

TRANSPORT AND PHOTOTRANSPORT IN AMORPHOUS AND NANOSTRUCTURED SEMICONDUCTORS

I. Balberg

The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

The basic physical ideas, concepts and pictures that are used for the understanding of the electronic properties of crystalline and amorphous semiconductors and their nanostructures are briefly reviewed. The emphasis is put in particular on the physical ideas that are encountered in the description of the transport and phototransport in crystalline and amorphous chalcogens and chalcogenides, and their recently developed nanostructures.

(Received June 8, 2001; accepted September 3, 2001)

Keywords: Band tails, Percolation, Tunneling, Extended states, Localized states, Mobility edge, Hopping, Quantum confinement, Resonant tunneling and Coulomb blockade

1. Introduction

The strong directed covalent bond yields solids with band separations that are of the order of an electron volt (eV), which makes them then part of the family of semiconductor materials [1]. In particular, in the solid chalcogens (S, Se and Te) the sp_z bonding-antibonding and the lone-pair p_x and p_y non-bonding orbitals yield such band separations and these are also carried over to the chalcogenides, where such and other sp covalent bonds exist [2]. The low coordination number Z in these two groups of materials has profound implications on the corresponding atomic-network structures and thus on the electronic properties of these materials. To appreciate the implication of this low Z value, let us consider [3] the constraints in a covalent network with a given Z . In such a network the bond length between two adjacent atoms is fixed and so is the bond angle between two bonds of a given atom. We have then $Z/2$ bond-length constraints and $Z(Z-1)/2$ bond-angle constraints per atom. Hence, the location of each atom in the network is determined by $Z^2/2$ constraints. Since in the three dimensional space the rigid structure is determined by three coordinates per atom, if $Z^2/2 \leq 3$ we have more degrees of freedom than constraints and thus a quasi-random network can be constructed. In contrast, if $Z > \sqrt{6}$ no random structure is possible and there may be only a few (e.g. crystalline) structures that are compatible with all the constraints. Since the low Z is a special property of the chalcogens and the chalcogenides let us examine the consequence of the above conclusion for the family of these materials. For example, in the chalcogenides the alternating $Z = 2$ and $Z = 3$ combinations enable a flat quasi-random network [2], while, for silicon ($Z = 4 > \sqrt{6}$) a diamond-like structure is enforced [1]. In the latter case any randomness can be introduced only by lifting some of the constraints of the ideal network. Indeed, we do know that in amorphous silicon the basic tetrahedral structure is conserved and it is only the long-range order that is destroyed. The latter is thus a consequence of the accumulated effect of strained bond lengths and distorted bond angles [4]. Moreover, in the latter case the removal of constraints also brings about broken (dangling) bonds. While relatively few in their number (less than 0.01% of the atoms) the effect of these dangling bonds is very significant when one considers the electronic properties of the material, as are even lower defect concentrations in crystalline semiconductors [5]. We note then that while in the amorphous chalcogens and chalcogenides, the potential fluctuations result from fluctuations in the (ring) arrangements of the atoms, i.e. the density of the atoms, in amorphous silicon they are primarily localized on the atomic-bond scale. Hence, we would expect in the former case that the potential fluctuations spectrum will be spread over a larger length, yielding a broader energy distribution of disorder-induced quantum states. In this sense the amorphous chalcogenides provide an experimental system that is closer to the ideal picture of a disordered semiconductor with a monotonic continuous

distribution of states. In view of these considerations we will limit our discussion to this type of a disordered semiconductor, and use it to review briefly the concepts of bands, band-tails, extended states, localization, mobility gap and hopping. The fact, then, that the chalcogenides are the natural test grounds for experimental checks of the corresponding physical ideas, as well as the fact that they can yield significant applications, such as xerography [2] and switching [6], makes the latter an exciting systems to study from both the basic-physics and practical-applications points of view.

Recently, the science of semiconductors became more and more concerned with the special properties of artificial nanostructures that are based on the traditional single-phase semiconductor materials. Such are the quantum wells [7], the quantum wires [8] and the quantum dots [9]. The success in the understanding and applications of various crystalline [7-9] as well as amorphous [10] nanostructures in general, and recently on chalcogens and chalcogenides [11,12] in particular, suggests that interesting effects may be found and understood in the latter structures. This is because of their structural flexibility and the rich phenomena that can result from the combination of their properties in the crystalline and amorphous phases.

The purpose of this paper is to review then, from the electronic point of view, the main ideas in the understanding of crystalline, amorphous and nanostructured semiconductors. In view of the limited space allocated for this review, we confine ourselves to qualitative-intuitive pictures of the current understanding of the electronic structure and the electrical transport of semiconductors and their nanostructures. We will try to introduce the relevant, rather general, concepts from the point of view of the chalcogenides in order to facilitate their grasp by researchers of these materials. Also, we will show how the understanding of the above systems can be derived by analogies with, and extrapolations of, other, much more familiar systems. In particular, we will show that the concepts of tunneling and percolation are the keys to our understanding of amorphous and nanostructured semiconductors. For the interested reader we provide a list of text-books and references in which experimental data, mathematical details and illuminating discussions are given.

We start our review in Sec. 2 by considering briefly the physical picture that explains intuitively the electronic properties of crystalline semiconductors. Then, in Sec. 3, we describe how these properties are varied when we turn to the chalcogenide-like, ideal, disordered semiconductors, and we bring the new concepts that were found necessary for an adequate description of these systems. Following the recent interest and success in the understanding of nanostructures in general and the potential of their construction from chalcogenides in particular, we review in Sec. 4 the fundamental ideas in the description of the electronic structure and transport properties of semiconductor nanostructures. The conclusions of this review will be given in Sec. 5.

2. Concepts in the theory of crystalline semiconductors

Since in the picture of the electronic properties of a solid we consider electrons that are present in an “infinite” block, the bulk, the simplest quantum picture that we can attribute to an electron is that of a free electron. Such an electron is characterized by its quantum momentum $\hbar\mathbf{k}$ where $\mathbf{k}$ is its wave-vector that is associated with a wavelength $\lambda = 2\pi/k$, where $k = |\mathbf{k}|$. If the electron has a kinetic energy $E(\mathbf{k})$ that is higher than the potential undulations on the atomic scale, the above free electron picture can be used with the potential undulations treated as a perturbation [13]. The perturbation in a crystal, i.e. when the potential is periodic, implies a periodicity of the electronic wave function throughout the bulk so that the macroscopic cyclic boundary conditions can be applied naturally. Expressing these conditions by the lattice constant yields that there are as many allowed wave-vectors (or allowed states) as there are unit cells, in the bulk. Considering the fact that the energies of interest are of the order of an eV and that the lattice constant is of the order of an angström, we can consider the energy distribution of the density of states $g(E)$ in a macroscopic crystal to be quasicontinuous. The second observation is that the wave function of the electron is determined by the propagation and reflection of a free electron-like wave as it travels “above” the potential undulations. This yields strong interference effects as one can find in the nearly free electron-like model [13] and in the Kronig-Penny model [7]. The destructive interference of the electron waves when its wavelength matches the periodicity of the crystal lattice yields then forbidden quantum states that are known as the edges of the Brillouin zone. These states interrupt the quasi

continuous, $E(\mathbf{k}) = \hbar^2 k^2 / 2m$ spectrum of states, yielding gaps in the state distribution. The size of the gaps is determined by the magnitude of the periodic potential. Here $\hbar (=h/2\pi)$ is Planck's constant and m is the free electron mass. The quasicontinuous distribution of states between the energy gaps are known as the allowed energy bands, and thus the energy ranges or forbidden quantum states are known as the bandgaps. It is obvious then that the smaller the magnitude of the potential undulations compared with $E(\mathbf{k})$ the smaller will be its effect on the free electron-like state distribution. In particular, we note in passing, that if the low-amplitude potential is not periodic, the number of allowed states is not expected to change and $g(E)$ will be very much the same as the one that is determined by the above given $E(\mathbf{k})$ dependence. On the other hand the absence of "exact" interference conditions under non-periodic conditions will not yield forbidden states in the entire bulk, and thus no bandgap in $g(E)$ is to be, a priori, expected.

