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I. Introduction

The work described within this report represents the fruits of our first six months' efforts to study the relationships among structure, bonding, electronic structure and transport properties of amorphous semiconductors. This initial report tends to emphasize the work of three groups working in individual areas, and to neglect the collaborative efforts which are just beginning. It deals, therefore, first with structural studies of Ge-Te alloys, doped As_2Se_3 and group IV elements. The second portion of the report describes optical and photoemission studies of some of these materials, while the third section deals with transport properties of more complex systems.

This separation in the early stages has been dictated by the necessity of obtaining reliable data through the individual approaches. Studies of the relationships among them are now beginning and will be dealt with in the next report. We should also mention that collaboration on matters related to sample preparation and other experimental techniques has already proved quite valuable and increased the efficiency of our operation. Since, for the most part, these collaborations involve equipment which has just recently been installed in Stanford's Center for Materials Research, they cannot yet be described in a report dealing, primarily, with the actual results obtained in the program thus far.

II. X-Ray and Neutron Diffraction Radial Distribution Studies (F. Betts, A. Bienestock, K. Connell, D. Keating, and S. C. Rowland)

In earlier work[1,2] we examined the structures of amorphous GeTe and various Ge_xTe_{1-x} alloy films by means of x-ray diffraction radial distributions. The most important result of these studies was that the interatomic distances throughout the composition range studied ($.1< x < .7$) appeared covalent. This result is consistent with the Mott[3] or Cohen, Fritzsche and Ovshinsky[4] pictures of why many amorphous semiconductor conductivities are so insensitive to many impurities. In these pictures, each atom is coordinated such that covalent bonding requirements are satisfied locally. As a result, no significant number of donor or acceptor states are formed. The result is particularly striking because the crystalline GeTe, which would appear throughout the composition range studied, in equilibrium, has significantly larger nearest neighbor GeTe separations which cannot be described in terms of simple covalent bonding.

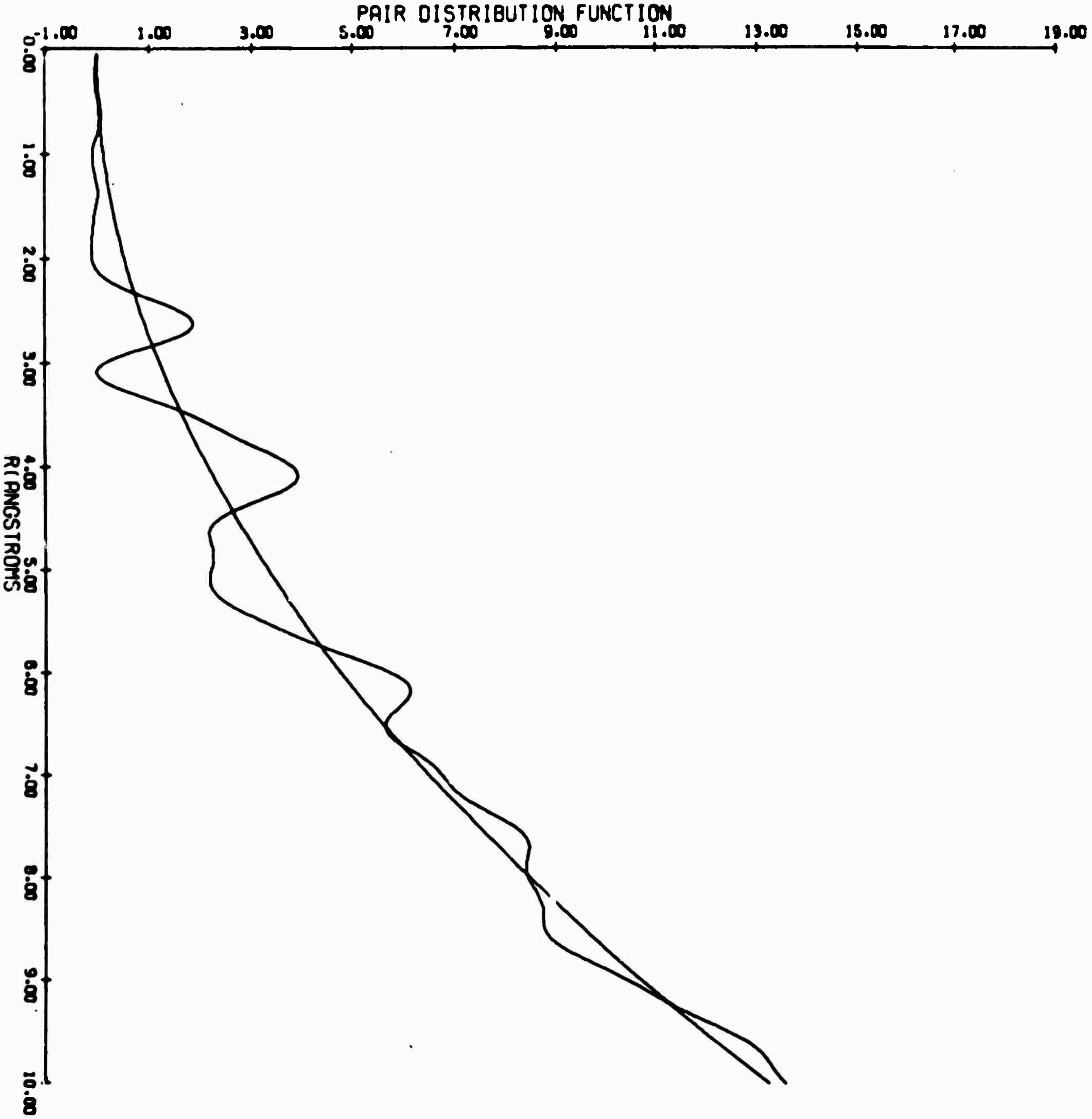
For the alloys which are dilute in Ge, it was proposed by us[2] that the structure is one in which Ge atoms cross-link Te chains. The best evidence for this structure came from careful analysis of an x-ray diffraction radial distribution obtained from a film of composition $Ge_{.11}Te_{.89}$.

This x-ray diffraction study was inconclusive for a number of reasons. The first is that any such x-ray radial distribution study is necessarily ambiguous, as discussed by Keating.[5] More important. however, is the fact that it was difficult to make strong statements about the Ge coordination because the Ge concentration in the alloy is low and because the Ge x-ray scattering factor is significantly smaller than that of Te. As a result, Ge bonding contributions to the area of the first radial distribution peak were small.

In an effort to attach greater certainty to the above-mentioned bonding picture, we have performed[6] both x-ray and neutron diffraction radial distribution studies of amorphous $Ge_{.17}Te_{.83}$. Of these, the neutron diffraction study is most important and is discussed here extensively. Neutron diffraction offers a number of significant advantages for such studies in this system. First, the scattering factors of the two species are independent of scattering angle. As a result, certain approximations which must be made in the analysis of x-ray diffraction data need not be made in the neutron case. Second, since the scattering is truly nuclear, and because the above mentioned approximations are not necessary, significantly higher resolution can be obtained in the final radial distribution. Third, and extremely important, is the fact that the neutron scattering factor of Ge is approximately 50% larger than that of Te. As a result, the radial distribution obtained is significantly more sensitive to Ge coordination than is the corresponding x-ray diffraction radial distribution on the same sample. These virtues have shown themselves to be extremely important, as is indicated below.

