STRUCTURE AND THE EXISTENCE OF THE FIRST SHARP DIFFRACTION PEAK IN AMORPHOUS GERMANIUM PREPARED IN UHV AND MEASURED IN-SITU

by

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ABSTRACT.

The structure of "glassy" germanium films prepared by slow sublimation of germanium on heated substrates in ultra high vacuum was investigated using in-situ high energy transmission electron elastic scattering up to the scattering vector $s = 4\pi/\lambda \cdot \sin \theta \propto 10^{-1}$ Å. It is shown that on the basis of the presently available experimental evidence, there exists a number of important physical constraints as to the structure of amorphous germanium. Furthermore, a diffraction pre-peak at the scattering vector $s \approx 1.2\text{Å}^{-1}$ has been observed, that first such observation in tetrahedrally bonded elemental amorphous semiconductors. This results is discussed in light of similar observations in other disordered systems. A significance of short and medium range real space correlations in disordered systems is pointed out.
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1. INTRODUCTION

The most important parameters controlling the physical
properties of amorphous germanium (a-Ge) films (and other group IV elements) are the substrate temperature, the evaporation rate and the cleanliness of the vacuum environment during the deposition. Films prepared on heated substrates (∼ 400 K) at small evaporation rates (keeping the vacuum in the ultra high vacuum range ≤ 5 \times 10^{-10} \text{ torr}) and referred to here as class A a-Ge films, differ markedly in their physical properties from those films (referred here to as class B a-Ge films) prepared on low temperature substrates (≤ 300 K) using high evaporation rates (≥ 5 \sim 10^6 \text{Å/sec}).

The difference is most noticeable in such properties as electron spin resonance (≤ 10^{18} \text{ spins/cm}^3 in class A and ≥ 10^{20}-10^{21} \text{ spins/cm}^3 in class B), optical properties (very little or no shift in the optical absorption edge on annealing in class A and "large" shifts of the optical absorption edge on annealing in class B), d.c. electrical transport (no parallel shifts of the log of the d.c. electrical conductivity \sigma_{d.c.} versus T^{-1/4} on annealing in class A and large parallel shifts of the log of the \sigma_{d.c.} versus T^{-1/4} on annealing in class B films) the atomic structure (a homogeneous structure down to the electron microscope "resolution limit" 5-8 Å in class A films and an inhomogeneous, "crack-like" columnar structure (characteristic dimension of ∼ 10 - 40Å - small angle scattering) seen by the electron microscopy studies of class B films).
The stable, relaxed form of amorphous germanium exhibited in class A films will be referred to in the present work also as a "glassy state" of germanium in order to indicate the resemblance to bulk glasses (materials prepared by cooling from the melt). The supporting evidence for the existence of this "stable" form of germanium (stable on a time scale of some 5 years - electron microscopy study of the present work) comes also from other experiments such as an early photo-emission work on a-Ge (class A) by Laude et al\(^1\). The conclusions about the stable, glassy form of germanium from this work were later confirmed by the measurements of the optical and d.c. electrical transport properties on the same kind of films\(^2,3\). The recent measurements of the X-ray absorption near-edge structure of a-Ge\(^4\) give yet another support to this notion. In this context it should be pointed out that there is a very clear tendency of class B films to anneal towards state A as was shown in\(^5\) when comparing the temperature \(T\) dependence of the d.c. electrical transport of a-Ge films prepared by different methods and coming from different laboratories. Since the structural measurements (both X-ray\(^6\) and neutron\(^7\) elastic diffraction) have been performed on class B films, the present structural investigation has concentrated on thin class A films. A-Ge films in the present work were prepared in ultra high vacuum (UHV) by slow sublimation
of ultra pure germanium charge onto hot (400 K) substrates and they exhibited physical properties that did not change on annealing until the temperature of crystallisation (~ 250° C) has been reached. They therefore seem to represent the relaxed and stable state of a-Ge not unlike that of proper bulk glasses. To characterise the structure of these films, in-situ measurements of the density and the transmission high energy electron diffraction were performed and they were supplemented by high resolution electron microscopy. The results of the diffraction study will be reported here.

The paper is structured as follows. The next section describes the sample preparation and the experimental procedure. The obtained structural experimental results are presented in section three. In section four the available structural data on a-Ge from different measurements are brought together in order to point out the important experimentally determined constraints for possible structural models of a-Ge and there are discussed in section five in light of the concepts regarding the electron bonding in glasses as suggested by Anderson and further developed by Klinger. Finally the first observation of the First sharp diffraction peak (FSDP) in a-Ge is discussed in section six and some speculations are presented for its possible origin in disordered materials.
II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The experiments described here, were performed in the UHV-system with the base pressure of $1.10^{-10}$ torr after several days bake-out. The schematic diagram of the experimental arrangement is shown in Fig. 1.

The standard electron microscope grids, coated with approximately 100 Å of amorphous carbon and 25 Å of amorphous sapphire were used as the substrates and were placed onto a sample block which was attached to a cold finger of the rotatable liquid helium cryostat.

There were two reasons for which the amorphous sapphire was used as a substrate. Firstly, it was found\(^{(2)}\) that other substrate films such as amorphous carbon or some of the usual metallic thin film substrates (Au, Cu, Ni) reacted strongly with growing amorphous germanium film and under the UHV conditions and at the elevated substrate temperatures during the deposition, induced the partial crystallisation of germanium films already during the deposition. The situation was found to be particularly bad in the case of gold films which induced partial crystallisation of amorphous germanium even when held at room temperature during the deposition. Contrary to these materials the amorphous sapphire (experiments to produce an ultra-thin crystalline sapphire substrate were unsuccessful) and silica substrates were found
to be sufficiently chemically inert as not to interact strongly with the growing film of amorphous germanium (as deduced from other independent experiments such as optical and electrical conductivity measurements), thereby making it possible to study the properties of amorphous germanium films in their own right. Secondly, the sapphire substrates were used so that the correlation could be made with other measurements which were all performed on films grown on the single crystal sapphire substrates.