When we "introduce" electrons into the solid, the allowed states are filled according to the Fermi-Dirac statistics that follows the Pauli principle. In particular, if the number of electrons in the last non-empty band is less (but not negligible) in comparison with the number of states, $2N$ (where N is the number of unit cells), we have a metal and we call the highest occupied state, the Fermi level, E_F . If there are only fully occupied and fully empty bands the material is an insulator. In the particular case of an insulator with a small band gap, i.e. of the order of an eV or less, the material is known as a semiconductor. One particular property of semiconductors is that at room temperature it is possible to have thermally excited electrons in the (zero-temperature electron-empty) "conduction band" and thermally excited (left behind) holes in the "valence band". The above definition of E_F does not hold in this case. However a very simple generalization of it, i.e. that it is the energy level at which the occupation probability is $1/2$, can be carried over to the semiconductor case. The naming of a material, as an insulator, is compatible with the above picture of the electronic structure since an externally applied electric field cannot shift the distribution of the electron velocities, as all the $\mathbf{k}$ -states in the last electron-occupied band are already filled. In contrast, in a semiconductor at a finite temperature, thermal excitation (interband or from a dopant) of some electrons and/or holes is possible and they can move (due to the availability of empty states) in their respective bands.

While the above brief description is helpful for the introduction of some concepts of the theory of the electronic structure of solids, it does not give a clue as to the calculation of the band structures, i.e. the $E(\mathbf{k})$ dependence, in real solids. The latter is determined by the particular geometry of the structure, the special character of the atoms and, in covalent materials, the nature of the bonds. This is in particular important for semiconductor materials, where (in contrast to, say, alkali metals) the energy of the charge carriers is of the order of the amplitude of the potential undulations [5].

The breakthrough in solving the above problem in crystalline solids was made by the suggestion of Bloch that the wave function of the electron in the crystal can be presented by the product of the free electron wave function and a function that has the periodicity of the lattice [13]. While this appears at first sight as a technical tool, the Bloch theorem had far-reaching consequences on the understanding of the electronic properties of solids, beyond the above-sketched nearly free electron-like picture. First, it suggests that $\mathbf{k}$ is always a "good quantum number in a crystalline solid" i.e. that regardless of the details of the system, the essence of the above free electron-like picture is always valid in crystals. All the specific features of a system are enclosed however in the $E(\mathbf{k})$ dependence and an electron can be considered free except for having an $E(\mathbf{k})$ -defined effective mass m^* . This quantity contains the resultant effect of the lattice interactions so that m^* replaces the free electron mass m and plays then the same role as m in the electron dynamics. In particular, for semiconductors [5], where one is interested in the few carriers around the extremas of the $E(\mathbf{k})$ function the nearly free electron picture applies and all the electrons (and similarly all the holes) have practically the same m^* .

The fact that $\mathbf{k}$ is a "good quantum number" in a periodic lattice gives us also an intuitive insight as to the motion of an electron in such a lattice. One can think then on a corresponding analogous picture as follows. Suppose there is a car moving on a straight road with periodic intersections, the traffic though which is controlled by traffic lights. If the traffic lights are synchronized, the driver can program the car to go at a fixed speed such that, on the one hand, the car does not stop at intersections, but on the other hand the driver will not be able to choose his speed, which is predetermined by the road (i.e. the $E(\mathbf{k})$) conditions. In a crystal this means that on the macroscopic scale the electron moves with a constant-like velocity and that, when an electric field is

applied, the response of the electron will be determined by its effective mass. We see then that the concepts of $\mathbf{k}$ and m^* are very helpful in describing both the electronic states structure and the adoption of the classical picture of transport. In particular, the conservation of the crystal momentum $\hbar\mathbf{k}$ in optical and electrical interactions enables a classical analysis of the corresponding processes in crystals.

For the transport in the real crystal [13] we note that the main perturbation to the exact periodicity comes from the thermally induced vibrations of the lattice that can be described as quantum mechanical particles. These phonons, have an energy $\hbar\omega$ and momentum $\hbar\mathbf{k}$, where ω is the corresponding vibration frequency and $2\pi/|\mathbf{k}|$ is their wave length. The conservation of energy and momentum can be used then as in the corresponding classical picture. When one considers the contribution of all the electrons one finds an average scattering time τ_s and correspondingly one can compress all the information concerning the transport into an effective mobility, $\mu = q\tau_s/m^*$ where q is the electronic charge. When the main interaction is with phonons, the concentration of which increases with the temperature T , the value of τ_s is expected to decrease with increasing T . In semiconductors where the velocity is proportional to $T^{1/2}$ this yields that $\mu \propto \tau_s \propto T^{-3/2}$.

Since the electrical conductivity σ is determined by μ and the carrier (say, the electron) concentration n , i.e. by $\sigma = q\mu n$, we must, in the case of a semiconductor, where carriers are thermally excited into the bands, consider the $n(T)$ dependence. We note that at very low temperatures (shallow defect ionization) $n(T) \propto \exp(-E_a/k_B T)$ where k_B is the Boltzmann constant, and E_a , the activation energy, is the corresponding ionization energy. At high temperatures (band to band excitations) $n(T) \propto \exp(-E_g/2k_B T)$ where E_g is the forbidden-gap energy. Only in the intermediate temperature range of complete defect ionization (well known as the extrinsic regime) n may be considered to be a constant.

Of course the carrier concentration in a semiconductor can be increased by optical excitation, primarily from the valence band to the conduction band. This creates electrons-hole pairs that are responsible for the well-known phenomenon of photoconductivity [14]. The corresponding steady state that results is determined by the balance between the generation rate of the charge carriers, G , and the corresponding recombination rate. For commonly applied illumination intensities the main recombination processes take place in the defects that exist within the (otherwise forbidden) band gap. The concentration of the excess, optically excited carriers n_{op} is presented via the concept of the recombination (or life) time τ_r . This quantity is defined by the measurable ratio of n_{op}/G . The microscopic parameters that determine τ_r via the relation $\tau_r = 1/P_t C_t$ are the concentration of the available trapping defects P_t and their capture coefficient C_t that is determined by the special characteristics of the defect. In general, both P_t and C_t depend on the energy of the defect [14], E_t , the temperature [15] and the position of E_F [16]. In particular, we note that under a given E_F and T , the thermal release rate from E_t competes with the recombination rate of the carriers of the other type that originate from the other band. The energy, E_D , above which (for electrons) the thermal emission dominates the recombination, is known as the demarcation line. States for which $E_t > E_D$ are called trapping centers and states for which $E_t < E_D$ are called recombination centers. It is generally assumed that the mobility of the optically excited carriers is the same as that of the thermally excited carriers and thus the photoconductivity is given by $\sigma_{ph} = q\mu n_{op}$.

