film consists of closely packed clusters with a minimal interparticle distance achieved. To increase the interparticle distance in the films a variable amount of polyethylene glycol (PEG) (M.W.=100 000) was added to the colloidal solution prior to the dropping. Polyethylene glycol is a well-known inert polymer that does not influence the structure and optical properties of individual CdSe clusters. We suggest that each CdSe cluster in the dried film is well surrounded by linear chains of PEG and the average interparticle distance can be calculated from the relative concentration of CdSe clusters and PEG in colloidal solution. Assuming a nearly spherical shape of CdSe clusters with 1.6-nm diameter and using the tabulated data on PEG parameters, we calculated the average interparticle distance (the wall-to-wall spacing between neighboring particles). A variation between 0 and 3.3 Å is found that corresponds to an interdot distance of approximately 6 . . . 10 Å when taking into account the presence of organic shell around a crystallite.

The optical absorption spectra of the samples investigated show a successive evolution from a clusterlike spectrum with a finite number of discrete absorption subbands to a smooth nearly structureless absorption spectrum. The absorption onset exhibits a monotonous shift towards lower energies by

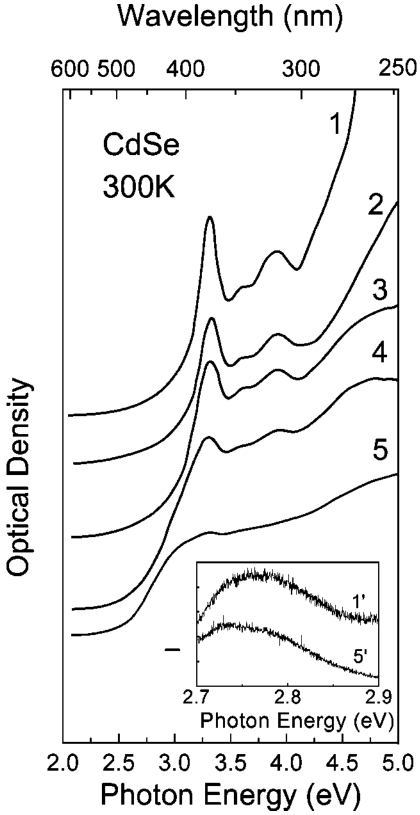

FIG. 1. A set of absorption spectra of CdSe nanoparticles, average radius is 1.6 nm. Nanoparticle concentration progressively rises up from upper to lower curves. Curve 5 corresponds to a CdSe film consisting of close-packed clusters capped with organic groups, curves 1-4 correspond to cluster/polymer composition, polymer volume fraction being 37%, 18%, 3%, 1%, respectively. The insert shows emission spectra 1′ and 5′ of the two samples whose absorption spectra represented by curves 1 and 5, respectively.

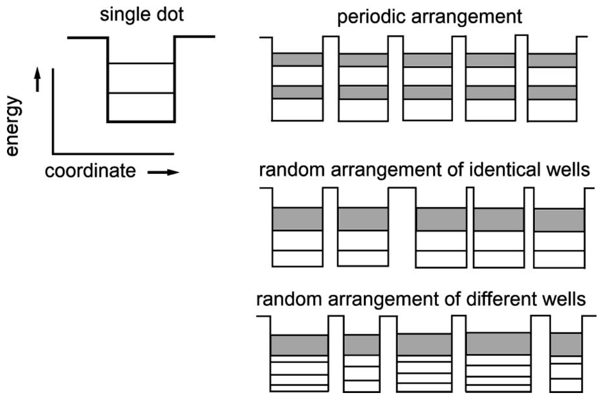

FIG. 2. A sketch of electron levels in an isolated quantum well and in periodically and randomly arranged ensembles of identical wells.

about 300 meV (Fig. 1). Along with the evolution of absorption, a steady redshift of the luminescence spectrum with concentration has been observed, the luminescence intensity exhibiting a monotonic decrease with increasing concentration (insert in Fig. 1). Concentration effects on the luminescence spectrum and intensity have been observed earlier and explained self consistently in terms of resonance energy transfer by means of dipole-dipole interaction.[9] In what follows, we shall discuss the evolution of absorption spectrum with concentration. The effect gains a reasonable explanation in terms of collective phenomena in a system of quantum dots.