After the pump-down and the bake-out of the UHV system, the liquid helium cryostat with coated electron microscope grids was rotated so as to bring the plane of the substrate perpendicular to the axis of the UHV evaporator (see Fig.1). The a-Ge films were evaporated onto amorphous sapphire layers using evaporation rates of the order of 0.1 Å sec⁻¹.

The temperature $T_s$ of the substrate was 400 K and the pressure in the UHV chamber during evaporation was not allowed to rise above $5 \times 10^{-10}$ torr. The material used for the evaporation was high purity germanium ($10^{13}$ electrically active impurities per cm³). Once the film of the required thickness (400-500 Å) was deposited, the cryostat was rotated again (now to bring the plane of the film perpendicular to the electron optical axis). The calibration of the electron diffraction camera was done using
thin polycrystalline film of aluminium. Linearity of the scanning system was found to be better than one percent over the whole of the scanned region. The energy resolution of the energy analyser was estimated by measured aluminium plasma losses and was found to be approximately two electron volts. The energy of the electron beam, used in the diffraction experiments was 50 keV.

Amorphous germanium diffraction patterns were recorded up to $s_{\text{max}} = 10 \, \text{Å}^{-1}$ at liquid nitrogen temperature, using scintillation-photomultiplier combination to detect the individual scattered electrons and photon counting electronics to increase the signal to noise ratio. In order to be able to remove the films from the UHV system for the electron microscopy studies without breaking the vacuum, an UHV transfer device was constructed\(^\text{10}\) and could be attached to the UHV system (see Fig. 1). In this way it was possible to study the specimen by in-situ electron diffraction and to check their structure down to 5-8 Å by using the transfer device in conjunction with JEOL 220 high resolution electron microscope.

III. THE EXPERIMENTAL RESULTS
The principal result of the present investigation is shown in Fig. 2. Here the scattered intensity (not normalised) from a-Ge film is plotted against the scattering vector $s$. As can be seen from the
Fig. 2, the four first diffraction maxima are well resolved in the raw data and their positions agree well with previous electron diffraction studies. In order to be able to compare the present results with other structural data in the literature (X-ray, neutron and other electron diffraction experiments), the diffraction data of Fig. 2 were analysed to yield the total interference function

$$F(s) = \frac{I_n - f_{e1}^2(s)}{f_{e1}^2(s)} \cdot s,$$

(1)

where $I_n$ is the normalised coherent, scattered intensity, $f_{e1}(s)$ is the atomic scattering factor (Born approximation and spherically symmetrical atomic scattering potential assumed) and $s$ is the scattering vector.

The important and qualitatively new is a feature observed at approximately $s \sim 1 \text{Å}^{-1}$ (marked FSDP). Although relatively small in amplitude, it stands clearly above the noise level and there can be little doubt that it is a real feature corresponding to the interference of the electron wave scattered by the a-Ge film. The experiment was a simple sample-in - sample-out experiment and a possible artifact of the experimental set-up causing this peak in the scattered el-intensity $I(s)$
would have been picked up in the sample-out run (sample-out was a diffraction run involving only the substrate film - dashed line in Fig. 2). The significance of the observed FSDP when related to similar observations in other glassy materials will be discussed later, but it should be stressed at this point that although its effect in real space transform is obviously small (the smallness of the FSDP amplitude), its significance as for possible structural models of a-Ge is undiminished, since any structural model has to reproduce it, when the appropriate scattered intensity is calculated from the model in question. Finally it has to be pointed out also that a-Ge films investigated in the present work were microscopically homogeneous as is demonstrated in Fig. 3, where high resolution electron micrograph of the studied a-Ge films does not resolve any inhomogeneities down to the resolution limit (some 5-8 Å). Below this size the term "inhomogeneities" (inhomogeneities referring now for example to atomic size empty spaces, groups of weakly bonded atoms\(^{9,11}\) etc.) homogeneously distributed throughout the structure loses its physical meaning and the above mentioned entities have to be considered rather as an integral part of the glassy state\(^{12}\).
The incoherent contributions to the total scattered intensity due to the background, the substrate, the elastic multiple scattering and the inelastic thermal diffuse scattering were substracted using the selfconsistent method proposed by Nabitovich et al.\textsuperscript{(13)}. The resulting coherent scattered intensity was normalised to the independent atomic scattering factor $f_{el}(s)\textsuperscript{(13)}$ and $F(s)$ was then calculated according to the equation (1) and is displayed in Fig. 4.

Because of the termination of $F(s)$ at $s_{max} \approx 9.0 \text{ Å}^{-1}$ and the inevitable errors caused by the incoherent contributions to the total elastic scattered intensity just mentioned, the real space data are of limited value and should serve only as qualitative estimates of trends in real space. They are displayed, together with the measured reciprocal space parameters, in Table 1, where they are compared with work of Paul et al.\textsuperscript{(6)} and Etherington et al.\textsuperscript{(7)}.

