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Section 1. Mott Lecture

The localization of electrons in amorphous semiconductors: A twenty-first century perspective

P. Craig Taylor

Colorado School of Mines, Department of Physics, Golden, CO 80401, USA

Abstract

This review covers those consequences of the localization of electronic states that appear to be universal features embracing all amorphous semiconducting materials where the electron–lattice interaction can be neglected, such as hydrogenated amorphous silicon. Several experimental measurements of these features are described. The role of strong electron–lattice interactions in some amorphous semiconducting systems, such as many chalcogenide glasses, is also discussed. In these systems, the electron–lattice interaction is so strong that it more than offsets the coulomb repulsion needed to put two electrons in the same energy state. Some experimental consequences of these so-called negative-U_{eff} systems are described. In addition, some universal features of metastable excitations for systems with both weak and strong electron–lattice interactions are discussed in the light of some recent experimental results.

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1. General classes of disorder

It has been 50 years since the original realization that sufficient disorder produces localization of the electronic states within an energy band [1]. If the disorder is insufficient to localize all of the states within the band, then only some of the electronic states, namely those at the edges of the allowed energy bands, are localized [2]. Even for infinitesimal disorder there exist localized states, albeit at infinitesimally small densities. The separation between the lowest energy localized states at the top of the valence band and the highest energy localized states at the bottom of the conduction band provides a sharp demarcation energy, which has come to be known as the mobility gap [3]. For amorphous semiconductors such localization has profound consequences for many of the electronic and optical properties. Although there has been considerable progress in understanding the details of these states, many important problems remain.

Even crystalline solids are disordered. In fact, all real solids are disordered. Real solids are grown at finite temperature, which produces defects thermodynamically. At some level, impurities always exist in real solids. Even if one imagines a perfect elemental solid, such as Si or Ge, with no defects or impurities, there will be disorder due to the presence of more than one isotope. It is therefore not surprising that the only remaining standard that is a physical sample is the standard kilogram stored outside Paris. Making a solid that is perfect enough to replace this physical standard is not easy [4].

If all real solids are disordered, it seems at first glance that the influence of localized electronic states must be all encompassing. In the purest sense this may be true, but it is obvious that the theory of crystalline solids has been extremely successful in describing the bulk properties of most solids whose atoms are arranged on a periodic lattice. In fact, some properties, such as electrical conductivity, can

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E-mail address: craig@physics.utah.edu

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be explained in some detail with no reference to a periodic lattice other than that necessary to count quantum states. The free electron Fermi gas is the most prominent example. Therefore, it makes sense to restrict our discussion of disorder to include only those cases where the disorder itself is important in determining the bulk physical properties, such as the thermal, vibrational, optical, or electrical properties. In the amorphous semiconductors this is always the case.

We begin with a brief introduction into the types of disorder found in solids, starting with the simplest and moving to the more complex. *Homogeneous disorder* occurs when all regions with large numbers of atoms or molecules have the same average, or bulk, properties, such as density, velocity of sound, specific heat, electrical and thermal conductivities, and so forth. The simplest example of homogeneous disorder is *disorder on a periodic lattice*. Such disorder is inherently topologically ordered because one can always determine a lattice site using well-determined translation vectors (linear combinations of primitive vectors of a unit cell). The disorder occurs in the type of atom or molecule that is present at a specific lattice site. The atoms or molecules are arranged on an ordered lattice, but at any specific lattice site there may be uncertainty as to the type of atom or molecule that is present. Homogeneous disorder on a periodic lattice is sometimes called *substitutional disorder* or *cellular disorder*. Examples include ternary alkali halides, ternary III–V semiconductors, crystalline C_{60} at room temperature, and Fe, where the disorder is in the magnetic moments.

The second category of homogeneous disorder is disorder with no long-range periodic order. These solids, of which the amorphous solids are an important class, are inherently *topologically disordered*, but they remain homogeneous on a macroscopic scale. Although the long-range order is not periodic, all solids in this class exhibit local atomic arrangements that have some order. This fact is a statement of simple chemistry because nature prefers specific *chemical bonds* that are remarkably invariant throughout the lattice. In particular, for a specific chemical composition, inter-atomic distances are very well defined. For such solids, the order in the local atomic arrangements disappears rapidly with distance away from an individual lattice site. Perhaps the simplest example of this second category of disorder is the so-called *quasi-crystal* where long-range rotational order exists, but at least in our spatially three-dimensional world, there is no well defined long-range periodic order.

Many materials that exhibit homogeneous disorder with no long-range periodic order can be described as *amorphous*, *vitreous*, or *glassy*. A homogeneous, disordered solid is amorphous if there exists no periodic array of lattice sites. Therefore, in a homogeneous amorphous solid there exists no long-range periodic order, although vestiges of short-range order will remain. In these systems some of the topological connections between atoms or molecules exhibit randomness, but the details depend of the specific materials system.

In what follows we shall treat vitreous and glassy as synonymous. Neither of these terms is well defined, and we shall adopt the usual operational definition that vitreous or glassy solids are those that can be quenched from the liquid phase to the solid phase without crystallization. It is clear from this definition that the more rapid the quench, the more likely the resulting solid is amorphous. Therefore, whether or not the resulting material is glassy may depend on the details of the quenching procedure and the volume of the sample.

More complex than homogeneous disorder is *inhomogeneous disorder*. In these solids the average properties vary from region to region. By analogy with homogeneous disordered solids, one can break up the inhomogeneous disordered solids into those that are primarily topologically ordered and those that are primarily topologically disordered. Examples of the former sub-class are polycrystalline solids, phase-separated crystals, and crystalline precipitates. Examples of the latter sub-class are phase-separated glasses and ceramics. Thin films of nanocrystalline and microcrystalline silicon are usually a mixture of these two classes.

2. Fluctuating potentials and localized electronic states

Disorder produces fluctuating potentials for electrons, which in turn localize some of the wavefunctions for electrons and holes. This problem was first treated by Anderson, who considered a three-dimensional Kronig–Penny model with potential wells that fluctuated randomly about some average value [1]. Although this model is clearly simplified, it produces most of the attributes that we currently associate with amorphous solids, including the localization of the electronic states at the edges of the bands. A symbolic diagram of the densities of electronic states for such a solid is shown in Fig. 1. The energies E_V, $E_{V'}$, E_C, and $E_{C'}$, represent the demarcation energies between localized and extended states. Although difficult to measure, these energies are well defined since quantum mechanics dictates that one cannot have both localized and extended states coexisting at the same energy. Experimentally, we find that the densities of the localized states at the edges of the bands decay exponentially into the energy 'gap'. Therefore, on a

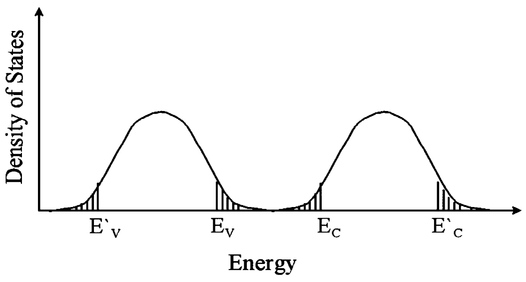

Fig. 1. Schematic diagram of the electronic density of states in the valance and conduction bands in a disordered solid. The cross-hatched regions indicate where the electronic states are localized.