Consider the evolution of the electron state of a nanocrystal from an individual to a collective state when the spatial arrangement changes from a dilute to a dense quantum dot ensemble. In the case of a perfect one-, two-, or three-dimensional periodic arrangement of identical quantum dots, one can expect a formation of minisubbands from a discrete set of electron (and hole) levels (Fig. 2). This effect is similar to the formation of minibands in a one-dimensional superlattice of quantum wells. Noteworthy, in the case of quantum dots a three-dimensional superlattice can be developed, i.e., a colloidal crystal consisting of nanocrystals. Such a superstructure has no analogy among the other nanostructures and offers, in principle, a new type of solids with a three-dimensional band structure on a superatomic scale. Because no long-range order occurs in the structures investigated, we consider electron properties of a disordered solid as a relevant example among atomic structures. In disordered solids, at certain degree of disorder a transition occurs from localized electron states to coexisting delocalized and localized ones separated by a border. With increase in concentration, delocalization occurs with respect to nearest-neighbor wells resulting in small conducting clusters involving several wells. At higher concentrations, the cluster size grows up and at certain arrangement electrical conductivity appears throughout a whole ensemble of potential wells. In physics of disordered solids the effect is known as the Anderson transition since 1958.[18] It was extensively examined in disordered solids[19,20] and is being investigated with respect to classical waves like electromagnetic and acoustic waves.[21–24] Coexisting discrete (localized) and bandlike (delocalized) states in randomly arranged wells are depicted schematically in Fig. 2. In the case of a one-dimensional system such a structure possesses localized electron states only.[20,25] Delocalization is possible in the case of higher dimensions of the system.

Basically, the above considerations remain valid for quantum dots and can explain the observed dependence of the absorption spectrum on concentration of quantum dots. A development of electron (and hole) collective states result in the appearance of a broad absorption band relevant to higher delocalized electron and lower hole states along with a few discrete absorption lines due to transitions that couple lower (localized) electron and higher hole states. However, even at high concentration of dots, the contribution to the absorption spectrum from localized states may be negligible similarly to the case of impurities in semiconductors, and a bulklike structureless absorption spectrum develops.

To verify the above consideration, we made numerical estimates using model displacement of 3375 (15^3) potential wells randomly distributed within a fragment of a cubic lattice with a period L. The aim of calculations was to estimate the number of delocalized states as a function of concentration C of nanocrystals, their radius R, and electron (hole) effective mass $m_e^*(m_h^*)$. Following Ref. 20, we considered a particle state as delocalized when the energy overlap integral is larger than the difference of energy level shifts in the nearest-neighbor wells because of the influence of all other wells within the system under consideration. Random displacement of wells was described in terms of a deviation of their coordinates with respect to nodes of a regular cubic lattice of a period L according to a Gaussian distribution. The maximal deviation value was chosen to be no larger than one half of the lattice period by means of the truncated distribution function.

Statistical analysis has been performed over 500 configurations of a quantum dot ensemble for each of several sets of parameters $\{C,R,m^*\}$. The detailed description of calculations and results for various semiconductor substances will be published elsewhere.[26] The results indicate the steady growth of delocalized electron states with increasing concentration of quantum dots. In the case of larger dots, even packing of particles up to volume fraction 0.5 does not result in a noticeable fraction of delocalized states. This result provides an explanation, why modification of absorption spectra with increasing concentration was not observed in the previous work[8] in which larger CdSe nanocrystals were examined. Taking into account presence of an organic shell in our experiments and in Ref. 8, even close-packed ensembles of larger crystallites may not satisfy the delocalization condition. Therefore, close-packed larger CdSe quantum dots reproduce rather properties of molecular solids with resonant long-range energy transfer.[9] However, for smaller dots a noticeable delocalization occurs at concentration far from close-packing, e.g., for $R\sim1$ nm, 75% of electron states were found to be delocalized at $2R/L<0.6$. This value corresponds to quantum dot volume fraction of 0.1 versus a fraction of 0.52 and 0.74 relevant to maximal fraction of close-packed solid spheres in a simple and face-centered cubic lattice, respectively. Therefore, close-packed smaller quantum dots will reproduce, to a large extent, properties of atomic solids, including not only energy and charge transfer but a formation of collective energy states.[27]

In conclusion, we observed a steady evolution of the optical absorption spectrum of a semiconductor quantum dot ensemble from discrete individual bands towards structureless band-edge behavior and put forward an interpretation of the observed evolution in terms of the systematic transition from individual to collective electron states that are delocalized within a cluster consisiting of several nanoparticles. We consider these results as a precursor for a possible Anderson transition in a quantum dot ensemble. These findings are believed to pose a number of issues related to electron properties of quantum dot superlattices like, e.g., electron band structure of a quantum dot super crystal, renormalized electron (hole) effective masses within a superstructure, modified electron-hole interaction (super exciton?) and other.