**IV. THE STRUCTURAL DATA - GENERAL TRENDS**

The general trends in the Table 1 regarding the usual standard parameters can be summarized as follows:
1) In accord with previous results\textsuperscript{(6,7)}, there does not seem to be any experimental evidence in the present work for the disorder induced variation in first nearest neighbour distance (the strength of the basic covalent sp\textsuperscript{3} bond is the same as in the crystalline phase and does not have any measurable dispersion around the mean value), the whole of the first nearest neighbour peak width being accounted for by the temperature broadening (assuming approximately the same Debye-Waller factor parameters as in the crystal\textsuperscript{(7)}).

2) The present work results indicate quite a large decrease in the number of first nearest neighbours relative to the crystalline phase. The deduced value of \( n_1 = 3.5 \) is smaller than both in the X-ray work of Paul et al.\textsuperscript{(6)} (value of 3.8 quoted) and in the neutron data of Etherington et al.\textsuperscript{(7)}, where the value of 3.68 was deduced. In view of the different preparation conditions this discrepancy should not be considered to be too serious. One very important conclusion can be drawn from the present work and the results of X-ray and the neutron investigations, namely that the first nearest neighbour co-ordination in amorphous germanium is appreciably less (3.6 - depending on the preparation conditions) than in the corresponding crystalline phase (4.0). This decrease (of the order of 10\%) relative to the crystal has
to be considered as an important difference and it is bound to affect even the calculations of the electronic ground state of amorphous germanium\(^{(14)}\), especially at the extremities of the respective bands. It is interesting to note that as the preparation conditions are improved and the resulting amorphous germanium films are more stable, the number of the first nearest neighbours tends to decrease giving an indirect support to the topological constraints when forming a "good", stable, bulk glass as suggested by Phillips\(^{(15)}\) (the best glass formers having the nearest neighbour co-ordination number between two and three).

The nearest neighbour co-ordination number of some 3.5 in thin a-Ge films found in this work correlates well with in-situ density measurements on the same films\(^{(16)}\) where an appreciable density deficit (~15\%) relative to the crystalline phase was found. Although the result was somewhat thickness dependent (for thicker samples the density deficit was less - some 3\% for 1 micron thick film) it indicated that contrary to the previous measurements there is a clear tendency towards a formation of less dense structures in class A a-Ge films. Further confirmation of this result came from in-situ optical measurements\(^{(17)}\) where the low energy (E ≤ 0.5 eV) refractive index n in the same films was found to be lower than in the crystalline phase (the value of
n ≈ 3.6 was found in thin films with density deficit of 15%.

It has to be stressed that the low value of the nearest neighbour co-ordination number found in the present work merely confirms the previous and more precise structural investigations of \( \alpha \)-Ge using X-rays\(^6\) and slow neutrons\(^7\) and therefore it has to be considered as an important and general experimental fact. It is surprising that this valuable structural information has gone unnoticed in the previous discussions of the structure of amorphous germanium.

3) The number of atoms in the second co-ordination shell-\( n_2 \) has been found to be 13.5 and it is somewhat larger than the value deduced from both X-ray\(^6\) and the neutron\(^7\) investigations. This trend however (increase in the second nearest neighbour co-ordination number with improvement of the preparation conditions - such as the increase of the substrate temperature during the deposition) is apparent already in the X-ray work of Paul et al.\(^6\). Also interesting in this context is the fact that a similar trend is observed in some glassy metals\(^{18,19}\), although the cause of this tendency there (chemical short range order) is formally somewhat different from the present case (the point to be discussed further in the following paragraph).
4) It could be argued that the results of the present work also indicate a slight increase in the first nearest neighbour distance (from 2.47 Å to 2.50 Å - "softening" of the basic covalent bond) and slight decrease in the second nearest neighbour distance (from 4.0 Å to 3.97 Å). These differences are however within the experimental error of the present investigation and should be therefore considered only with a caution. Clearly, more careful experiments on samples prepared under the same conditions as in the present work are called for, to clarify this potentially important point.

V. PHYSICAL CONSTRAINTS CONCERNING THE STRUCTURE OF a-Ge

In view of the presented structural results and those of other investigations\(^\text{(6,7)}\), it seems now worthwhile to summarise those experimental findings which are most relevant when considering various models for the structure of a-Ge. These findings lead to some definite constrains and requirements as to what general physical principles and approaches one has to adopt when addressing the question of the structure of a-Ge. These constraints can be summarised in the following four points:

1) **Nearest-neighbour co-ordination number is low relative to crystalline value** (approximately
3.6-3.8 compared with a value of 4.00 in the crystalline phase).

2) **The basic covalent bond is sp³ hybrid and there is no measurable distribution in its length.**

3) **The electron spin density in class A films especially is low - some 10¹⁸ spins/cm³.**

4) **The density of the films tends to be appreciably lower than in the crystal.**

At first sight there seems to be a conflict. On one hand the atoms are bonded by sp³ bonds with some 10% of them being apparently only 3 fold co-ordinated and one therefore expects a relatively large (~ 10²¹ cm⁻³) free spin density coming from the unpaired valence electrons. On the other hand however the experiments also show that the number of free, unpaired spins in class A films especially is some factor of 10³ less. It is therefore clear that most of the "free", unpaired electrons have to pair and form diamagnetic entities, but these are not sp³ bonds.

A possible and quite natural explanation to this problem is offered by Anderson's concept⁸ of an attractive effective interaction between two electrons in some diamagnetic glassy semiconductors.
The local distortion of the lattice due to the charge-lattice interaction when two electrons are placed on a "site" can be so large, that it offsets the repulsive Coulomb interaction between them and the electron pair together with the lattice distortion form a "diamagnetic bond" which can be nearly as stable as the standard sp³ bond itself. Using this concept it is therefore easy to understand why most of the valence electrons in a-Ge which do not participate in directed covalent sp³ bonds pair diamagnetically any way.

