Glassy, Amorphous
and Nano-Crystalline Materials

Hot Topics in Thermal Analysis and Calorimetry

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Editors

Glassy, Amorphous and Nano-Crystalline Materials

Thermal Physics, Analysis, Structure and Properties

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Preface

Early Research into Amorphous Semiconductors

Numerous aspects of physics and chemistry of non-crystalline solids and glassy state which are discussed in the present book can only hardly be prefaced without rude simplification. Therefore, let us make instead a short excursion to the prehistory of research into amorphous semiconductors, the topic on which the common epistemological features of the other subjects treated in this book may be demonstrated.

It is a matter of fact that in everyday life we encounter more frequently non-crystalline than crystalline solids. We can even with some exaggeration say that in the Nature the perfect crystals are as rare as diamonds. In spite of that, the existence of the class of non-crystalline materials has been recognized only recently. One of the reasons for such a state of the art is probably the fact that the positivistic continuous model of matter dominated till the end of the nineteenth century and that the fundamental conjectures of atomism were too closely bound up with the idea of the regular ordering of atoms; early atomic theories accounting for the regular shape of snow flakes [1] and for the anisotropy of optical properties of transparent crystals [2], namely, exploited the idea that such a regularity is due to the closest filling of the space by identical hard polyhedrons or spheres, atoms. Denying atomic order in solids would thus undermine the strongest intuitive argument in favour of atomism, namely, that just the satisfaction of geometrical constrains between neighbouring atoms and their close packing accounts for actually observed regular shape of crystals. Interestingly enough, in the scientific disputations about the structure of matter, the existence of glass, for a long time known amorphous, i.e. "shapeless" material par excellence, was tacitly ignored.

The serious attempts to treat the atomic structure of amorphous or glassy state are thus relatively recent, belonging to the first half of the twentieth century. The glass was at that time considered to be nothing but undercooled liquid i.e. a solid having essentially the atomic structure of original melt. Such a picture was an immediate consequence of phenomenological principle of continuity between

liquid and solid state proposed by Frenkel [3], which was, among others, partially confirmed by means of X-ray analysis. Accordingly, namely, some characteristic structural patterns observed in the solid phase are, as a rule, observed in the liquid melt as well. From the broadening of X-ray diffraction patterns it was even possible to conclude that the glass comprises nanocrystals of typical size ~2 nm. (Today such a material would be classified rather as a nanocrystalline aggregate than glass.) Nevertheless, the phenomenological model provided neither the algorithm for the reconstruction of atomic lattice of glass nor the basis for the derivation of its physical properties from the structural ones. The first realistic model of glass lattice due to Zachariasen [4] was thus rather a result of physical reasoning than of a purely descriptive phenomenology. Crucial for the establishment of the model was the observation (from today's point of view not very exact!) that the mechanical properties of a glass, e.g. elastic bulk modulus or hardness, and of a corresponding crystal are similar. Consequently, the underlying building blocks have to have similar structural energies and must be matched together without further expense of energy. In order to satisfy these conditions it was suggested to identify the "underlying building blocks" with the nearest neighbourhood of each atom, the arrangement of which was only slightly changed with respect to that in a crystal. Cumulating small deviations of bond lengths (~1%) and tiny variations of bond angles (~1°) made it possible to match building blocks together and to construct a random amorphous lattice without appreciable increase of structural energy. It can be shown that such a random lattice being locally almost identical with the periodic lattice of the corresponding crystal should reveal up to the second or the third coordination sphere practically the same radial distribution of atoms. For the following coordination spheres, however, huge differences are expected. The overall structural properties of amorphous solid may then be characterized quite simply by saying that the short-range order of atoms is preserved while the long-range order is absent. Evidently, this is quite a new concept of disorder, differing essentially from that encountered e.g. in gases. Being once established, the model of locally ordered homogeneous random network based on the absence of long-range order started to play more and more important role in modern solid state physics and chemistry.