The most striking disadvantage of neutron diffraction for studies of many amorphous semiconductors is that fairly large quantities of bulk material are required, whereas most of these samples can only be prepared through vapor deposition. Fortunately, Dr. J. deNeufville of Energy Conversion Devices, Inc. developed a technique for preparing bulk samples of $Ge_{17}Te_{83}$ and made them available for this study.

The most striking features of this distribution, indicating its high quality, are the absence of structure for R less than 2Å, and the almost perfect resolution of the first neighbor peak. The absence of structure indicates that there are no serious errors in the intensity data, or its


PAIR DISTRIBUTION FUNCTION
-1.00
1.00
3.00
5.00
7.00
9.00
11.00
13.00
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17.00
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0.00
1.00
2.00
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9.00
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Figure II-1

analysis. This, coupled with the high resolution, has allowed us to obtain an extremely accurate area.

Our analysis of the radial distribution leads to the following conclusions.

1) The area of the first neighbor peak agrees to 1 part in 900 with the area calculated from the Random Covalent Model of Betts et al.[2] While such good agreement is probably fortuitous, it lends strong support for the validity of the model. Nevertheless, we cannot conclude that this model is truly valid, as we have been able to construct models on the basis of phase separation in the system which agree to 2% with the observed area. It is quite possible that the measured area is inaccurate by 2%.

2) The first peak of the radial distribution is at 2.65Å. This is only slightly longer than the expected covalent GeTe separation of 2.57Å. This slight discrepancy is to be expected, since Te-Te bonds still account for approximately 40% of the area. Note, however, that this distance is significantly smaller than the 2.84Å nearest neighbor Ge-Te separation in crystalline GeTe, where the bonding is almost semi-metallic in nature.

Hence, we believe the results point strongly towards a picture of covalent bonding. The validity of the Random Covalent Model still, however, remains slightly in doubt because of the possibility of phase separation. We shall return to these points later in the report.

In order to further test the validity of the Mott-Cohen, Fritzsche and Ovshinsky structural picture, we have undertaken two studies. First, we are performing x-ray diffraction radial distribution studies of $Ge_{1-x}S_x$ amorphous semiconducting alloys. These alloys have the advantage that they can be prepared in bulk throughout the range x less than 0.5 and that the Ge scattering factor is significantly larger than that of S. Careful x-ray diffraction data have been taken[7] on a number of samples of different composition. Radial distributions are now being calculated from them.

We are also in the midst of determining whether we should undertake such a study of amorphous $SiTe_2$. This system is important because, like GeTe, the crystalline structure is relatively close packed and cannot be explained on the basis of simple covalent bonding pictures. Should the amorphous structure be loosely packed and covalent in nature, it would lend even stronger evidence for the above-mentioned picture. Our one source of hesitation is that the sample reacts readily with water in the atmosphere, so that sample handling demands are rather stringent. We have decided, therefore, to spend some time searching for a similar system, in which the crystal structure is relatively close-packed, and sample maintenance is simpler, before undertaking experiments on this compound.

Finally, I should note that we have refined significantly our x-ray diffraction techniques during the past six months and are, consequently, obtaining better radial distributions than those published by us previously.[1,2] As a result, the samples studied in those papers are now being reanalyzed.

III. X-Ray Induced Photoemission and X-Ray Absorption Edge Studies

(C. Bates, F. Betts, and A. Bienenstock)

In the original research proposal for this contract, it was indicated that we intended to explore the possibility of examining the feasibility of using x-ray induced photoemission and x-ray absorption edge measurements for the study of bonding and coordination of impurities in amorphous materials. Results[8] obtained thus far indicate that these are, indeed, most valuable techniques.

In the preceding section, it has been shown that the Ge-Te amorphous alloys can be characterized by covalent bond distances. The existence of the covalent bonding is obtained by inference. The results obtained with the techniques used here are much more direct in their indication of covalent bonding. Both work on the same principle. When an atom loses an electron through, say, the classical type of ionic bonding, its core levels are more strongly bound to its nucleus, and have lower energies. As a result, the energy required to create a free core electron of fixed kinetic energy through the x-ray photoemission effect, or to transfer a core electron to the lowest lying unoccupied states, as in the x-ray absorption experiment, are greater. These energies are measured by measuring the kinetic energies of photoemitted electrons using a monochromatic x-ray source[9] or by direct measurements of the x-ray absorption edge.

In the work described here, we have studied Ge core shell binding energies in various Ge-Te alloys. The work shows, quite definitively, that the core shell binding energies are significantly greater in crystalline GeTe, GeSe and GeS than they are in the amorphous materials, so that the bonding in the amorphous materials is significantly more covalent.

In Table I, the measured shifts of the Ge $3d^{5/2}$ binding energies, relative to the energy in crystalline Ge, are tabulated for a number of materials. The sign convention is chosen such that a positive shift indicates stronger binding and implies, hence, more ionicity. These are shifts determined by the IEE technique.

TABLE I

X-Ray Photoelectron Spectroscopy - Binding Energy Shifts of the Ge $3d^{5/2}$ Core Level Relative to Crystalline Ge.

Sample	Shift (eV)
GeTe (crystalline)	3.6 ± 0.2
GeSe (crystalline)	2.9 ± 0.2
$^xGe_{.15}Te_{.81}Sb_{.02}S_{.02}$(amorphous)	1.1 ± 0.1
$^xGe_{.15}Te_{.81}As_{.02}S_{.02}$(amorphous)	1.1 ± 0.1
$^xGe_{.15}Te_{.81}As_{.02}S_{.02}$(crystalline)	3.1 ± 0.2

[x] These are memory type materials of the general form $Ge_{15}Te_{81}X_4$. Some samples were provided by Energy Conversion Devices, Inc.

It is apparent from these results that the shifts in the crystalline materials are all of the order of 3 eV, while those in the amorphous are of the order of 1 eV. These results are, to our knowledge, the first direct indications that the bonding in the amorphous materials is significantly more covalent than that in the crystalline. The sample compositions studied were determined, primarily, by the sample requirements of Varian's IEE apparatus.

Similar results were obtained through studies of the Ge K_α x-ray absorption edge energy. These are summarized in Table II.

TABLE II

Shifts of the Ge K_α Absorption Edge Relative to Crystalline Ge.

Sample	Shift (eV)
GeTe	2.48 ± 0.1
GeSe	2.35 ± 0.1
* $Ge_{.34}Te_{.66}$(amorphous)	1.16 ± 0.1
* $Ge_{.38}Te_{.62}$(amorphous)	1.13 ± 0.1
* $Ge_{.57}Te_{.43}$(amorphous)	1.11 ± 0.1
* $Ge_{.15}Te_{.81}Sb_{.02}S_{.02}$(amorphous)	1.31 ± 0.2

*The amorphous films used here were supplied by Energy Conversion Devices, Inc.

Again, it is apparent that the core electrons are more deeply bound in the crystalline material than in the amorphous, indicating that the bonding is more covalent in the amorphous materials than in the crystalline.

Taken together, the two sets of results have some interesting features other than those mentioned above.