The question remains what are the "sites" where the electron pairing (to be distinguished from sp³ covalent bonding) occurs, how many of them there are in an amorphous semiconductor such as stable a-Ge film and what is their possible origin? From the above arguments it follows that the density of these "sites" should be some 5-10% of the atomic number density and for this reason they can not really be considered as defects, but rather as an integral part of the structure itself. As to the possible nature of the electron pairing sites, a very plausible and interesting theoretical model was developed recently by Klinger⁹,¹⁰ to account for low temperature behaviour in amorphous and glassy semiconductors, which is general enough to be extended to present case. The essence of the model lies in postulating an existence in the random network of
relatively large number of microscopic regions (one to few atoms) where the interatomic potential is highly non-linear and large atomic displacements are possible with no appreciable increase in the lattice strain energy ("critical atomic potentials"\(^{(9,10)}\).

Extending Anderson's concept to this atomic model, it was possible to account for a number of electronic phenomena observed in glasses such as light-induced metastable paramagnetism, photostructural changes, quenching of the photoluminescence, presence of the non-radiative recombination channels in the photoluminescence and others. In particular it was possible to show that electron selftrapping can indeed occur at the "critical atomic potential sites" and that two electron states are more stable than the single electron ones. If the electron pairing "sites" discussed above are identified with Klinger's "critical atomic potential sites", it is also possible to speculate about their origin as coming from the preparation process itself. In glassy semiconductors (prepared by quenching the melt) they can be considered as frozen-in fluidity modes reflecting the highly non-linear nature of the interatomic potential in the fluid state. They are identified by Klinger somewhat differently - simply as frozen-in fluid atomic density fluctuations.

In the recent work\(^{(12)}\) the idea of viewing the chalcogenide glasses as thermodynamic "defect" semi-
conductors was raised and can be related to Klinger's "critical potential sites".
In this context the formation of an amorphous germanium should be considered as spatially local (non-ergodic) minimisation of the total energy of the system through covalent bonding plus electron pairing with the appropriate lattice distortions at the electron pairing "sites". It is important to stress at this point that in this picture the 8-N bonding rule is assumed not to be valid, the assumption which is of course born out by experiment. The relative concentration of the electron pairing "sites" is determined by the energy and time considerations during the preparation process.

VI. THE DIFFRACTION PRE-PEAK AT 1.2 Å⁻¹
The second important and qualitatively new feature in the diffraction pattern shown in Fig. 2 (the feature is of course seen also in Fig. 4, although here it is somewhat smaller due to scaling with s and possible normalisation errors) is the observation of an extra maximum (relatively sharp!) in the total scattered intensity at the value of s = 1.2 Å⁻¹. This is the first time that what is known in literature as the "First Sharp Diffraction Peak" - FSDP has been identified also in the elemental tetrahedrally bonded amorphous semiconductor. Although relatively weak (comparable in strength only with higher order diffraction peaks), this feature is nevertheless
sharp and strong enough (see Fig. 2) to be considered as an important new experimental finding (the trace in Fig. 2 is a direct output from the diffraction experiment independent of any possible subsequent analysis in terms of normalisation and/or separation into a coherent, single scattering event elastic part and an incoherent part).

The significance of the FSDP observed in the present work on amorphous germanium lies therefore clearly in its very existence rather than in the possible way it might affect the real space structural results; here the effect will be understandably small because of the pre-peak's relative weakness when compared with the first two diffraction peaks (see Fig. 3) which will carry the main weight in the Fourier analysis. In this sense it is therefore its existence that might serve as an important test for any real space structural model for the stable, amorphous germanium (class A films) since it represents an extra feature in the diffraction pattern at low values of \( s \) that has to be reproduced, when any such model is Fourier transformed into the scattering space.

It should be mentioned at this point that although it is not clear precisely why the FSDP has not been observed in \( \alpha \)-Ge in the previous structural investigations, the most likely explanation is the difference in the preparation conditions between films of class B (the previous investigations) and thin films of
class A (present work). The other important difference lies in the temperature of the measurements (300 K in the previous investigations and 77 K in the present work).

**FSDP - The general trends.**

The existence of the FSDP in disordered systems has been known for some time. It has been observed in "proper" bulk covalent glasses such as As$_2$S$_3$\textsuperscript{(20)}, As$_2$Se$_3$\textsuperscript{(21)}, Ge S$_2$\textsuperscript{(22)}, Ge Se$_2$\textsuperscript{(23)}, SiO$_2$\textsuperscript{(24)}, but also in elemental amorphous Sb\textsuperscript{(25)}, P\textsuperscript{(26)}, As\textsuperscript{(27,28)}, and even in some metallic glasses and liquid metal alloys (18,19,29). The experimental and theoretical situation around FSDP has been reviewed by Phillips\textsuperscript{(15)} and more recently by Moss and Price\textsuperscript{(30)}. Various models have been put forward to explain the existence of the FSDP in each particular material or group of materials. They range from the concept of local chemical order\textsuperscript{(19,31)} (metallic glasses and liquid metal alloys) to various cluster models\textsuperscript{(30,31)} and layered structures\textsuperscript{(15)} (covalent bulk glasses). However, despite the occurrence of this phenomenon in different disordered materials, only recently an attempt to look for a more general explanation has been made\textsuperscript{(30)} in terms of Random Packing of Structural (molecular-like) Units (RPSU). Bearing in mind the obvious differences among the various disordered systems exhibiting the FSDP (and
therefore the possibility of different physical causes for the occurrence of the FSDP), it is tempting, in the light of the present work and the experimental evidence available so far, to look for some underlying principles and tendencies, common to all of these systems. To characterise the FSDP, when it is observed, it can be said, that the existence of the FSDP does not seem to depend on

a) nearest neighbour coordination (from 2–3 in chalcogenides glasses to more than ten in metallic glasses),

b) the nature of bonding and/or the electronic structure of the system (amorphous metals, semiconductors and insulators, exhibiting what is believed to be metallic, covalent and partially ionic bonding all show FSDP) and

c) the number of the constituents in the system (both elemental and the multi-component disordered system exhibit FSDP).