3. Electronic properties of disordered semiconductors

The relatively simple picture and concepts sketched in Sec. 1 cannot be carried over as such to the disordered semiconductors because of the loss of translational symmetry. The importance of this loss is that the resultant interference of the free carrier-like wave is not the same at the various unit cells. In particular, if a $\mathbf{k}$ value is assigned to an electronic waves there will not be a particular $\mathbf{k}$ value for which a total destructive interference will be found, and consequently there will be no forbidden states throughout the solid. Similarly, a relation such as $E(\mathbf{k})$ is not well defined since different amounts of interference may yield different energy levels in the solid for an a priori assumed value of $\mathbf{k}$. Hence, one cannot describe the electron interactions by E - $\mathbf{k}$ conservation laws. The great advantages of having the concept of crystal momentum as introduced by Bloch are lost then and we usually summarize all these facts by saying that $\mathbf{k}$ is no more a “good quantum number”. How can we

picture then the, conceptually new, situation encountered in the disordered solids? In what follows we present the simplest picture, mainly due to Anderson and Mott [2,17], for the description of the electronic properties of a disordered solid. For that purpose let us introduce first the concepts that enabled to suggest such a picture for disordered semiconductors.

We start then by returning to the pre-Bloch area with the nearly free electron model. We recall that this model is based on the assumption that the amplitude of the potential undulations in the solid is much smaller than the kinetic energy of the electron [13]. Under these conditions the fact that the potential is not periodic should have little effect on the free-electron-like nature for quantum states that are allowed (in the corresponding crystals), i.e. for states for which no exact destructive interference occurs. We may conclude then that for energies and states “deep” in the bands of the corresponding solid the features of the free-electron-like states, will be similar to those in the crystalline solid, in spite of the fact that $\mathbf{k}$ is no more a “good quantum number”. We can call such states band-like states. These considerations suggest, for example, that there will not be much difference between a crystalline alkaline-metal and its “amorphous” counterpart if such would exist. However, while setting the stage, the above conclusion is not too helpful for the consideration of semiconductors, where the states of interest are precisely those that (in the crystalline counterparts) lie at, or close to, the band edges. This is since the energies involved there are of the order of the potential undulation. While bearing the above consideration in mind, we see that we have to start our discussion from a different point of view. The easiest choice is to take the other extreme, i.e. the electronic states in the space-limited atomic orbitals.

The point of view we take then is that of atomic orbitals and/or bond orbitals in a covalent semiconductor. We start by adopting the N fold degeneracy of the atomic orbital within the solid (as we have for the crystalline bands) and the lifting of this degeneracy by the interaction with the other atoms [1]. These effects can simply be considered as quasicontinuous splitting of the atomic or covalent bond levels, as the inter-atomic distance is decreased, into bands [15]. Again, as in the above metallic picture, this point of view enables us to conclude that the existence of a band of allowed states is independent of the order within the structure of the solid. As the atoms come close together, the bands may even overlap and consequently split in two [1,5]. However, for disordered semiconductors, in view of the above discussion, the effect of the disorder will be important at energies around the levels that were band edges in the crystalline counterparts. We conclude then that the gross features of the band structure will be similar in the crystalline and the disordered semiconductors, and that the main difference is that in the latter systems the “edges” will be “blurred”. Correspondingly, the common quantity by which we can describe the electronic structure of both types of solids is the density of states (DOS) distribution function $g(E)$. What we concluded already then is that in the disordered case $g(E)$ will have a broad maximum (rather than peaks that are due to well defined interference effects in the crystalline phase) and a broad minimum. The maximum will be found in the energy interval where, in the crystalline counterpart, there was the center-of-band maximum of $g(E)$, and the minimum will be found in the energy interval where there was a “band” of forbidden states (i.e. the band gap where $g(E) = 0$). From the conservation of the number of states and the above discussion we would expect then that $g(E)$ between two bands that originate from two different “atomic” (or bond) orbitals, will be relatively low. We call then the region of finite $g(E)$ in the amorphous phase, in which we had $g(E) = 0$ in the crystalline counterpart, the pseudogap. Since the band edges and band gap are the more interesting regimes of $g(E)$ in the crystalline semiconductors it is natural that we will be mainly interested in the regions of relatively low $g(E)$ when we discuss amorphous semiconductors.

For a more quantitative evaluation of the shape of $g(E)$ in the above mentioned regions we can use the following considerations. In a disordered covalent network in which $Z^2 \geq 6$ (such as amorphous silicon) the disorder is manifested by stretched bonds or distorted bond-angles. In this case we may see the amorphous structure as a topologically distorted crystalline structure and think of the local potential fluctuation as we think of the potential of an impurity in a crystal. This approach suggests that we will have now states that lie in the energy interval that was forbidden in the crystalline state. In particular, since there are no new atoms introduced by the disorder there will be an “immigration” of states from the bands of the crystalline phase into the pseudo gap. The larger the distortion of the bond the larger will be the local potential fluctuation and thus the deeper (i.e. towards the mid-pseudogap) will lie the corresponding state. On the other hand, we expect that the larger the

concentration of the potential fluctuations the larger will be $g(E)$ in the region for which $g(E)$ was zero in the pseudogap. We further expect that the probability for having a distortion is smaller, the larger the distortion. Hence, fewer larger distortions and fewer deeper states are expected. This consideration suggests that there will be a decay of $g(E)$ from the pseudogap edges towards the center of the pseudogap. Similar considerations apply for the random-like (topologically different) structures such as the structure of the chalcogens and the chalcogenides, for which $6 \geq Z^2$. This is since the concentration of the structural deviations from the crystalline (e.g. honeycomb decorated) structure to larger or smaller atom-membered rings will decrease [2]. Hence, in this case, we also expect that $g(E)$ will decrease from the pseudogap edges to the pseudogap center. In fact in the chalcogenides we have, in addition to the topological disorder, a chemical disorder that may induce even larger potential fluctuations. Correspondingly, the value of $g(E)$ around midgap is expected to be larger than in chalcogens or in the tetrahedrally-bonded semiconductors [18]. This, rather general, decrease of the function $g(E)$ towards the center of the pseudogap makes the states distribution in the pseudogap look like “tails” of the states distribution in the bands. We thus call these DOS tails the band tails. The natural expectation from the above argument is that the tails will be characterized by an exponential decrease of the form (for the conduction band tail) of $g_c = g_{co} \exp[-(E_c - E)/E_{co}]$ where E_c is the conduction band-edge, g_{co} is roughly the density of states in the $k_B T$ interval at the conduction band edge of the pseudogap and E_{co} is the “width” of the tail [19]. Of course the blurring of $g(E)$ around the pseudogap edges and the conservation of states suggest that g_{co} is somewhat lower than the corresponding value in the crystalline counterpart. This value is usually taken then to be of the order of $10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$ [4], suggesting that the total concentration of band tail states is only about one thousand's of the band-like states in the disordered semiconductor. However, as we know for crystalline semiconductors, this is a huge number when one considers the possible contribution of the defects to the concentration of the charge transporting carriers in a semiconductor. We also note in passing that the exponential dependence of $g(E)$ is not universal, and $g(E)$ can be different depending on the particular energy distribution of the potential fluctuation in the amorphous semiconductor [20].