First, we note that the x-ray absorption edge measurements indicate that the Ge K_α shift of the amorphous materials remains essentially constant, within experimental accuracy, over the composition range of 15 to 57 atomic percent Ge. This tends to imply that the type of bonding remains relatively constant over this range. This is important for the following reason. Betts et al.[2] have claimed that the strong differences in interatomic distances in crystalline and amorphous GeTe rule out any microcrystalline model for amorphous GeTe in which the microcrystallites are similar in structure to crystalline GeTe. They noted, however, that the nearest neighbor coordination in the amorphous compound could be interpreted as three-fold, rather than as in their Random Covalent Model. Such a coordination could be ascribed to crystalline GeSe, although there are three further nearest neighbors in that compound. Hence, it has been suggested by a number of workers in private communcations that amorphous GeTe could have a microcrystalline structure which is closely related to crystalline GeSe. The data presented in Table II tend to rule out the possibility that the bonding in amorphous GeTe is similar to that in crystalline GeSe, since the shifts in crystalline GeTe and GeSe are quite similar to each other and quite different from the shifts in the amorphous materials. It should also be noted that Chopra's statement[10] that stoichiometric amorphous GeTe might be quite different in structure and bonding from the amorphous alloys of composition close to it has now been withdrawn as a result of the structure studies of Dove et al.[11] on the amorphous stoichiometric materials. It appears as if the general form of the bonding and structure remains relatively constant throughout the composition region, with no unique characteristics present in the stoichiometric material.

Second, it is apparent from Tables I and II that crystalline GeTe shows a larger shift than do crystalline GeSe and GeS. This result appears to imply that crystalline GeTe is more ionic than the other crystalline materials, although the differences are much smaller than the differences between the average of the crystalline materials and the average of the amorphous materials. On the basis of electronegativity differences, one would anticipate that crystalline GeS and GeSe would be more ionic than crystalline GeTe. We do not understand this difference between theory and experiment and do not intend, for the time being, to investigate it further. The differences between the various crystalline materials are sufficiently small so that uncertainties in our understanding of the fundamental physics of photoemission may be important. What's more, this is a contract for the study of amorphous materials.

Our experimence with these two techniques makes us believe that they can be extremely valuable for studying bonding in other amorphous materials. They have the distinct advantage, relative to radial distribution studies, that individual atomic species can be studied. For this reason we are pushing ahead with them in two directions.

First of all, it is our intention to modify the x-ray absorption edge equipment to obtain significantly higher resolution. We are considering modifications which include both a double crystal spectrometer system and a low-temperature sample holder, in an attempt to obtain more accurate knowledge of the edge position and fine structure.

Second, we will use this technique to study the bonding of various impurities in As_2Se_3. As indicated in the original proposal, some impurities, at concentration levels up to 10 atomic percent, leave the conductivity and its temperature dependence essentially unchanged, while others lead to drastic changes. It is our expectation that these two techniques will provide considerable understanding of these phenomena.

IV. Phase Separation Studies (A. Bienenstock and Y. Verhelle)

As indicated in Section I, the possibility of phase-separation has always made our structural results somewhat ambiguous. In particular, we have found that it is usually possible to fit a first neighbor radial distribution peak area by a model in which, for Te-rich Ge-Te alloys, the system is considered to be phase separated into amorphous GeTe and Te. Hence, we have begun phase separation studies. We might also point out that it is our intention to become quite familiar with a variety of techniques for observing such separation because electronic properties of systems which are more likely to phase separate are to be studied under this program. It is our intention to always compliment electronic properties studies with structural studies.

At any rate, our initial attention has been concentrated on the memory material $Ge_{.15}Te_{.81}As_{.02}S_{.02}$ because it is so easily made in a variety of forms. Even here, activity has been limited by the preparations necessary for the use of our new sputtering system. Indeed, such preparations have occupied an appreciable portion of our time. Nevertheless, we do have some preliminary results to report.

First, bulk samples of this materials have been prepared by water quenching a melt which had been rocked at 800°C in vitreous silica ampules. These have been studied, first, by replication of fracture surfaces. The replicas show spheroidal particles whose sizes are distributed between 0.05 and 0.2 μ and which represent approximately 2% of the volume. Because of the small second phase particle sizes, it has been impossible for us to determine its composition.

This small volume fraction of phase separated material in the quenched bulk samples would tend to imply that phase separation is an unimportant phenomenon in the evaporated films used for the radial distribution structural studies. Such a conclusion is unwarranted for a variety of reasons. It is possible to miss phase separation when studying replicas of fracture surfaces since, for example, the different phases may have very similar mechanical properties. Hence, it is possible that there is grosser phase separation which we have missed. In addition, phase separation can be extremely sensitive to composition. Thus, it may be gross in the composition regions of the radial distributions, but not in the region studied here. Hence, we are continuing these studies.

There is another reason for continuing such studies. We have hints that the small spheroidal particles act as crystallization nucleation centers. If this is the case, their understanding would be important for the understanding of memory devices.

Our more recent studies involve the use of the newly arrived scanning electron microscope. Initial efforts have been on both the $Ge_{.15}Te_{.81}As_{.02}S_{.02}$ material mentioned above and the $Ge_{.17}Te_{.83}$ glass, supplied by Energy Conversion Devices, Inc., and used in the neutron diffraction studies. These studies also reveal the characteristics seen in the replica studies, and no other observable separation. Again, however, we are hesitant to make strong conclusions because of our own inexperience with the technique.

It is our intention to continue this work on a variety of materials. With the imminent availability of sputtering equipment, it is our intention to deposit materials directly onto carbon coated electron microscope grids to perform transmission electron microscopy on samples of varied composition and heat treatment. With these studies, we may also learn, for ourselves, the reliability of the scanning electron microscope studies.

V. Infrared Absorption Studies (A. Bienenstock and K. Liang)

As indicated in the original proposal, it is also our intention to assess the possibility of using local mode infrared spectroscopy to understand the role of Be and Mg impurities in the conductivity of As_2Se_3. A student has just started on this work, so that no results of interest might be anticipated. We have, however, found something by accident which may be rather important.

For practice, it was decided that he should polish two samples of materials to a form which is useful for infrared absorption studies. These were bulk glass As_2Se_3 and As_2Se_3-5% Mg samples which had been sitting in air for about one year.

The As_2Se_3 samples show absorption peaks which can be associated with the amorphous compound, as well as strong peaks which are probably indicative, according to Hilton and Jones,[12] of oxidation. These peaks increase markedly the absorption between 550 and 850 cm^{-1}. The sample containing 5% Mg, however, shows no such oxidation peaks and was virtually (except for reflection losses) transparent in the range from 550 to 3000 cm^{-1}.

These results, in terms of the original goals of the investigation, are interesting because there does not appear to be any local mode absorption due to the Mg in the range studied. This could be because the local modes are not in this frequency range, or because they are not infrared active. If the latter is the case, they may show up in Raman spectroscopy, which would be quite revealing. We are starting such studies.

They are more important, however, because they suggest a method of retarding the degradation, through oxidation, of infrared windows. To be frank, we do not know if such degradation is an important problem, or if the addition of such metals would be generally applicable, or if the addition of such metals leads to other undesirable characteristics. The possible importance of this observation, however, prevents us from neglecting it, although it is an aside from our basic program. We are, therefore, attempting to determine if oxidation is an important problem, and will also mix a bit of Mg into important infrared window glasses to see the effect on optical properties, glass transition behavior and oxidation behavior. Any comments of contract monitors who have been following developments in the window problem would be most appreciated. It may be that the problem is unimportant. It should also be mentioned that Lacourse et al.[13] have observed similar effects in glassy selenium. Hence, it is probably a quite general phenomenon.