The strength of the FSDP on the other hand does seem to depend generally on the "quality" of the glass (at least in the covalent disordered solids). Better the glass is, stronger and more persistent is the FSDP\(^{(15)}\) (the definition of the quality of the glass as given by Phillips\(^{(15)}\) is adopted here i.e. as the inverse of its minimal quenching rate - the slowest cooling rate which can be employed without crystallisation of the supercooled liquid). The second very important
property of the FSDP is the dependence of its strength on temperature. In well annealed films and in bulk glasses this does not follow the usual Debye-Waller factor temperature dependence, but on contrary it seems that the amplitude of the FSDP if anything, increases with increasing temperature\(^{(21)}\) and in some cases it does so all the way through glass transition temperature and into the liquid phase\(^{(23)}\). This suggests strongly that there are some definite dynamical effects that have to be taken into account when an attempt is made to explain the origin of FSDP.

This temperature caused dynamical effect observed in well annealed films (and in bulk glasses) should be considered separately from the effect of annealing on the strength of the FSDP in as-deposited films of for example \(a\)-\(\text{As}_2\text{S}_3\)\(^{(20)}\) where structural relaxation seems to play a dominant role (a point to be discussed in the following paragraph).

Two characteristic features seem to be common to all disordered systems, exhibiting the FSDP. These are the existence of the disorder (manifestation of non-ergodicity of the system) itself and the density deficit (usually \(\geq 10\%\) below the crystalline phase, where such phase exists, although only a few percent in metallic glasses, the difference reflecting the effect of the nature of bonding and the easiness of denser packing in these systems - increased nearest-neighbour co-ordination). The present work on \(a\)-\(\text{Ge}\)
supports this view since, contrary to previous results, in-situ measurements of the density in this work revealed a relatively large density deficit with respect to crystal\(^{(16)}\).

The previous attempts\(^{(15,31)}\) to explain the existence of the FSDP were usually quite specific, relating to some real space feature, characteristic of the particular system under investigation. However, in view of the "sharpness" (FWHM) of the FSDP (all real space correlations have to contribute through a weighted Fourier transform to the scattered intensity) and the generality of occurrence, these models are too restrictive and therefore somewhat unlikely. A step in the right direction has been taken recently by Moss and Price\(^{(30)}\) who showed that a number of structural observations can be explained qualitatively (and in some cases also quantitatively) by viewing the structure of disordered systems exhibiting the FSDP as random packing of microscopic (molecular like) structural units (RPSU).

Here the word random means averaging over all spatially possible orientations of the elemental molecular structural unit. The spacing between the centers of the structural units has a reasonably well defined mean value over a characteristic correlation (coherence) length. It is the size of the elemental structural units and the characteristic coherence length that gives rise to the FSDP and its width respectively.
There is some evidence that this approach (RPSU) correlated reasonably well also with some aspects of the electronic structure (electron band structure). An amorphous Arsenic for example (32) when prepared on low temperature substrates (77 K) (atomic mobility low), seemed to form a molecular-like insulating solid film which was transparent in the optical frequency spectrum and had a very high resistivity, supporting the RPSU model, structural units being here As\textsubscript{n} "molecules" where n is a small number (electronic structure based on very weakly coupled set of a single units leading to large optical gap and very high electrical resistivity typical of a molecular As\textsubscript{n}).

On annealing the electronic structure changed drastically, the "intermolecular" interactions becoming increasingly important, leading eventually to the formation of Continuos Random Network (CRN) with a typical semiconducting behaviour (lower electronic band gap and appreciably lower electrical resistivity). The strength of the FSDP in this temperature range (annealing up to a "glassy", stable CRN state) would be expected to decrease with increasing temperature through this structural relaxation and the experiments on As\textsubscript{2}S\textsubscript{3} films indicate that this is indeed the case (20, 33) (the amplitude of the FSDP in as-deposited evaporated films decreased on annealing to the value characteristic of the bulk glass). On further
increase in the temperature however the FSDP generally increases in amplitude through the temperature dynamical effect as had been mentioned previously. It is in this respect that the RPSU model must not be taken too literally but should be rather considered as an indicator of a tendency of a system to "order" (minimise its total energy) on an increasingly smaller spatial scale with increasing degree of non-ergodicity (limiting the atomic motions) in the system during the preparation process (for example by increasing the quenching rate when preparing a glass from the melt or by increasing the evaporation rate and/or decreasing the substrate temperature when preparing an amorphous film by vapour condensation).

It will be argued in the next section that in well-annealed, stable films and in bulk glasses this range reflects the spatial range over which the effective one-electron bonding interactions are finite\(^{(14,34,35)}\) and that it is this spatial range that is responsible for the "real space range of atomic correlations" and the existence of the FSDP. A decrease of the range of electronic bonding interactions through an increased degree of non-ergodicity will eventually lead to the above discussed RPSU model describing more or less correctly both the electronic and the structural properties of the system under consideration. The tendency for short range chemical order seen in some
metallic glasses\(^{(19)}\) can be also linked in this way to the finite spatial range of the effective one-electron Hamiltonian. On the other hand an increase of the spatial range over which the system will minimise its energy (increasing the degree of ergodicity through increased atomic mobility) will lead to the formation of the microcrystalline, poly-crystalline and monocristalline phase.

