# PHASE TRANSITION IN SOME SIMPLE GLASSY SEMICONDUCTORS

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**By**

*El-Sayed Mahmoud Abd El-Rehman Osman*
*( B. Sc. )*

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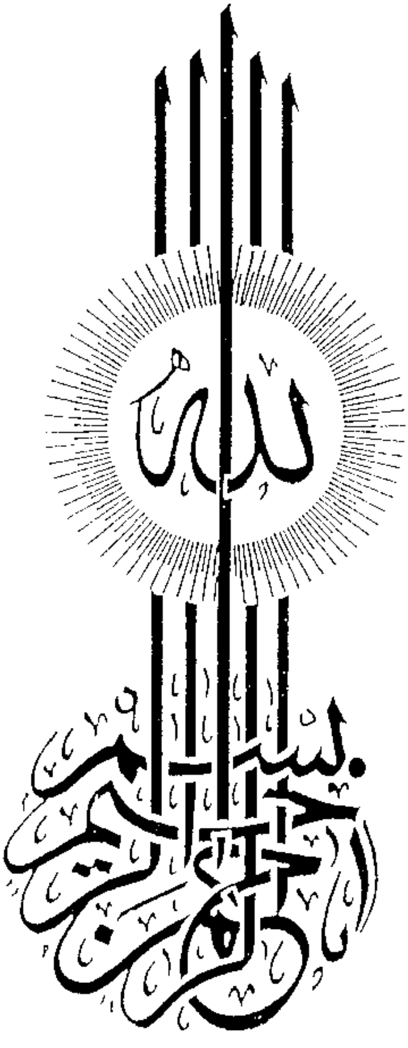
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# VITAE

Mr. El sayed Mahmoud Abd El-Rohman has graduated from Ain-Shams University, Faculty of Science in 1973 obtaining his B.Sc. degree in Physics "Special Degree". He was born in Monofia in May 1950. His primary, secondary and University educations were completed in Egyptian Institutes in Cairo.

Mr. Abd El-Rohman was appointed in Ain-Shams University as a full-time assistant instructore in the physics Department in Octoper 1973.

Mr. El-Sayed Mohmoud Abd El-Rohman attemted and completed successfully the following post graduate courses.

Theoretical Physics
Computer Programing
Advanced Electronics
Semiconductors
Crystal structure
Deffect of solids
Polymers
Transport Theory
Essay, (Amorphous semiconductors)
German Language,

These courses have been offered by the physical department, in partial fulfilment of the requirements for the M.Sc. degree, during the academic year 1973/74.

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# ABSTRACT

The effective properties of a two-phase system during phase transition used to define the volume fraction of each phase, may be helpful in understanding the mechanism of such transformation. Both the problem of studying the property-content distribution, especially the electrical conductivity and its dependance on volume part of each phase and their relative distribution, as well as the mechanism of phase transition have great theoretical and technological value.

This thesis is concerned with a theoretical investigation of the kinetic of phase transformation of pure Se, on the basis of Avrami equation in conjunction with two different models for the electrical conductivity-content dependance of a double phase system (a modified Kirkpartrick and a suggested empirical models). Two distinguished transitions have been considered; a morphous-crystalline($a \rightarrow C$) and liquid-crystalline($\ell \rightarrow C$) transitions.

As the electrical conductivity is a temperature dependant, a procedure was assumed to exclude heat effect in order to identify the volume fraction ($\alpha$) as reflected by the conductivity changes associated with phase transition only and compared to that without excluding such heat effect.

The order n characterising the mode of crystallisation, the rate k of growth and the activation energy E of phase transition in all cases have been deduced and correlated with a model reported for the crystallisation of Se through primary and secondary processes.

Crystallization of Se (in both a --> c and $\ell$ --> c transitions) occurs mainly through two subsequent processes; formation and growth of isolated fine crystallites dispersed into parent amorphous phase followed by welding of the grain boundaries to form more ordered nonisolated crystalline network.

In case where heat effect is excluded, the order n of the primary process ranges between 1.03 - 2.88 ...... for a --> c transition and between 1.13 - 3.76 for $\ell$ --> c transition (on basis of $\sigma$ ) whereas n for the secondary process ranges between 1.11 - 1.72 for a --> c transition and between ... 0.75 - 1.47, ... for $\ell$ → c transition, indicating a one-dimensional mode of crystallization. The activation energy of this second process is 20.94K Cal/mole in the ranges 100-150°C in consistent with those theoretically reported previously for pure Se.