By admitting new structural model, the problem of amorphous state was by no means definitely solved but just on the contrary. The researchers had to struggle with qualitatively new difficulties which appeared by computing the mechanical, optical and electronic properties of amorphous solids. As the semiconductors are materials which are known to be most sensitive to the changes of structural and chemical disorder, they may serve as a good example illustrating the fascinating development of solid state physics which followed. The quantum band model of solids as established in the 1930s was tailor-made for crystals having perfectly periodic lattice disturbed by only a small number of imperfections. Accordingly to Wilson's classification [5], the semiconductors were materials characterized by a "not very large" energy gap (~1 eV) in their electronic band structure. The very existence of the electronic band structure of solids was at that time treated as a direct consequence of periodicity of crystal lattice. Such an opinion was basically

due to the establishment of famous Bloch's theorem [6] which enabled one to solve electronic structure of periodically arranged atoms even analytically (see e.g. Kronig-Penney model [7]). According to Bloch's theorem, namely, the interaction of an electron with the periodic crystal lattice may be replaced by its movement in a certain periodic potential. The solution of Schrödinger equation in such a periodic field has a special form of harmonic wave with periodically modulated amplitude. In amorphous solids such a marvelous mathematical simplicity due to the perfect translational symmetry and long range order of crystals was lost forever and researchers have to learn how to do without Bloch's theorem. Moreover, the situation was further complicated by quite an astonishing experimental observation of Kolomiets [8] that chalcogenide glasses behave like intrinsic semiconductors which are essentially non-sensitive to the doping. Unexpectedly enough, theorists had to account for the surviving of the band model in the absence of lattice periodicity and for experimentalists quite a new field of research was opened, amorphous semiconductors. It should be stressed here that just these two circumstances had enormous impact on the further development of semiconductor science and technology.

The real boom of research into amorphous semiconductors was initialized by works of Ovshinski who reported about switching between a highly resistive and conductive state effected by an electric field and memory effects in chalcogenide glasses [9]. Immediately afterwards a plenty of new effects such as photodoping, reversible photostructural changes and optical memory effect having a huge application potential for imaging and electrophotography (e.g. Xerox process) were discovered. Hand in hand with the promise of further applications steeply increased interest not only in chalcogenide glasses but also in other types of amorphous semiconductors (e.g. tetrahedrally bounded semiconductors) and in non-crystalline materials in general. Quite naturally there appeared a demand for a new scientific journal (Journal of Non-Crystalline Solids, 1st issue 1969) covering all these hot topics.

What were actually the main achievements in amorphous semiconductors during the decade from1965 to 1975? First of all it was recognized that the band gap does exists also in amorphous semiconductors in spite of the absence of atomic long-range order. The band gap is, however, not empty but it contains an appreciable amount of localized states and its edges are no more sharp [10]. The position of the band gap edges and actual width of the band gap thus depends on the method of measurement. Transport band edges coincide with so called mobility edges where the mobility of carriers dramatically changes while the optical band gap (Tauc's optical gap [11, 12]) is determined by means of extrapolation of absorption curve. The localized states within the gap are, moreover, no passive entity. As a rule, at room and lower temperatures, they enable a special type of carrier transport via localized states, the so called hopping [13]. A new light on the character of localized states within the gap shed the path-breaking discovery of possibility of effective doping of amorphous silicon prepared by glow-discharge technique [14]. Passivation of localized gap states by hydrogen or other chemicals opened a new way to the tailoring of these materials. Besides the purely technological progress,

the research into amorphous semiconductors stimulated development of qualitatively new methods of computing electronic structure of disordered solids and brought about changes in understanding to apparently closed topics [15].

We can thus claim that the research into amorphous semiconductors completely changed, within practically 1 decade, the gist of solid state physics as a whole. The concept of disorder became a corner stone of a lot of theories; the era of order was shared by the era where the concept of disorder dominated. And finally, in epistemological context provided the discovery of various aspects of disorder a valuable key to our understanding of a lot of natural systems and phenomena belonging not only to the scope of solid state physics and chemistry but also to biology, astrophysics and even to sociology.

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