VI. Calculations of Scattering by Microcrystallites (F. Betts and A. Bienenstock)

The question of whether the structures of amorphous materials are best described by a microcrystalline or random network model has been with us now for nearly forty years. It takes on added importance in a period when scientists are attempting to understand charge transport in them, for each model would dictate a different interpretation of the low conductivities.

In recent years, however, there appears to be a strong shift in favor of the random network type models for amorphous semiconductors. The strongest case provided is that by Betts et al.[2] for amorphous GeTe, where no crystalline analogue is apparent, as discussed above. In addition, however, the work of Moss and Graczyk[14] presents strong evidence for the inapplicability of the microcrystalline model to amorphous silicon.

These authors obtained careful electron diffraction data on the material. They then calculated the diffraction pattern to be expected from a variety of microcrystalline models and showed that none of the calculations could yield the measured intensities.

A potential shortcoming of their work was that they neglected to include the effects of intercrystallite scattering in their calculations. That is, they assumed that each crystallite scatters independently. The justification for this neglect was uncertain.

The difficulty of assessing the role of interparticle interference comes from the fact that no one has a clear idea of how the crystallites would be arranged in a microcrystalline array of the high packing fractions necessary to achieve amorphous densities. To circumvent this problem and obtain an estimate of the order of magnitude of the interparticle interference terms, we have approximated the microcrystalline system with a rather simple model.

The model assumes, first of all, that there is no correlation in the orientation of neighboring crystallites. This may be its most serious flaw. Nevertheless, it does allow for considerable simplification of the mathematics and should give reasonable order of magnitude results.

The second assumption of the model is that the probability of finding two crystallites separated by a given distance is given by the Finney[15] radial distribution function for the "liquid" packing of hard spheres.

Finally, we note that in using the hard sphere radial distribution, it is necessary to ascribe a hard sphere radius to the microcrystallites. If one uses a radius characteristic of the crystallite size, it is apparent that the high density of amorphous silicon will not be achieved. Hence, we have adjusted the hard sphere radius in the pair distribution function to match the density. This implies that some crystallites overlap.

Under these three approximations, we have calculated the effects of interparticle interference for the most important of the models considered by Moss and Graczyk and found them to be negligible at all but very small angles, where our approximations are unreliable. Since the discrepancies between the model calculations and the observed intensities are most important at higher angles, our calculations indicate that it is extremely unlikely that the discrepancies can be explained on the basis of interparticle interference. Hence, they provide added support for a random network model of amorphous silicon.

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VII. Discussion of the Electronic Structure of Amorphous Ge (W. Spicer)

In this section, we will examine the information which we obtained previously about the electronic structure of amorphous Ge, try to systemize this, and propose a model which can be tested through studies on other materials.

The optical density of states of amorphous Ge is presented in Fig. 1. Also plotted in that figure is the calculated density of states of crystalline Ge. In Figure 2, a plot is given of the optical density of states which emphasizes the states in the band gap region. This is shown in order to emphasize the sharp band edges deduced from the optical and photoemission studies.

When one compares the optical density of states from amorphous Ge to the crystalline density of states, one is struck by two things: (1) the sharp structure away from the band edge in the crystalline material completely disappears in the amorphous Ge, and yet (2) the edges of the forbidden band remain as sharp in the amorphous as the crystalline material. At first glance, these results appear contradictory; why should the peaks away from the edge disappear but the edge keep its sharpness? If one looks for the source of the structure, it is, perhaps, not so surprising. The peaks in the density of states of crystalline Ge are principally associated with the Bragg reflection at the zone boundaries. The Bragg reflection, and thus, these peaks disappear when the long range order is destroyed in the amorphous material. On the other hand, if one associates the sharp absorption edge with the covalent bond, it is not surprising that it does not disappear in the amorphous material since the covalent bond is clearly retained.

One peak appears in the valence band about 1.5 eV below the valence band maximum. Inspection of the density of states of crystalline Ge indicates that there is a shoulder near 1.5 eV. This is due principally to states which lie near the (111) crystal direction, i.e., to states which lie along the direction of the covalent bond. Thus, there appears to be a correspondence between the valence band density of states peak in the amorphous material and states along the bond direction in the crystalline material. This may be accidental, but it is suggestive that the valence band peak in amorphous Ge may be associated with the Ge covalent bond. The width of the valence band in the crystal and amorphous materials is comparable. In both cases the width is probably due to the overlap associated with the covalent bond.

All of this speculation on the covalent bond and the electronic structure of amorphous Ge provides a tentative model which can be tested by data from other materials. This model associates peaks in the amorphous valence band density of states with the covalent bond and relates the position of the peak with the energy of states along the bond direction in the crystalline material.

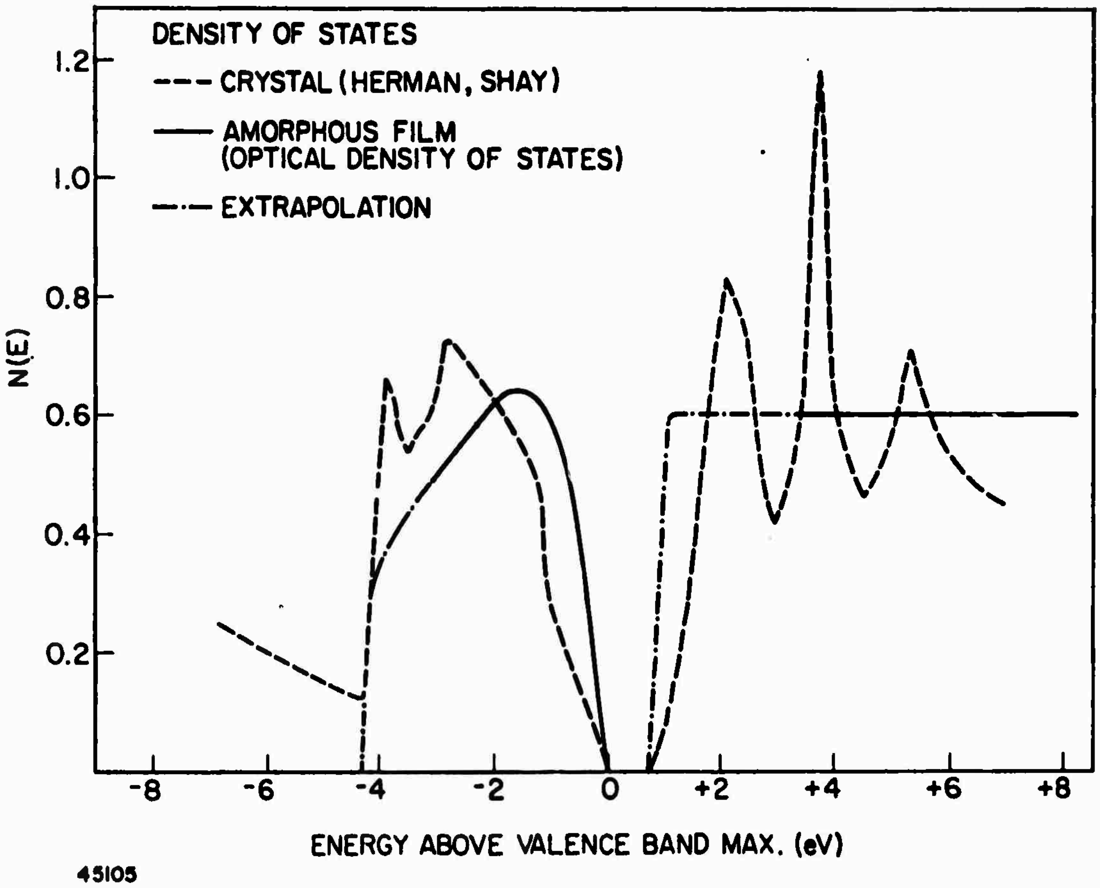
DENSITY OF STATES
--- CRYSTAL (HERMAN, SHAY)
— AMORPHOUS FILM (OPTICAL DENSITY OF STATES)
—·— EXTRAPOLATION
N(E)
1.2
1.0
0.8
0.6
0.4
0.2
-8
-6
-4
-2
0
+2
+4
+6
+8
ENERGY ABOVE VALENCE BAND MAX. (eV)
45105