**THE POSSIBLE ORIGIN OF THE FSDP**

In view of the experimental evidence and models discussed above, the present attempt to explain the FSDP rests on the general concept of non-ergodicity in disordered systems\(^{(35)}\) and on the dynamics of atomic motions. The basic notion is that through limiting the energy and/or time scales during the formation of a disordered solid (either from the melt or by evaporation), the system is effectively forced to search for a minimum energy state on a progressively smaller spatial scale (the system is idealised by assuming that effects due to walls and surfaces can be neglected - at least in the first approximation). This spatial scale is not a single, precisely defined length scale, but it should be rather considered as an "effective spatial range", described perhaps by some algebraic decay \(R^{-\eta(16)}\), where \(R\) is a spatial co-ordinate and \(\eta\) is a characteristic exponent expressing the degree of non-ergodicity \((\eta\) increases with increasing degree of non-ergodicity).
The effective attractive atomic potential which will be "seen" by a valence electron responsible for binding and cohesion is postulated to come from within this "effective spatial range" $R^{-n}$, the rest of the potential being effectively screened out very much in the spirit of the chemical pseudopotential concept\(^{(14,35)}\) used for the real space calculations of the electronic structure (bonding and cohesion) in disordered systems. Here a clear reference is being made to now increasingly well-established notion in modern theory of Condensed Matter, namely that the essential properties of solids (such as for example the overall density of one-electron states and the existence of the band gaps, cohesion, general rigidity and others) are almost completely determined by short range effective one-particle interactions (and/or by the local atomic environment\(^{(14,34)}\)). The new aspect in this context is an attempt in the present work to link the "effectiveness" of screening out more distant parts of the one-electron attractive atomic potential with the degree of non-ergodicity in the system, which in the present model manifests itself through limiting the atomic motions of the system. It is these motions (quite often diffusive rather than just oscillatory) that allow the changes in the bonding (and therefore in the topology of the atomic structure) to take place and thereby allowing the system to choose the structure with minimum total energy. If impeded, other
bonding arrangements (topologies) will be taken up by the system, including some more exotic possibilities such as electron pairing in a homogeneous structure as suggested by Anderson\(^8\), electron pairing at frozen-in fluid density fluctuations ("critical potentials") suggested by Klinger\(^9\), formation of polarons and/or solitons, and possibly other structure stabilising "defects"\(^{12}\).

Different topologies of these non-ergodic atomic structures (as manifested for example by a-Ge with nearest neighbour co-ordination of some 3.6) makes them temporally stable at low enough temperatures although in many cases they can be stable all the way up to and through the glass transition temperature.

Having made link between the degree of non-ergodicity during the preparation of a disordered film or a glass and the corresponding "effective range" \(R^{-\eta}\) of the one-electron attractive atomic potential seen by the valence bonding electrons (it has to be stressed at this point that the effective range \(R^{-\eta}\) is the same at each atomic site in the system), it can be further argued that it is this range and the corresponding effective one-electron Hamiltonian describing the major electron bonding interactions that in turn will determine the range of the atomic structural correlations and the final static atomic structure.

It is suggested that it is the range of the real
space atomic correlations and the way they decay in space that gives rise to the existence and the form of the FSDP in many disordered materials. To make a connection between the present model (finite spatial range of the effective one-electron bonding interactions caused by the non-ergodicity of the system during the preparation) and the Random-Packings of Structural Units model put forward by Moss and Price\(^{30}\), it is only necessary to realise that in the limit of very large degree of non-ergodicity, the valence electrons' orbitals will be so atomic-like (molecular-like) that only a minimum interatomic (intermolecular) interaction will occur leading to a solid comprised of an assembly of very weakly coupled (for example through Van-der Waals forces) atoms and/or molecular units. The RPSU model can be therefore considered as a strong non-ergodicity limit of the present model. Finally some few more remarks should be made concerning the present model.

Firstly, an increase in the amplitude of the FSDP with temperature (of the well annealed, stable films or glassy specimen) means a further decrease of the spatial range of the effective bonding interactions. The proposed model therefore implies a relatively very short range of the effective one-particle (electron) interactions for a liquid in thermodynamical equilibrium.
Secondly, the existence of the crystalline phase in the proposed model is related to the ergodic conditions of the preparation process in the following way. Firstly a sufficient energy (coming from the external energy source such as oven, substrate or a laser) is transferred quickly into the atomic motions (energy scales mentioned previously) and then it is subsequently released slowly (ergodically) to the external environment (time scales mentioned previously). In this way a gradual increase of the long range order parameter is possible.

It is believed also that although the range of the effective one-electron bonding interactions in the crystalline phase (of for example germanium) is not appreciably larger than in the disordered phase\(^{14}\) the main reason for non-existence of the FSDP in the crystal is related to its destruction through established "infinite" range of real space correlations (the formation and growth of the crystalline order parameter - three dimensional mass density wave for example\(^{34}\)).

Thirdly, in one-component systems, the local spatial range of one-electron bonding interactions seems to manifest itself through changes in the number of neighbours in the first and second co-ordination shell together with finite density deficit, leaving the basic bond unaltered (in the first approximation), all relative to the crystalline phase. In the multi-
component systems on the other hand (glassy metals in particular) its manifestation seems to be through a strong tendency towards a chemical short range order\textsuperscript{(19)}.