The empirical formula (based on log $\sigma$ ) could not detect the primary process due to the low sensitivity of log $\sigma$ to the small changes in conductivity associated with this process, it could predict only the secondary process where the conductivity increases by several orders of magnitude, Meanwhile, the modified, Kirkpatrick formula proved to be more convenient in predicting both processes of crystallization in particular when the heat effect is excluded as the primary process becomes more pronounced.

# INTRODUCTION

Solids which do not meet the criterion of a long - range periodically repeated pattern of atoms are known as non - crystalline or amorphous solids(1). A distinctive class of such solids is "glasses" which can be prepared by quenching from the melt. This is to distinguish them from other amorphous solids which can be formed by various deposition techniques(2,3); e.g. by slow condensation of vapours on cold substrates. However, it is doubtful that "glasses", so defined, differ sharply in microscopic character from amorphous solids with the same composition formed in other ways.(4)

There seems to be no rigorous theoretical proof that the most stable form of a substance, even if it is monatomic, must at low temperature be crystalline rather than glassy or liquid(5). However, experience has shown that, with the exception of helium, the most stable low temperature forms of pure substances are crystalline. This may be due to that the energy of the ordered atomic arrangement is lower than that of an irregular packing of atoms.(6)

Transition from noncrystalline to crystalline state can be acheived by any activating means such as thermal energy(1) or light illumination(7). This transformation takes place through two temperature-dependent processes, a nucleation of fine crystalline centres (nuclei) and a growth of these nuclei(8). The former is very sensitive to the thermal history and the impurity centres in the material(9), while the latter may be correlated with the motion of brocken bonds, hole formation and hole motion(7). Both processes may assist hetrogeneous nucleation in Se.

The free energy of formation of nuclei or the energy threshold depends on the rate at which these new centres of the new phase are created in the parent phase. This implies the dependence on the process of diffusion and the free surface energy between the solid crystal and the parent phase(9).

Phase transformation is accompanied by remarkable changes is various physical, chemical and mechanical properties of the amorphous material(4). The determination of the changes of a certain property may be useful for qualitative and quantitative investigations of such transformation. Of these are density measurements,(10,11) optical and electrical measurements, x-ray diffraction(12,13) electron microscope spectroscopy(14,15), magnetic suscept-ibility measurements(16) as well as ESR spectroscopy(17).

It has been shown that the dc electrical conductivity can be successfully considered as experimental parameter to account for phase transformation in particular for Se and Se-like structures. This may be mainly due to the strong variation in conductivity during crystallization process; e.g. $10^6$ times for pure Se(18), and the ease with which this technique may be applied(19).

At any intermediate point during transformation, the system can be considered as a two-phase system (amorphous and crystalline existing simultanaously). The effective properties of such system used to define the volume fraction of each phase, may be helpful in understanding the transformation mechanism. Both the problem of studying the property - content characterization, especially the electrical conductivity and its dependence on volume part of each phase and their relative distribution, as well as the mechanism of phase transition have great theoretical and technological value.

This thesis is concerned with a theoretical investigation of the kinetics of phase transformation of pure Se based on a data obtained previously at our lab. Using dc electrical conductivity as an experimental parameter to follow the transformation process. Avrami equation(20,21,22) was used in conjunction with two different models of the electrical conductivity - content dependence of a double phase system.

As a matter of fact that compositional and structural heterogeneity as well as potential fluctuations seem to play an important role in noncrystalline systems. Conduction must then be treated as a percolation process" favoring pathes of high conductivity"(23,24). Part of the work is devoted to put kirkpatrick equation(25) in a modified form, which is represents the first model. The suggested familiar empirical formula(26) is the second model

Two distinguished transitions have been considered; amorphous-crystalline and Liquid ⟶ crystalline transitions.

As the electrical conductivity is a temperature dependent a procedure was assumed to exclude heat effect in order to identify the volume fraction ($\alpha$ (t)) as reflected by the conductivity changes associated with phase transition only and compared to that without excluding such heat effect. The order n characterising the mode of crystallization, the rate K of growth and the activation energy E of phase transition in all cases have been deduced and correlated with current theories now in discussion for the crystallization of Se through primary and secondary processes.