Figure VII-1

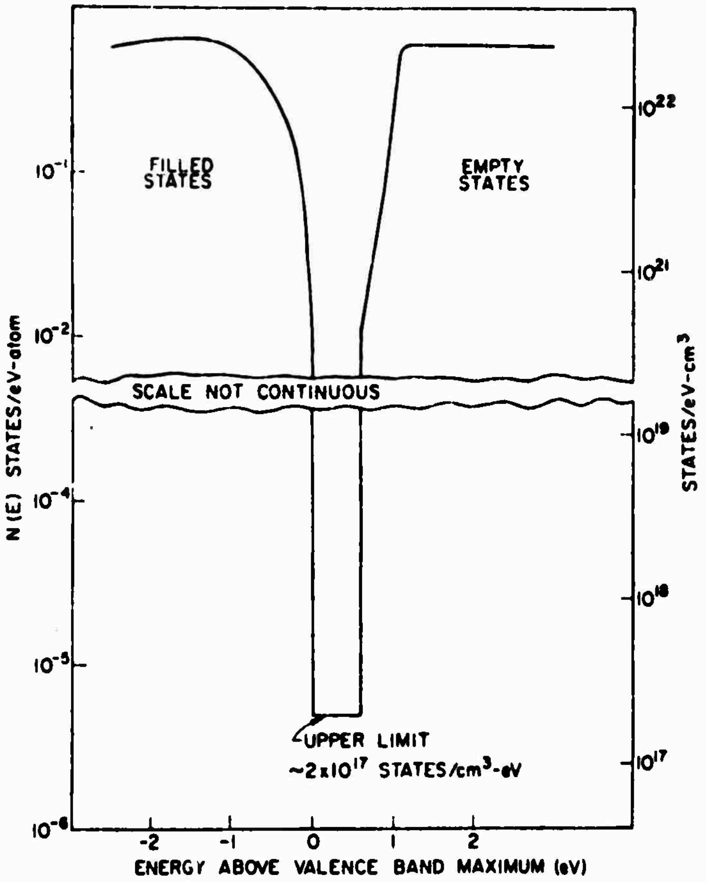
FILLED STATES
EMPTY STATES
SCALE NOT CONTINUOUS
UPPER LIMIT
~2x10^{17} STATES/cm^3-eV
N(E) STATES/eV-atom
STATES/eV-cm^3
10^{-1}
10^{-2}
10^{-4}
10^{-5}
10^{-6}
10^{22}
10^{21}
10^{19}
10^{18}
10^{17}
-2
-1
0
1
2
ENERGY ABOVE VALENCE BAND MAXIMUM (eV)

Figure VII-2

VIII. Photoemission Studies of GeTe (G. Fisher and W. Spicer)

A photoemission study of amorphous GeTe is well underway at Stanford. The results obtained thus far (Fig. 1) are intriguing. We hope to gain a knowledge of the density of states in the amorphous material and upper limit on the density of bulk states existing within the forbidden gap.

Measurements of photoelectric yield and electron energy distributions (EDC's) have been taken on films sublimed from a source of polycrystalline GeTe in a geometry which has previously given amorphous samples. A polycrystalline Mo substrate was at room temperature throughout the evaporation. A quartz oscillator thickness monitor measures the thickness between 1000Å and 2000Å. The pressure during evaporation reached 10^{-7}Torr in a system with a base pressure of 2×10^{-11}Torr.

The un-normalized EDC's in Fig. 1 at three photon energies show the results for our sample. There are two relatively sharp peaks, 1.5 eV and 3.0 eV below the high energy cutoff. The peaks retain their shape as they move out with increments of photon energy. The high energy cutoff is sharp with the minimal leading edge to be expected from instrumental resolution.

The photoelectric yield (Fig. 2) rises slowly and smoothly from threshold, leveling off at a yield of .015 electrons/incident photon at high energies. The shoulder above 9 eV corresponds to the appearance of the second peak in the EDC's.

The first question is whether we are looking at amorphous GeTe. A conclusive test would be to crystallize the film detecting changes in optical properties (e.g. direct transitions). The process of annealing the sample at 70°C, 100°C, and 125°C (T_c = 120°C) is in progress now.

If we compare with studies on amorphous Ge[2], the movement of peaks of constant shape is characteristic of an amorphous material. The yield curve of our film is very similar to that of amorphous Ge as opposed to the sharp threshold and structure usually found in crystals. Both materials also share a sharp high energy cutoff in the EDC's. The annealing studies will be the final word, but it seems likely we have an amorphous film.

It is also intriguing to note that both amorphous Ge and the present data have a peak 1.5 eV below the high energy edge. However, the data on amorphous Ge shows a peak significantly broader than that in our present work (Fig. 3). To ascribe the electrons in each peak to the same source would be presumptuous at this time.

Current plans are to test the effect of the threshold on our data by cesiating an amorphous sample and a crystallized film. An attempt will be made to grow single crystal GeTe here at Stanford. Data on such samples would provide a standard against which to compare our amorphous data.

References:

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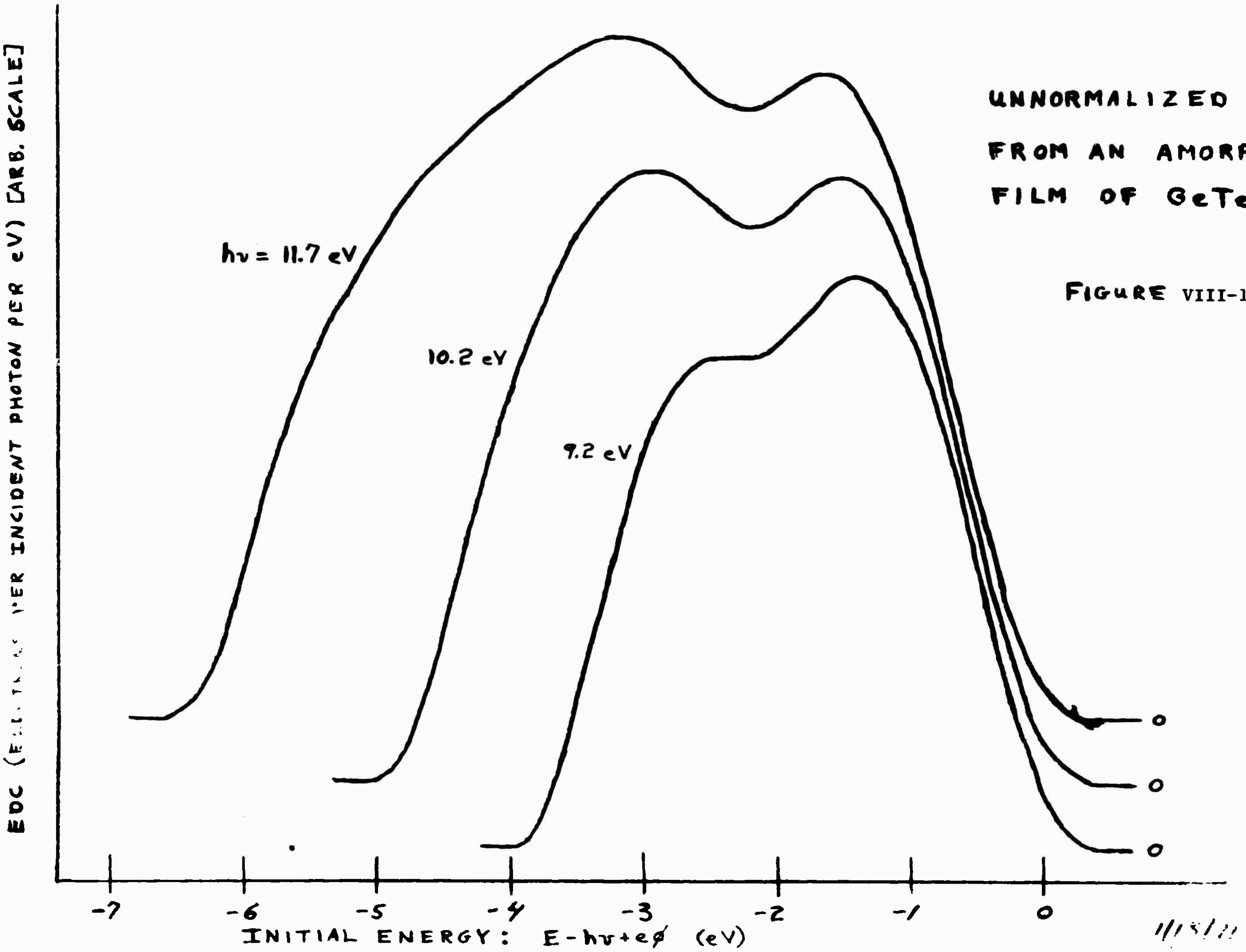
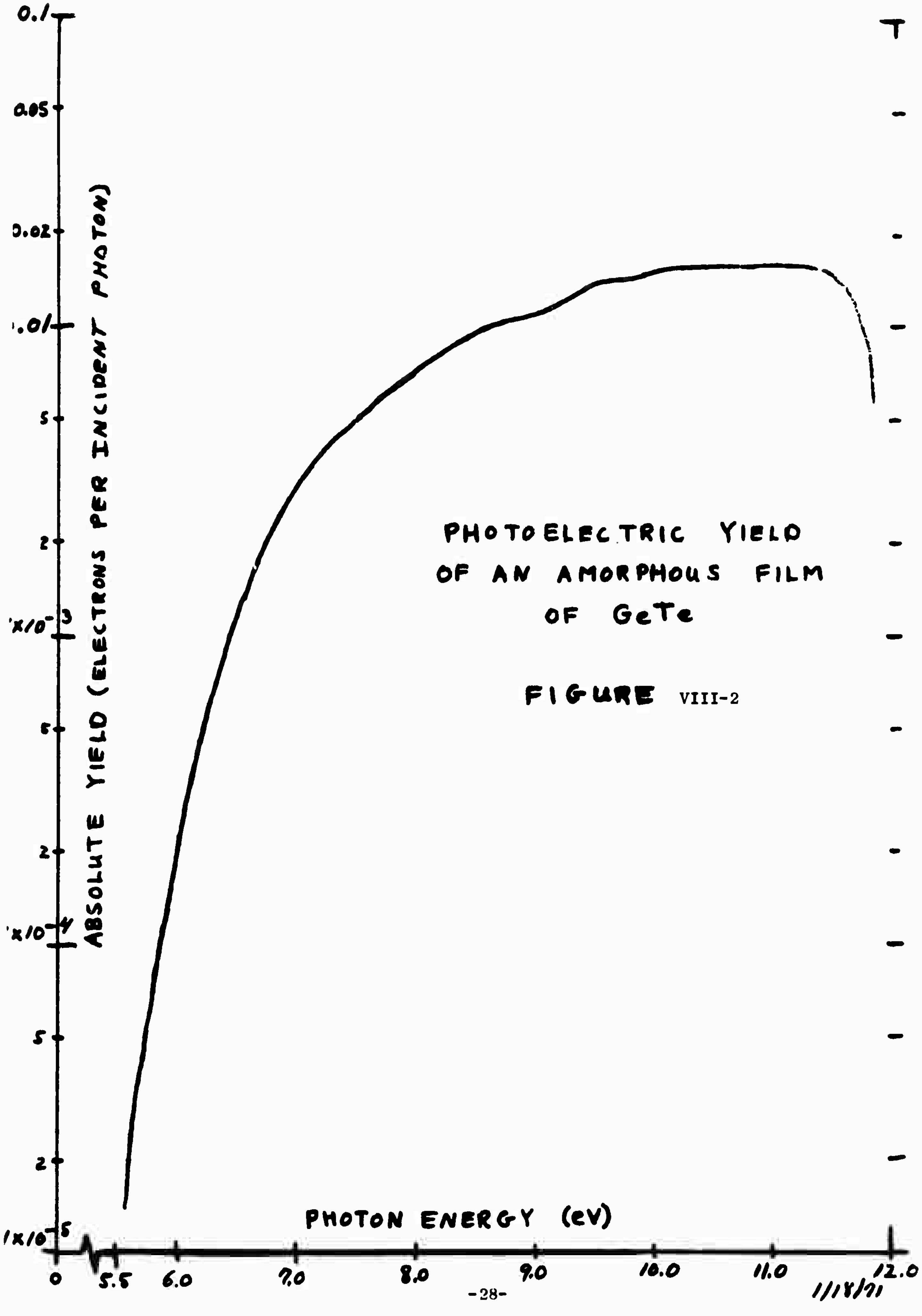
2. T. M. Donovan and W. E. Spicer, Phys. Rev. Letters 21, 1572 (1968).