From the above discussion we saw that the overall picture and the density of states concepts are basically similar to those used for the crystalline materials, but now we have a “pseudo gap”, i.e. a region of a relatively small, but not negligible, DOS. On the other hand, the above discussion did not yield a characterization of the states as we had in the crystalline case, where we were able to characterize a state by its $\mathbf{k}$ vector. To do that let us recall that we have already concluded that deep in the bands the nature of the states should be very similar to that in the crystal since they are effected weakly by the potential undulations in the solid. This is obvious both classically and quantum mechanically, and can be well formulated by the nearly free electron model. Correspondingly we call these states band-like states. In contrast, for states deep in the pseudogap their energy is relatively low, in comparison with the features of the potential undulations, as are impurities in crystalline semiconductors. Again, both classically and quantum mechanically we would expect the electrons in these states to be limited in the spatial extent to the scale of the corresponding potential fluctuations around their location. We can, however, quantum mechanically, refine the distinction between the band-like states and the spatially limited states by noting that for the higher energies in the pseudogap quantum mechanical tunneling can enable diffusion in the lattice even when the electrons energy is lower than the features of the surrounding potential. For these states conduction can take place in a path that is classically forbidden for percolation but is allowed for “quantum mechanical” percolation [2]. This process can be described as follows. If the spatially limited equal energy states are separated in space on a scale much larger than the fluctuation confining range their tunneling probability is so small that in practice they can be assumed to be localized within the scale of the limiting fluctuation. Such states are known as localized states [17]. If however, the spatial separation of these states is small enough to enable significant tunneling between them, a continuous percolation path can form. We call these types of states extended states. Quantum mechanically we have then that as the state energy is increased from the center of the “pseudogap” towards the center of the bands the character of the states will change from localized to extended to band-like.

As pointed out above, for semiconductors the interesting states are those of the energy range in the transition between localized and extended states. This is since we know that the transport in crystalline semiconductors is taking place at the “band edges”, i.e. it is expected to be somewhere in the bandtails of the disordered material. This rather more delicate, then the above rather course,

characterization of the corresponding types of states, was given by Anderson. His approach, that relies on the percolation-diffusion and quantum mechanical tunneling concepts can be presented [2,21] in the following qualitative way. We know that in the quantum theory of solids the width of the band, B , accounts for the overlap of the wave functions of two atoms in the solid. Hence, the larger the value of B , i.e. the larger the overlap of the atomic wave-functions of a given pair of atoms, the larger the tunneling probability between them. We have also mentioned above that the larger the spread in the potential fluctuations, W , the broader will be the width of the tail. Correspondingly, the larger the W the farther will be the distance between two states of the same E . Recognizing the “equal E requirement” for tunneling between two sites, the larger the W/B the lower the probability for tunneling and then for the quantum diffusion of an electron throughout the disordered solid. It is obvious also that the larger the value of E , the larger is $g(E)$ and thus the larger the probability for the delocalization of the electrons. What is not obvious is how sharp in this delocalization transition with the increase of E . A simple picture that is helpful in considering this question is the percolation picture. We assume that two sites in the solid are connected if B is large enough to yield the requested overlap of the wave functions for an electron to belong to both of them, as in the crystalline solid. For low $g(E)$ there will be only few such states and the average spatial distance between them will be too large to enable the above requested overlap. With the increase of E there will be more and more pairs and then clusters of “tunneling connected sites”. As E is further increased there will be an energy E_c' at which a macroscopic-percolative path of “connected site” will be formed, and the “quantum diffusion” will rise abruptly from zero to a finite value. This energy is known as the conduction band mobility edge [17]. Similarly, we have for the holes the valence band mobility edge E_v' , and the energy range between E_v' and E_c' is correspondingly known as the mobility gap. As is apparent from its definition this gap differs from the optical (and the same mobility) gap in the crystalline semiconductor. On the other hand considering the exponential decay of $g(E)$ towards the center of the pseudogap we do not expect the respective gaps in the two systems to differ too much, on the energy gap scale.

Let us turn now to the expected transport processes in the extended states and in the (finite temperature possible) localized states. Starting with the extended states we can go back to the pre-Bloch concepts of diffusive transport interrupted by scatterers, as in the Drude-model [4], except that we do not consider the interaction with atoms or lattice vibration, but rather, we assume that the dominant scattering is by potential fluctuations. This (much more) effective scattering and the low mobility that results can be accounted for by considering the Einstein relation between mobility and diffusion [22]. In particular, in the limit of potential fluctuations on the inter-atomic distance scale a , we expect that the diffusion (random-walk scattering) process [23] will yield a mobility that is given by $\mu_e = (qa^2v)/(6k_B T)$, where v is the “nearest neighbor hopping probability” (which is proportional to the quantum transfer probability between neighboring atoms). Since μ_e is also the mobility in the lowest lying extended state this μ_e is also expected to be the mobility just above the mobility edge, E_c' . Considering the fact that we are dealing with a semiconductor, the concentration of carriers at E_c' is expected to be given by $n_c' = N_c' \exp[-(E_c' - E_F)/k_B T]$, where N_c' is the effective DOS at the mobility edge ($\approx g(E_c')k_B T$). The electrical conductivity will be given then by $\sigma = q\mu_e n_c'$.

Turning to the localized states, our previous discussion shows that at $T = 0$ there will be no conduction between localized states [2,17]. However, at finite temperatures, the restriction of equal-energy tunneling is eased, since phonons may provide the difference in energy between two states that are within the above overlap-distance, thus enabling tunneling between these states. The energy of the phonon W_p is smaller than about $k_B \theta_D$ where θ_D is the Debye temperature of the material. This finite temperature activation can enable then a (phonon assisted hopping) percolating route at $E > E_c''$ where E_c'' is the lowest energy of localized states for which there is a sufficiently high $g(E)$, to provide (at a given $T > 0$) conduction. This yields (assuming the expected decay of the DOS towards the center of the pseudogap) the lowest (non-zero) finite temperature mobility for localized states. The mobility then is thermally activated and is thus proportional to $\exp(-W_p/k_B T)$. However, for this process to take place the carrier has to be excited from the last (in a semiconductor possible) occupied level (i.e. E_F in the disordered semiconductor) to the various states above E_c'' . Hence, the activation energy for the electron excitation is of the order of, but not smaller than, $E_c'' - E_F$ ($< E_c' - E_F$) and the activation energy for this conduction process is at least $E_c'' - E_F + W_p$. At lower temperatures, such nearest neighbor, or so-called fixed range hopping [17,24], can take place only around E_F since the concentration of the

phonons drops and probability for the phonons to provide energies beyond W_p is reduced. The low $g(E_F)$ will limit this conduction process yielding that $\sigma \propto \exp(-W_p/k_B T)$. The smaller the $g(E_F)$ the larger the spread in energy differences between states of nearest neighbors, and thus there will be fewer adjacent sites with smaller energy differences than W_p . Hence, as the temperature is lowered even further the energy of the available phonons will be too small to enable enough nearest neighbor hopping-events to open a conducting percolation path.