Helpful discussions with N. A. Poklonskii are acknowledged. The work has been supported in part by the Volkswagen Stiftung and INTAS research grants.

---

*Author to whom correspondence should be addresssed. Electronic address: gaponen@imaph.bas-net.by, http://imaph.bas-net.by

[1] L. E. Brus, Appl. Phys. A: Solids Surf. **53**, 465 (1991).

[2] L. Banyai and S. W. Koch, *Semiconductor Quantum Dots* (World Scientific, Singapore, 1993).

[3] C. Klingshirn, *Semiconductor Optics* (Springer, Berlin, 1995).

[4] U. Woggon, *Optical Properties of Semiconductor Quantum Dots* (Springer, Berlin, 1996).

[5] S. V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals* (Cambridge University Press, Cambridge, 1998).

[6] *Spectroscopy of Isolated and Assembled Semiconductor Nanocrystals*, edited by L. E. Brus, Al. L. Efros, and T. Itoh, special issue of J. Lumines. **70**, 1 (1996).

[7] T. Vossmeyer, G. Reck, L. Katsikas, E. T. K. Haupt, B. Schulz, and H. Weller, Science **267**, 1476 (1995).

[8] C. B. Murray, C. R. Kagan, and M. G. Bawendi, Science **270**, 1335 (1995).

[9] C. R. Kagan, C. B. Murray, M. Nirmal, and M. G. Bawendi, Phys. Rev. Lett. **76**, 1517 (1996).

[10] N. F. Johnson, J. Phys. C **7**, 965 (1995).

[11] V. Colvin, A. Schlamp, and P. Alivisatos, Nature (London) **370**, 6488 (1994).

[12] B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, and M. F. Rubner, Appl. Phys. Lett. **66**, 1316 (1995).

[13] M. V. Artemyev, V. Sperling, and U. Woggon, J. Appl. Phys. **81**, 6975 (1997).

[14] S. V. Gaponenko, E. P. Petrov, U. Woggon, O. Wind, C. Klingshirn, Y. H. Xie, I. N. Germanenko, and A. P. Stupak, J. Lumin. **70**, 364 (1996).

[15] S. Lazarouk, P. Jaguiro, S. Katsouba, G. Masini, S. La Monica, G. Maiello, and A. Ferrari, Appl. Phys. Lett. **68**, 2108 (1996).

[16] F. Gindele, R. Westpaling, U. Woggon, L. Spanhel, and V. Ptatschek, Appl. Phys. Lett. **71**, 2181 (1997).

[17] V. Ptatshek, B. Schreder, K. Herz, U. Hilbert, W. Ossau, G. Schottner, O. Rahäuser, T. Bischof, G. Lermann, A. Materny, W. Kiefer, G. Bacher, A. Forchel, D. Su, M. Giersig, G. Müller, and L. Spanhel, J. Phys. Chem. B **101**, 8898 (1997).

[18] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[19] N. F. Mott and E. A. Davis, *Electron Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1979).

[20] B. I. Shklovskii and A. L. Efros, *Electron Properties of Doped Semiconductors* (Nauka, Moscow, 1979; Springer, Berlin, 1982).

[21] S. John, in *Confined Electrons and Photons: New Physics and Applications*, edited by E. Burstein and C. Weisbuch (Plenum Press, New York, 1995), pp. 523–584.

[22] R. H. J. Kop, P. de Vries, R. Sprik, and A. Lagendijk, Phys. Rev. Lett. **79**, 4369 (1997).

[23] S. John, Phys. Rev. Lett. **58**, 2486 (1987).

[24] P. W. Anderson, Philos. Mag. B **52**, 505 (1985).

[25] I. M. Lifshitz, Usp. Fiz. Nauk **83** 617 (1964) [Sov. Phys. Usp. **7**, 549 (1964)].

[26] M. V. Artemyev, A. I. Bibik, L. I. Gurinovich, S. V. Gaponenko, and U. Woggon, in *Physics, Chemistry, and Applications of Nanostructures*, edited by V. E. Borisenko *et al.* (World Scientific, Singapore, 1999), pp. 223–228.

[27] The above consideration is qualitatively valid for metal nanoparticles as well. In the case of two-dimensional arrangement of silver quantum dots, a localization-delocalization transition has been examined in the recent paper which appeared after the present manuscript has been completed [F. Remacle, Chem. Phys. Lett. **291**, 453 (1998)].