UNNORMALIZED EDCs FROM AN AMORPHOUS FILM OF GeTe

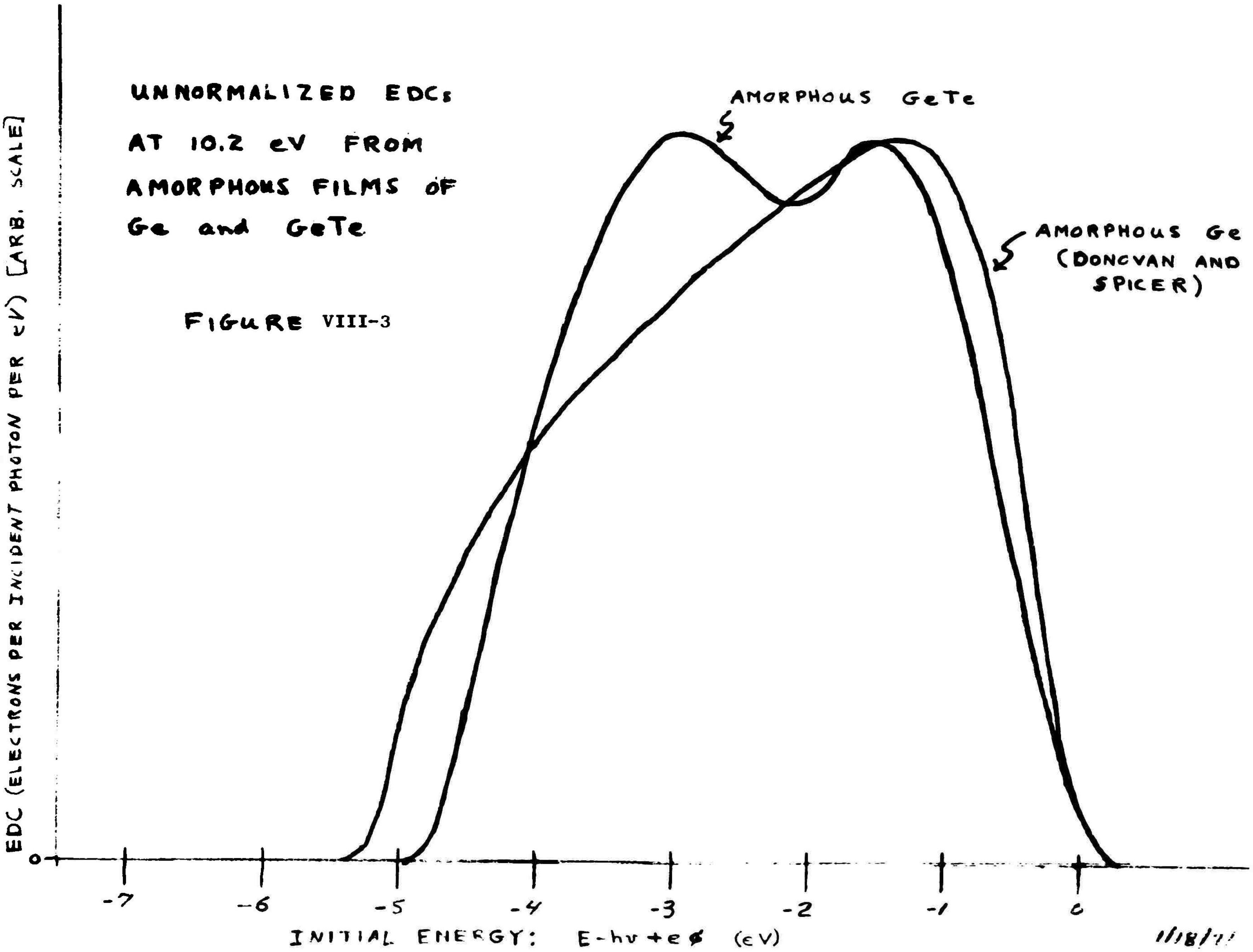
FIGURE VIII-1



PHOTOELECTRIC YIELD OF AN AMORPHOUS FILM OF GeTe

FIGURE VIII-2

1/18/71



UNNORMALIZED EDCs AT 10.2 eV FROM AMORPHOUS FILMS OF Ge and GeTe

FIGURE VIII-3

11/18/71

IX. Photoemission Studies of Amorphous Si (D. Pierce and W. Spicer)*

We recently began a photoemission investigation of amorphous silicon similar to the study of amorphous germanium by Donovan and Spicer. Initially, we have obtained photoelectron energy distribution curves (EDC's) and quantum yield spectra from an evaporated amorphous film. The changes in the EDC's were followed as the film was annealed through several stages to a polycrystalline film.

In preparation for this experiment a third harmonic generator was constructed in order to obtain the third derivative of the E-V curve which is the second derivative of the EDC. Second derivatives of EDC's have been shown to be useful in experiments on metals for detecting small structure on a broad background. We obtained second derivatives of the EDC's in searching for faint structure in the EDC's due to crystallinity as the film was annealed. In addition, the photoemission flange was modified so that EDC's can be obtained from the metal shutter at the rear of the collector and the collector work function determined. The workfunction of the sample and the location of the Fermi level can then be determined. The 2500Å thick amorphous film was electron gun evaporated from 1000 Si-cm p-type Si onto a mechanically polished and heat cleaned single crystal (111) 1000 Si-cm n-type substrate at an intermittent rate of 60-100Å/min. The pressure was maintained $< 5 \times 10^{-9}$ Torr during evaporation and returned to a base pressure of $< 5 \times 10^{-11}$ Torr. X-ray analysis of a test film deposited on a glass substrate nearer the evaporator showed the absence of characteristic crystalline Si different in peaks.

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* This work is only supported partially by this contract; however, it is reported here for completeness.

In Fig. 1 we show representative EDC's at $\hbar\omega = 10.2$ eV from the amorphous film and after two of the anneals. The amorphous film was annealed for 30 min. at 250°C, 30 min. at 400°C, 30 min. at 550°C, and 1.5 hr. at 660°C. After the final anneal strong structure was present which corresponds with structure in EDC's from cleaved single crystals indicating that our film had become polycrystalline. The EDC's of Fig. 1 are plotted with respect to initial state energy below the Fermi level.

EDC's from the amorphous film at other photon energies have broad maximum 1-2 eV below E_i similar to the EDC at 10.2 eV in Fig. 1. This is similar to the results from Ge. Again the peak lies in the energy range of states in crystalline Si along the bond direction. The broad maximum of the disordered film remains constant in initial state energy consistent with the nondirect model of optical transitions. Preliminary analysis of the data gives no evidence for tailing of states into the band gap. In fact, as can be seen in Fig. 1, the EDC's from the amorphous and partially annealed films have a somewhat sharper leading edge than the crystalline film. The slight sounding of the high energy tail due to resolution and instrumental broadening effects is the same for all three films of Fig. 1. Evidence was obtained that the Fermi level was close to the valence band maximum from the center of the gap. The reason for this is uncertain. Considerable data analysis and possible future photoemission and uv reflectivity measurements remain in this investigation.