For such low temperatures the only option left for possible contribution to the conductivity is hopping to sites beyond the nearest neighbors. In this case the possibility to find an energy difference within the value of available phonon energies, increases the larger the hopping distance. Mott suggested for this regime the process of variable range hopping that can be described as follows [17,25]. For the electron, at a site i and at the level $E_i \approx E_F$ (assumed to be the ground state), to find a state with energy $E_i + W_{ij}$ it has to tunnel a relatively large distance R_{ij} . In this case the probability for the electron hop is proportional to $\exp(-2R_{ij}/\xi - W_{ij}/k_B T)$, where ξ is the localization length of the electrons in the localized states of the system. How far a distance R_h , on the “average” (see however below), does the electron have to go in order to find a state of energy $E_i + W_p$ where W_p lies in the interval $W_{ij} \leq W_p \leq k_B \theta_D$. If we assume that $g(E_i) \approx g(E_F) \approx g(E_F + W_p)$, the concentration of states that can “accept” the hop in a unit volume is about $g(E_F)W_p$. Thus, to “secure” a hop the “average” minimum required R_h has to be given by $(4\pi/3)R_h^3 g(E_F)W_p = 1$. Considering this relation the value of R_h that will yield the highest hopping probability (i.e. the minimum value of $(2R_h/\xi + W_p/k_B T)$) will be $R_h = \{\xi/8\pi k_B T g(E_F)\}^{1/4}$ (or when “properly” [24,25] averaged $\{9\xi/8\pi k_B T g(E_F)\}^{1/4}$). Considering the above probability this yields the famous Mott’s $T^{-1/4}$ law, i.e. the conclusion that the hopping conductivity will have the $\exp[-(T_h/T)^{1/4}]$ dependence [24] where $T_h = (5\xi^3)/(18\pi k_B g(E_F))$. This process describes then a variable range of the hopping with the variation of temperature. The “properly derived” expression was found [26] by noting that the resultant resistance of the network is determined by the largest resistor that participates in the percolative network, and not by an unspecified “average” resistor [26]. This derivation was shown, however, to effect the exact value of T_h and the prefactor of the macroscopic conductivity [25], but not the temperature dependence which is a result of the optimization of the individual “resistors” that participate in the conduction process. For our purpose of an intuitive picture the important finding is that it is, at least in principle, possible to distinguish between different conduction mechanisms by the different temperatures dependencies of the electrical conductivity.

For the phototransport, the excitation of the carriers is provided by external illumination so that usually one considers the transport in extended states, and thus the photoconductivity is given by the extended-states mobility and, as mentioned in Sec. 2, by the concentration of the carriers $n_{op} \approx \tau_r G$. In the present case, however, the interesting effective state distribution that determines τ_r is that of the tail states [14,15]. The occupancy of these states is determined then as follows. For states, below, but close to E_c , the occupation is determined by thermal equilibrium of the localized state with the conduction band. For the deeper states the occupation is determined, as explained above, by the recombination in states that lie below the demarcation line [14]. Now we know that as the temperature is lowered the demarcation lines move towards the mobility edges and thus we have an increasing number of recombination centers that bring about a lower value for τ_r . The same role is played by the increase of the illumination i.e. the electron-hole generation rate, as to be expected from the larger recombination rate for a larger concentration of electrons and/or holes [27]. In the case of an exponential band tail the effect of the shift of the demarcation line will be particularly strong yielding an exponential-like decrease of τ_r with decreasing temperature [14]. For the photoconductivity, σ_{ph} , we note that its dependence on the optical generation rate is usually characterized by an exponent γ that is defined by the relation $\sigma_{ph} \propto G\tau_r \propto G^\gamma$. In the case of present interest, i.e. the case of the band tails, one correspondingly obtains [14] a value of $\gamma = E_{ct}/(E_{ct} + k_B T)$ where E_{ct} is the width of the bandtail, when the DOS of the latter is assumed to be given by $N_c \exp[-(E_c' - E)/E_{ct}]$. Hence, the measured temperature dependence of γ can reveal the value of E_{ct} . It turns out that the temperature dependence of γ is also sensitive to deviations from the exponential bandtail shape, and as such its measurement can provide a tool for the mapping of the $g(E)$ map.

4. Electronic properties of semiconductor nanostructures

As we saw above the well understood electronic structure of crystalline semiconductors is quite a good starting point for the analysis of the electronic properties of non-crystalline semiconductors. For the understanding of the electronic structure and electrical transport in nanostructures we begin then again with the Bloch-picture. This is in artificially made structures for which the scale is larger than the atomic or macromolecular scale ($\leq 10 \text{ \AA}$) but smaller than the macroscopic-bulk scale ($\geq 100 \text{ \AA}$) for which the electronic properties are independent of the size of the structure.

The most important fundamental effect that takes place in the nanostructures is that of the simple quantum confinement which is an immediate result of the uncertainty principle [28]. This principle in the present context can be understood as the consequence of limiting an a priori free electron into a space region of diameter d , say, in the x -direction, as can be done by infinitely high potential barriers. Here we assume, however, that d is not only larger than the lattice constant a , but is such that the carrier can be assumed to be well described by the Bloch wave function, i.e. that it can be assumed to behave a priori as a free particle with the same effective mass that it has in the bulk. This above confinement of the electron yields then an increase of the electron momentum by $\hbar/d$, and consequently, its kinetic energy increases by about $(\hbar/d)^2/(2m^*)$ or, more precisely [8], by $\Delta = (\hbar^2/2m^*)(\pi/d)^2$. It is important to note that if the electron has a mean free path ℓ such that $\ell < d$, a dephasing of the electron wave will take place and its amplitude will decrease within the distance ℓ , thus making the above picture inappropriate. This aspect of the confinement can also be discussed using the uncertainty principle by noting that if the electron has a mean free time for scattering τ_s , such that $\ell < d$, its energy is broadened by the amount of $\Gamma = \hbar/\tau_s$. Hence, the quantum confinement effect is expected to be observed only if $\Delta > \Gamma$, i.e. only if $\ell > d$. This is the reason that the fascinating phenomena associated with quantum confinement take place in high mobility semiconductors and in particular at low temperatures [28,29]. As a consequence we would expect that for a disordered solid these phenomena will be found for smaller nanostructures than in their crystalline counterparts [30]. We note in passing that over the scale of ℓ , the concept of m^* (though not with the same value) appears to be useful for the extended states in a disordered semiconductor. In what follows we discuss then the electronic structure in nanostructures of crystalline semiconductors, recalling that for small enough structures of disordered materials the results are expected to be qualitatively the same. On the other hand since ℓ is a statistical concept the potential fluctuations in disordered semiconductors, over their scales, will cause the smearing of the sharper features associated with the electronic properties of crystalline nanostructure even for $\ell > d$. Indeed, clear manifestations of the quantum confinement, i.e. the dependence of the electronic structure and transport on the size of structure, in the above $10 \leq d \leq 100 \text{ \AA}$ range, have been reported for chalcogenes [11], chalcogenides [12] and tetrahedrally bonded [30] amorphous semiconductors.

In addition to the increase of the electrons' energy there is another consequence of the confinement, i.e. the quantization of the states according to their standing waves in the potential well. To appreciate these effects let us start by a brief review of the electronic levels in a quantum well [8], i.e. in a two-dimensional geometry where the confinement takes place between two infinite barriers, the distance between which is d , and the direction of which is x . A particle within such a well is described by the product of the Bloch wave function for the y - z plane and the envelope wave function $\Xi(x)$ of the standing-wave that is determined by the corresponding solution of the one dimensional Schrödinger equation in the x -direction [9,28]. The solutions for $\Xi(x)$ yields then the energies $E_n = n^2\Delta$ where $n = 1, 2, 3, \dots$. In the more realistic case of a finite-depth well these value change somewhat but the main consequences of the confinement, i.e. energy shifts and discrete levels in the confinement direction, remain [8,28].