Fourthly, in well annealed, stable glassy films (class A films) and also in the well-prepared, stable bulk glasses the existence of the FSDP might be considered as a "range" parameter of one-electron bonding interactions in the material.

Finally, the FSDP should be considered as a very important test for man or computer built structural models in that when they are appropriately Fourier transformed into reciprocal (scattering) space, the FSDP has to be reproduced both in the position, but also in its form.

VII. CONCLUSION

The atomic structure of a-Ge films prepared in ultra high vacuum by slow sublimation on heated substrates was investigated by in-situ high energy electron diffraction. From these and other complementary measurements it was established that the films were homogeneous down to 5-8 Å, that they were stable temporally and that the density was appreciably lower than in the crystalline phase. The main structural results can be summarised as follows:
1) The strength of the basic sp\textsuperscript{3} bond is the same as in the crystal.

2) There is no evidence for disorder induced variation in the first nearest-neighbour distance (all of the observed width of the first nearest neighbour peak can be accounted for by temperature broadening).

3) The nearest neighbour co-ordination of some 3.5 is appreciably less than in the corresponding crystalline phase.

4) The free spin density in these films is low (~10\textsuperscript{18} cm\textsuperscript{-3}).

On the basis of these findings it is argued that an appreciable electron pairing (electrons not participating in the direct covalent sp\textsuperscript{3} bonds) has to occur in a-Ge films of class A. It seems also that the overall topology is not that of four fold co-ordinated continuous random network, but involves various other local bonding arrangements.

5) What is known as a "First Sharp Diffraction Peak" has been observed in these films at a scattering vector of s \approx 1.2\textpm{}1.

The existence of the FSDP was discussed in relation with other disordered materials exhibiting this feature in the diffraction pattern. An attempt was made to relate the non-ergodic nature of
the preparation process of amorphous films or bulk glasses to the finite spatial range of the effective one-electron bonding interactions. It is argued that it is this range of bonding interactions that is responsible for the formation of the real space static atomic correlations, but also for how these decay in real space. Both the range of the correlations and the decay parameter determine the existence and the exact shape of the observed FSDP.

VIII. ACKNOWLEDGEMENTS

The experimental part of the presented work has been performed at P.C.S., Cavendish Laboratory, University of Cambridge, England. It is a pleasure to acknowledge A.D. Yoffe for his continuous interest and support throughout this work.

The author also acknowledges very enlightening discussions with M.I. Klinger concerning various aspects of the electronic and structural properties of glasses and amorphous materials.
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Table 1  Scattering space and real space structural parameters determined from the present work and from the work of Paul et al. (6) and Etherington et al. (7).
<table>
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<td></td>
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<td>5</td>
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i - i'th nearest neighbour in real space

r_i(Å) - real space position of the i'th nearest neighbour

n_i - number of i'th nearest neighbours
FIGURE CAPTIONS.

Figure 1  Schematic diagram of the sample block, the evaporator, the high energy electron diffraction camera and the transfer device (es = evaporation source, rs = radiation shield ms = mechanical shutter, qc = quartz crystal oscillator, em = evaporation mask, sb = sample block, f = filament, W = Wehnelt, a = anode, ca = condenser aperture, dc = deflector coils, cl = condenser lens, sc = scanning coils, e, eg = energy analyser electrodes, ap = aperture, sc = scintillator).

Figure 2  Plot of elastically scattered unnormalized electron intensity versus scattering vector s for a-Ge films. Scattered intensity from the substrate is also shown (dashed line).

Figure 3  High resolution electron micrograph of a-Ge films investigated in this work (Bright field - magnification ~ 1,6\cdot10^6).

Figure 4  Plot of the total interference function $F(s)$ versus scattering vector $s$ for studied a-Ge films.
STRUCTURE AND THE EXISTENCE OF THE FIRST SHARP DIFFRACTION PEAK IN AMORPHOUS GERMANIUM PREPARED IN UHV AND MEASURED IN-SITU

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The structure of "glassy" germanium films prepared by slow sublimation of germanium on heated substrates in ultra high vacuum was investigated using in-situ high energy transmission electron elastic scattering up to the scattering vector \( s = (4\pi/\lambda) \sin \theta \approx 10 \text{ \AA}^{-1} \).

It is shown that on the basis of the presently available experimental evidence, there exists a number of important physical constraints as to the structure of amorphous germanium. Furthermore, a diffraction pre-peak at the scattering vector \( s \approx 1.2 \text{ \AA}^{-1} \) has been observed, the first such observation in tetrahedrally bonded elemental amorphous semiconductor. This result is discussed in light of similar observations in other disordered systems.

1. INTRODUCTION

The most important parameters controlling the physical properties of amorphous germanium (a-Ge) films (and other group IV elements) are the substrate temperature, the evaporation rate and the cleanliness of the vacuum environment during the deposition. Films prepared on heated substrates at small evaporation rates (keeping the vacuum in the ultra high vacuum range \( \approx 5 \cdot 10^{-10} \text{ torr} \)) and referred to here as class A a-Ge films, differ markedly in their physical properties from those films (referred here to as class B films) prepared on low temperature substrates (\( \approx 300 \text{ K} \)) using high evaporation rates (\( \gtrsim 5 - 10 \text{ \AA/sec.} \)).