As in our discussion in Sec. 3 the most general and informative feature of the electronic structure is the DOS. Let us examine then this property in the nanostructures. We do know that for the simple parabolic bands the density of states (per unit, of the corresponding dimensional, volume) within a band (the bottom of which lies at $E = 0$) is: $\rho_3 = [(2m^*)^{1/2}/(\pi^2\hbar^3)]E^{1/2}$ in three dimensions, $\rho_2 = (m^*/\pi\hbar^2)$ in two dimensions and $\rho_1 = (2/\pi\hbar)(m^*/2E)^{1/2}$ in one dimension [7,8]. We note here that the DOS is finite at the band edge in two-dimensional systems and that it diverges at the bottom of the

band in one-dimensional systems. In the simple quantum well-like structures we will have then that the energies are given by $E_n(\mathbf{k}_1) = n^2\Delta + \hbar^2|\mathbf{k}_1|^2/2m^*$, where $\mathbf{k}_1$ is the wave-vector in the y-z plane. The corresponding DOS will be then a “steps” function where at each n the DOS “jumps” by $m^*/\hbar\pi$. It is obvious then that as d increases, the separation between the E_n levels will be reduced and that the overall DOS will approximate that of the three dimensional system [8]. This is to be expected since with the increase of d the system approaches the situation of the Bloch’s macroscopic crystal where we consider the fact that $d = aN_d$, where N_d is the number of unit cells in the well. Indeed we mentioned above that $E_n = (\hbar^2/2m^*)(\pi n/aN_d)^2$. As d increases we get two simultaneous effects. First, the separation between the levels (the confinement energy) becomes smaller, and second, the number of allowed states ($2N_d$) becomes larger. Consequently the increase of d yields a transition from that of well-separated discrete states distribution to a quasicontinuous distribution as in the crystalline band. The states change their nature from standing waves to traveling-Bloch waves. Since for the latter states the crystal momentum is a good quantum number, we have that for a wide enough quantum well the expected three-dimensional crystalline DOS will be found.

In general, we are familiar with the evolvement of the electronic structure from that of the atom to that of the molecule to that of the crystalline solid. Let us follow then, in a similar way, the evolvement of the electronic structure when adjacent quantum wells are introduced, say, along the above x-direction. The double well structures, in which a barrier of finite height and finite width enables the tunneling of an electron from one well to the other, in a manner that is reminiscent of the hydrogen molecule, is expected to yield the removal of the double degeneracy of the original well states by the perturbation that is due to the effect of one potential well on the electron energy in the other potential well.

As we go to an array of finite-depth quantum wells, with a barrier width b we encounter the periodic situation of the well-known Kronig-Penney model [7] with a periodicity of $d+b$. The smaller the b the larger the overlap of the wave functions in adjacent wells and the broader the corresponding minibands that form by the broadening of the discrete confinement levels of the isolated well. The degeneracy of the states in each band will be N_w where N_w is the number of wells in the one-dimension arrays. We can use here exactly the same considerations that we have used for the broadening of the atomic levels into bands, in the crystalline bulk. When $d+b$ becomes so small to approach the lattice periodicity, the corresponding atomic potential becomes dominant and $g(E)$ transforms to the expected three-dimensional density of states of the original semiconductor bulk. One of the interesting outcomes of this “superlattice” is that the width of the Brillouin zone of the minibands is $2\pi/(b+d)$. Since the superlattice crystal momentum is conserved up to the reciprocal lattice vector $\pi/(b+d)$, the corresponding wave vector behaves as a zero wave vector and we can look at the original crystalline zone edge π/a to be folded into smaller zones. This view is known as the “zone folding” picture [7]. The significant effect of this folding is that it enables to transfer a chosen effective mass in the crystalline bulk band to the minimum of the next miniband, yielding an “effective mass engineering” [7,28]. In fact, by choosing the sequence of quantum well and quantum barrier materials, one can engineer many of the electronic properties of the semiconductor. In particular, one can tailor the properties of the electrons and the holes in the system to yield high efficiency light emitting diodes (LED’s) and solid-state lasers [8]. The reason for the higher efficiency, in comparison with the older pn-diodes, is that in the quantum wells we have both a wave guide-like structure due to the different refractive indices of the well and barrier materials and to the geometrical confinement of both electrons and holes that increases the overlap of their wave-functions and thus the probability for their radiative recombination.

Turning to lower dimensions, we find that in the one-dimensional system in the x-direction we have standing wave-like states due to the confinement in the y and z directions. For a wire with a rectangular cross section $L_y \times L_z$ this will yield the discrete levels to be given by $E_{x,y} = (\hbar^2\pi^2/2m^*)[(n_y/L_y)^2 + (n_z/L_z)^2]$ where n_y and n_z are the states of the confined wave function. Only in the x-direction we have then a free electron-like behavior. In the latter case, we can have elastic scattering only from the $-k_x$ to the k_x or the $-k_x$ states and vice versa. This, as we show below, yields then the interesting phenomenon of the quantization of the conductance [29]. An interesting result that we have mentioned before is the diverging of the DOS at the band edge. We note however that for a “quantum wire” of a finite length the separation of the energy levels and the control of the states occupation by the Fermi-Dirac statistics will cause the conduction to take place at a finite value

of k_x , as is the case of the Bloch metal. Consequently, we refer to the corresponding largest occupied k_x as the Fermi wave vector and denote it by k_F .

Further reduction of the dimensionality brings us to the quantum dot of which we can think of as a cubical box, or a sphere with radius R , where R is in the range considered above for quantum structures [9]. Following the above consideration this will yield discrete states such as $E_{e,n,l} = E_g + (\hbar^2/2m^*)(\kappa_{n,l}/R)^2$ for the electrons in the “conduction” band, and $E_{h,n,l} = (\hbar^2/2m_h^*)(\kappa_{n,l}/R)^2$ for the holes in the “valence” band. Here, the E_g is the bandgap of the original crystalline bulk and $\kappa_{n,l}$ are the quantum numbers of the confined states that are characterized by the integers n and l . The sum of the confinement energies gives then the increment in the widened “forbidden gap” that consists now of discrete states. In the ground state the “band gap” becomes then $E_g + E_R$, where $E_R = (\hbar^2/2m_r^*)(\pi/R)^2$ and m_r^* is the reduced electron-hole mass. In this simple treatment we ignore of course the Coulomb interactions, the importance of which will be considered below. It is obvious that as the size of dot increases, the above level separation and the confinement energies decrease, yielding again a smooth transition from the discrete, quantum confined states, behavior to that of the Bloch-bulk traveling-wave behavior. We note that as a consequence of the discreteness of the energy levels one defines the energy “band gap” in such a system by the energetic distance between the highest energy DOS peak in the valence band and the lowest DOS peak in the conduction band [31].