The difference is most noticeable in such properties as electron spin resonance (\( \gtrsim 10^{18} \text{ spins/cm}^3 \) in class A and \( \gtrsim 10^{20} - 10^{21} \text{ spins/cm}^3 \) in class B), optical properties (very little or no shift in the optical absorption edge on annealing in class A and "large" shifts of the optical absorption edge on annealing in class B), d.c. electrical transport (no parallel shifts of the log of the d.c. electrical conductivity \( \sigma \text{ d.c.} \) versus temperature \( T^{-1/4} \) on annealing in class A and large parallel shifts of the log of the \( \sigma \text{ d.c.} \) versus \( T^{-1/4} \) on annealing in class B) and the atomic structure (a homogeneous structure down to the electron microscope "resolution limit" 5-8 \( \text{ 	ext{\AA}} \) in class A and inhomogeneous, "crack-like" columnar structure (characteristic dimension of \( \approx 10-40 \text{ \AA} \) small angle scattering) seen by the electron microscopy studies of class B films). Despite the above mentioned differences there seems
to be a clear tendency of class B films to anneal towards state A (1). Since the structural measurements (both X-ray (2) and neutron (3) elastic diffraction) have been performed on class B films, the present structural investigation has concentrated on class A films.

2. THE EXPERIMENTAL RESULTS

The principal result of the present investigation is shown in Figure 1. Here the scattered intensity (not normalised) from a-Ge film is plotted against the scattering vector $s$.

![Graph showing scattered intensity vs. scattering vector $s$]

FIGURE 1

As can be seen from the Fig.1, the four first diffraction maxima are well resolved in the raw data and their positions agree well with previous diffraction studies.

The important and qualitatively new is however a feature observed at approximately $s \approx 1 \text{ Å}^{-1}$ (marked FSDP).

It has to be pointed out that a-Ge films investigated in the present work were microscopically homogeneous as is demonstrated in Fig.2, where bright field high resolution electron micrograph (magnification appr. $2.3 \times 10^5$) of the studied a-Ge films does not resolve any inhomogeneities down to the resolution limit (some 5-8 Å). Because of the termination of the scattering experiment at $s_{\text{max}} \approx 9.0 \text{ Å}^{-1}$ and because of the inevitable errors caused by the incoherent contributions to the total elastic scattered intensity, the real space data are of limited value and should serve only as qualitative estimates of trends in the real space. Nevertheless they are displayed together with the measured reciprocal space parameters in Table 1, where they are compared with work of
Paul et al. (2) and Etherington et al. (3).

TABLE 1

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<th>Diffraction ring</th>
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<th>present work ( s(A^{-1}) )</th>
<th>nearest neighbour ( r_i(A) )</th>
<th>( n_i )</th>
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</table>

1. \( i \)th nearest neighbour in real space
2. \( r_i(A) \) - real space position of the \( i \)th nearest neighbour
3. \( n_i \) - number of \( i \)th nearest neighbours

In view of the present investigation and those of others (2,3), it seems now worthwhile to summarise those experimental findings which are most relevant when considering various models for the structure of a-Ge. These findings lead to some definite constrains and requirements as to what general physical principles and approaches one has to adopt when addressing the question of the structure of a-Ge. These constrains can be summarised in the following four points:

1) Nearest-neighbour co-ordination number is low relative to crystalline value (approximately 3.5-3.8 compared with a value of 4.00 in the crystalline phase).
2) The basic covalent bond is \( sp^3 \) hybrid and there is no measureable distribution in its length.
3) The electron spin density in class A films is low - some \( 10^{18} \) spins/cm³.
4) The density of the films tends to be appreciably lower than in the crystal.

3. THE DIFFRACTION PRE-PEAK AT 1.2 \( A^{-1} \)

The important and qualitatively new feature in the diffraction pattern shown in Fig.1 is the observation of an extra maximum (relatively sharp!) in the total scattered intensity at the value of \( s = 1.2 \ A^{-1} \). The existence of the ESDP in disordered systems has been known for some time, but only recently an attempt to look for a more general explanation has been made (4) in terms of Random Packing of Structural (molecular-like) Units (RPSU) explaining a number of structural observations. The RPSU model should not be taken too literally, but should be rather considered as an indication of a tendency of a system to "order" (minimise its total energy) on an increasingly smaller spatial scale.
with increasing degree of non-ergodicity (limiting the atomic motions) in the system during the preparation process (for example by increasing the quenching rate when preparing a glass from the melt or by increasing the evaporation rate and/or decreasing the substrate temperature when preparing an amorphous film by vapour condensation). It is suggested that the effective atomic potential which will be "seen" by valence electrons responsible for binding and cohesion comes from within this "effective spatial range", the rest of the potential being effectively screened out very much in the spirit of the chemical pseudopotential concept (5). The new aspect in this context is an attempt in the present work to link the effectiveness of screening out increasingly closer parts of the one-electron attractive atomic potential with increasing degree of non-ergodicity. If the atomic motions (quite often diffusive rather than just oscillatory) that allow the changes in the bonding (and therefore in the topology of the atomic structure) to take place (thereby allowing the system to choose the structure with minimum total energy) are impeded, other than usual bonding arrangements (topologies) might be taken up by the system, including some more exotic possibilities such as electron pairing in a homogeneous structure as suggested by Anderson (6), electron pairing at frozen-in fluid density fluctuations ("critical potentials") suggested by Klinger (7), formation of polarons and/or bipolarons and possibly other structure stabilising "defects"(8). It can be then further argued that it is this spatial range describing the major electron bonding interactions that determines the atomic structural correlations in the final static atomic structure and that it is the range of these atomic correlations and the way these decay in space that gives rise to the existence and the form of the FSDP in disordered materials.

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