Turning to the transport properties we start by mentioning the most conspicuous transport phenomenon in each of the various dimensions, leaving the other phenomena to be found in the cited literature [8,29]. Starting with the two-dimensional quantum well structures the most known special feature is the resonant tunneling [8,28]. The essence of this very famous effect is quite simple considering the two requirements for tunneling as we presented them already in the context of hopping conduction. First, tunneling can take place from a given state to another state at the same energy level, and second, the latter state must be empty so that the electron can tunnel into it. Let us consider then a five-layer semiconductor structure such that the first and the last layers are made of a bulk semiconductor with a conduction band edge E_c . The second and fourth layers, made of another semiconductor, serve as the tunnel barriers. The third layer is a quantum-well semiconductor with say, a conduction band edge E_w and a confinement energy E_d . The carrier concentration in the well is usually lower than that of the bulk semiconductor. The assumption then is that in the semiconductor bulks E_c is occupied by electrons so that these states can be considered to be discrete occupied levels above which there are empty levels. Before a voltage V is applied, $E_w + E_d > E_c$ and thus no tunneling is possible throughout the structure. Upon the application of a voltage V the conduction band edge of the “left” bulk is raised to $E_c + V/2$ and that of the “right” bulk is lowered to $E_c - V/2$. Now, tunneling is not possible (at $T = 0$) as long as $E_w + E_d > E_c + V/2$. With further increase of V the alignment of $E_c + V/2$ with $E_w + E_d$ yields a strong increase of the tunneling current. Then, as $E_c + V/2$ is made larger than $E_w + E_d$ the tunneling probability drops again, and the current drops in spite of the rise in V . This provides then a region of V for which there is a “negative differential resistance”. The importance of this feature is that it is a condition for current instability. In particular this feature enables oscillations in the circuit [8] or even self-excited oscillations [32] as do (by other mechanisms) the Gunn [28] or the acoustoelectric [33] effects. It is interesting to note that such an effect has also been observed in double barrier structures of amorphous semiconductors [34], indicating the validity of the nearly free electron picture in small enough structures of these systems.

For the one-dimensional system of quantum wires the most striking feature is the quantization of the conductance [8,29]. As we saw in this case the only way for an elastic scattering process to take place is that of an electron in the k_x state to be scattered to the k_x state or the $-k_x$ state, or vice versa. In the “channels” (or the subbands, i.e. the two-dimensional confinement energies, $E_{x,y}$), if they are well separated (e.g. for $L_y \approx L_z \approx 100$ Å the separation between the confinement levels is 50 meV) this motion, with only elastic scattering, can yield very high mobilities. In the ideal case this motion yields a quantized (minimum) conductance as can be concluded from the following considerations. The conduction takes place at k_F such that the velocity of an electron contributing to the current is $v_e = (\hbar k_F/m^*)$. The time it takes to travel through a wire of length L_x is L_x/v_e and thus the current contributed by each electron at k_F is given by qv_e/L_x . The number of such electron states within the interval $qV/2$ (see below) is $L_x \rho_1(E_F) qV/2$. Considering the fact that $\rho_1 = (2/\pi \hbar) m^*/\hbar k_F$ we get then that the total current is $I = (2q^2/h)V$. Hence, each occupied channel contributes a quantized conductance of $2q^2/h$. In a system where only a single channel is occupied this quantized conductance

will be manifested by the corresponding quantized jumps in the conductance. In this simple picture the non-trivial point is that we considered $V/2$ rather than the intuitively expected V . The reason for that is that a system of only elastic collisions has no resistance and thus the voltage drops at the contacts [9]. Hence the quasi-Fermi level in the wire is shifted up on the “average” by only $V/2$.

As for the two-dimensional and the one-dimensional systems the transport in an array of quantum dots is expected to be controlled by the tunneling between adjacent quantum dots. Hence, the effective mobility of the carrier propagation μ_t is expected to be proportional to the inter-dot tunneling probability $\exp(-2\chi s)$ where χ is the tunneling (say, WKB) exponent and s is some typical (see however below) inter-dot distance. A priori then, the conditions for transport in the array resemble those between adjacent quantum wells. However, there is one significant difference that follows the relatively small size of the dots, i.e. the non-negligible charging energy of a dot which is a result of placing a single electronic charge on the dot. The dot size is typically a few tens of Å and thus, this energy is typically of the order of a tenth of an eV [35]. A rough upper estimate of that energy can be obtained as follows. The energy needed to be supplied by a single electron addition to a dot is $E_{cb} = q^2/2C$ where C is the capacitance of the dot within its environment. Assuming an isolated spherical dot, with a radius R , that is embedded in a dielectric with a constant $\epsilon\epsilon_0$, the capacitance is given by $C = 4\pi\epsilon\epsilon_0 R$. For a dot with $R = 20$ Å in a quartz matrix ($\epsilon = 3.9$) one gets that $E_{cb} = 0.175$ eV. Correspondingly, for a single electron to be injected to a system of dots an activation process that supplies the energy E_{cb} is required. Similarly, for the thermal “generation” of an electron-hole pair i.e. a negatively charged dot and a well-separated positively charged dot, from an a priori two neutral dots, the energy to be supplied is $2E_{cb}$. The latter situation can be viewed as the thermal electron-hole pair generation in an intrinsic semiconductor with an energy gap of E_g , for which we saw that the carrier concentration is proportional to $\exp(-E_g/2k_B T)$. Thus, in both cases mentioned here, the concentration of carriers available for tunneling is given by $n_{cb} \propto \exp(-E_{cb}/k_B T)$. Hence, conduction can take place only if the energy E_{cb} , to overcome this electrostatically-imposed Coulomb blockade, is provided. The conductivity will be given then by $\sigma_t = q\mu_t n_{cb} \propto \exp(-\chi s - E_{cb}/k_B T)$. This expression has simple consequences in two cases. If we have an ordered array of the same s and the same R , the conductivity σ_t will be activated in the same way as n_{cb} . This analogy can be carried over also to the case of a disordered array of dots if there is a continuous path of very small (of the order of atomic spacing) dot-separation. In the latter case, that resembles impurity-band-like conduction, this optimal conduction path shunts the other possible conduction routes and the conductivity of the system will be the same as that of the optimal conduction path [36]. In the other extreme of large s or very low temperature (so that there is a low probability for the supply of E_{cb}) we encounter the situation similar to that of variable range hopping and the expected $\exp(-T_0/T^{1/4})$ dependence, but of course with a T_0 that corresponds to the dots rather than to atoms [37]. The most interesting case takes place however for some distributions of s and R [37] and in particular for the simple correlated case for which the s/R ratio is assumed to be a constant [35]. Such a situation is a priori expected to occur in a composite where the fractional content of the material of which the dots are made (the other is the dielectric in which the dots are embedded) is a constant. In the latter case a region with larger dots is also expected to have large s values, and a region of smaller dots is expected to have small s values. There is here the obvious competition between the smaller barrier, that enhances the tunneling, and the smaller dot that requires higher activation energy. In that case the optimal conduction path will be determined by the s - R combination that will yield the highest conductivity. It is easy to see then that the maximum of σ_t for a given temperature will be determined by the s - R combination that will minimize the term $(\chi s + E_{cb}/k_B T)$. In the simple case of a constant s/R this will be obtained for $s \propto R \propto T^{-1/2}$, yielding that $\sigma_t \propto \exp(-AT^{-1/2})$, where A is a corresponding constant. Thus, there will be a shift of the optimal conduction path as a function of temperature. It is to be noted that while this argument resembles Mott’s argument for variable range hopping [17] which is a pure mobility argument, in the present case there is an interplay between the mobility and the carrier concentration, that yields the optimal path shift [35]. Here again there is a participation of relatively very few (as low as 1%) quantum dots in the effective conduction process [36].

Summarizing the above picture one would expect for a disordered system of quantum dots a temperature dependence of the type $\log(\sigma_t) \propto T^{-\alpha}$, where $1/4 \leq \alpha \leq 1$, for various systems of quantum dots. In particular a transition from $\alpha = 1/4$ to $\alpha = 1/2$ is to be expected with increasing temperature. If a

path of close enough adjacent dots is present a transition from $\alpha = 1/2$ to $\alpha = 1$ is also to be expected [37]. We should remark in passing that while the above ideas have been developed for granular metals their essence are valid for semiconductor quantum dots [38], for which the additional refined effects associated with the quantized levels in the dot have also been observed [39]. In particular deconfinement effects accompanied with [40,41] or without [42] their effect on the photoluminescence have been observed in disordered arrays of semiconductor quantum dots.

5. Conclusions

The fact that semiconductor chalcogens and chalcogenides can come with crystalline or amorphous forms and the fact that they can be made to have various nanostructures, make them a very good testing grounds for the ideas and concepts introduced into semiconductor physics in the second half of the 20th century. In addition they have the prospects of providing structures for various electronic and optoelectronic applications which benefit from their very special properties. The most notable example of the latter is of course the xerography.

It appears, following the above review, that the Bloch and the localized states pictures are very good starting points for the understanding of the electronic properties of disordered and nanostructured semiconductors. To better understand these systems one must apply the concepts and the theories of tunneling and percolation. The important new concepts, as well as some analogies and extrapolations from the theory of crystalline semiconductors and situations of other quantum systems, are found to be very helpful for the construction of pictures of the electronic properties of the above systems in general and for chalcogens and chalcogenides in particular. These concepts are in fact necessary tools for quantitative characterization of the latter systems.

Acknowledgement

This work was supported by the Israel Science Foundation.

References

- [1] J. C. Philips, Bonds and Bands in Semiconductors, Academic, New York (1973).
- [2] R. Zallen, The Physics of Amorphous Solids, John Wiley, New York (1983).
- [3] D. Adler in Amorphous Semiconductors, Eds. H. Fritzsche, D. Han, C. C. Tsai, World Scientific, Singapore, 1987, p. 3.
- [4] S. R. Elliot, Physics of Amorphous Materials, Longman, Hong Kong (1990).
- [5] C. M. Wolfe, N.J. Holonyak Jr. and G.E. Stillman, Physical Properties of Semiconductors, Prentice Hall, Englewood Cliffs (1989).
- [6] I. Balberg, Appl. Phys. Lett., **16**, 491 (1970).
- [7] J. Singh, Physics of Semiconductors and their Heterostructures, McGraw Hill, New York (1993).
- [8] C. Weisbuch, B. Vinter, Quantum Semiconductor Structures: Fundamentals and Applications, Academic, Boston (1991).
- [9] L. Ba'enjai, S. W. Koch, Semiconductor Quantum Dots, World Scientific, Singapore (1993).
- [10] For a collection of papers see, Optical Effects in Amorphous Semiconductors, Eds. P.C. Taylor and S. G. Bishop, AIP, New York, 1984.
- [11] E. Vateva, I. Georgieva, J. Non Cryst. Solids, **164-166**, 865 (1993).
- [12] See for example, I. Z. Indutnyi, P. E. Shepeljavy, J. Non Cryst. Solids, **227-230**, 700 (1998), and V. Palyok, M. Malyovanik, J. of Opt. and Adv. Mater., **1**, 77 (1999).
- [13] J. Ziman, Principles of the theory of Solids, Cambridge University, Cambridge (1965).
- [14] A. Rose, Concepts in Photoconductivity and Allied Problems, Wiley Interscience, New York (1963).
- [15] R. H. Bube, Photoelectronic Properties of Semiconductors, Cambridge University, Cambridge (1992).

- [16] I. Balberg, *J. Appl. Phys.*, **75**, 914 (1994).
- [17] N. F. Mott, E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Oxford University, Oxford (1979), and N. F. Mott, *Conduction in Non-Crystalline Materials*, Oxford University, Oxford (1993).
- [18] M. H. Cohen, H. Fritzsche, S. R. Ovshinsky, *Phys. Rev. Lett.*, **22**, 1065 (1969).
- [19] A. A. Klochikhin, S. G. Ogloblin, *Phys. Rev. B*, **48**, 3100 (1993).
- [20] See for example, E. N. Economou, C. M. Soukoulis, M. H. Cohen, A. D. Zdetsis, *Phys. Rev. B*, **31**, 6172 (1985), and S.K. Oley and P.K. Lim, *Solid State Commun.*, **101**, 513 (1997).
- [21] J. M. Ziman, *Models of Disorder*, Cambridge University, Cambridge (1979).
- [22] R. A. Smith, *Semiconductors*, Cambridge University, Cambridge (1961).
- [23] H. C. Berg, *Random Walk in Biology*, Princeton University, Princeton (1983).
- [24] O. Madelung, *Introduction to Solid State Theory*, Springer, Berlin (1978).
- [25] B. I. Shklovskii, A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer, Berlin (1984).
- [26] A. Ambegaokar, B. I. Halperin, J. S. Langer, *Phys. Rev. B*, **4**, 2612 (1971).
- [27] Y. Lubianiker, I. Balberg, L. Fonseca, *Phys. Rev. B*, **55**, R15997 (1997).
- [28] P. Y. Yu, M. Cardona, *Fundamentals of Semiconductors*, Springer, Berlin (1999).
- [29] S. Datta, *Electronic Transport in Mesoscopic Systems*, Cambridge University, Cambridge (1995).
- [30] As an example see B. Abeles, T. Tiedje, *Phys. Rev. Lett.*, **51**, 2003 (1983, and for a review see M. Hirose, S. Miyazaki, N. Murayama, in *Tetrahrally-Bonded Amorphous Semiconductors*, Eds. D. Adler and H. Fritzsche, Plenum, New York, 1985, p. 441.
- [31] See for example, N. A. Hill, K. B. Whaley, *J. Elect. Mater.*, **25**, 269 (1996), and S.V. Nair, L. M. Ramaniah and K. C. Rustagi, *Phys. Rev. B*, **45**, 5969 (1992).
- [32] P. Zhao, H. L. Cui, D. L. Wooland, *Phys. Rev. B*, **63**, 075302 (2001).
- [33] A. Many, I. Balberg, *Physics Letters*, **21**, 486 (1966).
- [34] Z. R. Yu, I. Pereyral, M. N. P. Carreno, *Jpn. J. Appl. Phys.*, **38**, 1317 (1999).
- [35] B. Abeles, *Applied Solid State Science*, **6**, 1 (1974).
- [36] G. A. Levin, *Physics Letters A*, **142**, 405 (1989).
- [37] P. Sheng, J. Klafter, *Phys. Rev. B*, **27**, 2583 (1983).
- [38] G. Y. Yu, R. F. O'Connell, Y. L. He, M. B. Yu, *J. Appl. Phys.*, **78**, 3945 (1995).
- [39] X. Gu, H. Qin, H. Lu, J. Xu, K. Chen, *Mater. Res. Soc. Symp. Proc.*, **467**, 367 (1997).
- [40] Y. Posada L. Fonseca, O. Resto, S. Z. Weisz, I. Balberg, *Mater. Res. Soc. Symp. Proc.*, to be published (2001).
- [41] Y. Lubianker, I. Balberg, *Phys. Rev. Lett.*, **78**, 2433 (1997).
- [42] Y. He, Y. Wei, G. Zheng, M. Yu, d M. Liu, *J. Appl. Phys.*, **82**, 3408 (1997).