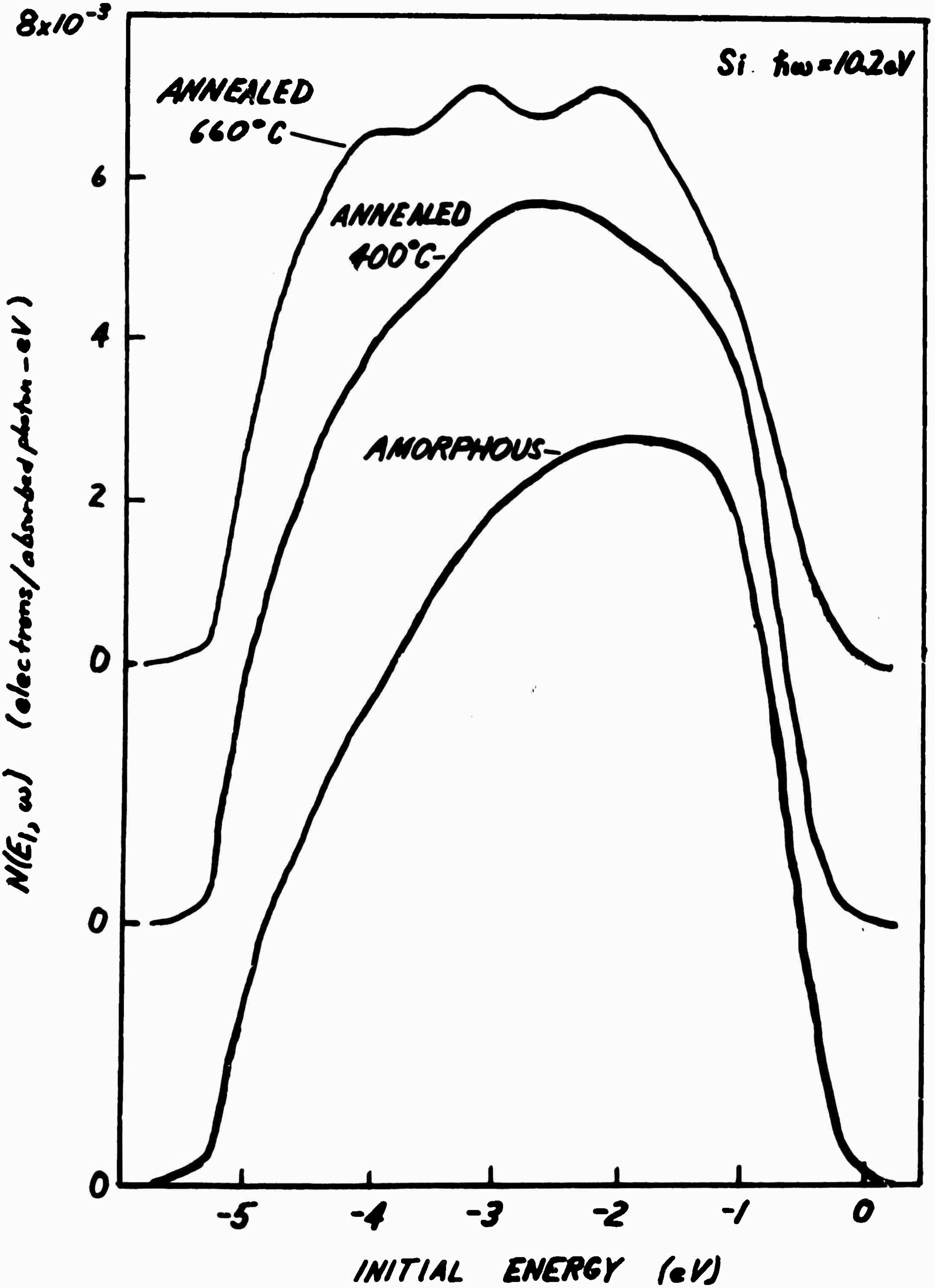

8x10⁻³
6
4
2
0
0
0
N(E₁, ω) (electrons/absorbed photon - eV)
Si ħω=10.2eV
ANNEALED 660°C
ANNEALED 400°C
AMORPHOUS
-5
-4
-3
-2
-1
0
INITIAL ENERGY (eV)

Figure IX-1

X. Proposed Experiments on Pure and Highly Doped Amorphous Ge (C. Ribbing and W. Spicer)

In spite of the intensive interest for amorphous materials during recent years we are still far from a well established understanding of the electronic structure in the amorphous elemental semiconductors silicon and germanium. Since photoemission has proved to be one of the most powerful tools to investigate the details of the electronic structure of almost any substance, it is hoped that careful uv photoemission measurements may give conclusive answers to some of the problems.

Therefore, the following two experiments are being planned and prepared in the Stanford photoemission laboratory.

1) Investigation of Amorphous Ge

The problems to be investigated are e.g. the possible influence of deposition rate on the position of the absorption edge, the position of the Fermi-level in film obtained by evaporation in ultra-high vacuum of heat-cleaned intrinsic grade germanium, and temperature-dependence of the EDC's.

2) Investigation of Group V-Doped Ge

The intention is to compare the effect of a donor-impurity on the EDC's of amorphous and crystalline germanium. If practicable this experiment offers a way to test Mott's hypothesis that the amorphous phase allows the host electronic structure to relax and satisfy the covalent bonding requirements of the impurities, so no localized impurity-states are created.

XI. Transport Studies in Ovonic Switching Type Alloys (T. C. Arnoldussen and R. H. Bube)

Initial measurements of photoelectronic propoerties of amorphous materials have been undertaken to test out a newly constructed cryostat for this purpose, using an interdigital-electrode structure Ovonic switching-type alloy with composition $Ge_{11}Si_{11}P_3As_{35}Te_{40}$. The three principal types of measurement performed are illustrated in Fig. 1. Curves 1 and 2 show the temperature dependence of the dark conductivity (90 volts applied) as measured initially and after a second exposure to air after a series of measurements in a 125 micron He pressure. The conductivity varies exponentially with 1/T with an activation energy of 0.47 eV. The dashed curve in Figure 1 shows the temperature variation of the light conductivity, which in the higher temperature range has an equivalent activation energy of about 0.20 eV. The dash-dot curve shows the thermally stimulated conductivity, produced by heating after photoexcitation at low temperature. All of these measurements have been previously reported by E. Fagen of ECD, and our measurements are in substantial agreement with his.

Our own research program will concentrate on materials chosen to simulate those involved in the chalcogenide switching phenomena, but with no more than three or four constituents, and with variations in composition achieved by an atomic substitution on procedure. Such materials will be described by the general formula: $Ge_xAs_{(40-x)}Se_yTe_{(60-y)}$. Fifteen possible such materials have been chosen for investigation corresponding to x = 0, 10, 20, 30, 40; and y = 18, 30, 42.

Figure 2 shows the bulk glass-forming regions of the As-Ge-Se and the As-Ge-Te systems, as well as the line of compositions which are to be studied. The introduction of Te into the As-Ge-Se system would be expected not to decrease appreciably the As-Ge-Se glass-forming region and perhaps even to increase it. Therefore it is expected that measurements on bulk glass samples can also be compared with measurements on thin-film sputtered layers for the same compositions.

There are two reasons for choosing a combination of Se and Te, rather than limiting the material to either one or the other alone: (1) the desirability of obtaining a large glass-forming region, and (2) the desirability of obtaining a resistivity range suitable for the wide variety of measurements planned. From the standpoint of extended glass-forming regions, the As-Ge-Se system is characterized by large bandgaps and very high resistivities, whereas the As-Ge-Te system is characterized by small bandgaps and low resistivities. By combining Se and Te, we expect to be able to vary the bandgap and resistivity over a wide range and still maintain a large glass-forming region. For example, the system $As_2(Se_{1-x}Te_x)_3$ forms bulk glasses from $x = 0$ to $x = 0.85$, while the resistivity at room temperature varies from about 10^{12} ohm-cm for As_2Se_3 to about 10^4 ohm-cm for $As_2(Se_{.15}Te_{.85})_3$.

For a given Se:Te ratio, we plan to investigate the effect on conductivity, mobility, trap distribution etc. of replacing As with Ge. This substitution can be made for both the higher resistivity system $As\text{-}Ge\text{-}(Se_{.7}Te_{.3})$ and the lower resistivity system $As\text{-}Ge\text{-}(Se_{.3}Te_{.7})$.

It is desirable to choose the Se:Te ratios that give intermediate resistivity of 10^6 to 10^9 ohm-cm at room temperature in order to maximize the variety of measurements that can be meaningfully made. Measurements planned include (a) dark conductivity vs. 1/T under DC and AC electric fields, (b) transient space-charge injection, (c) thermoelectric power, (d) photoemission from a metal contact into the material, (e) steady-state and transient photoconductivity vs. T, (f) photoconductivity vs. light intensity, (g) photoconductivity vs. wavelength of light for DC and AC electric fields, and (h) thermally stimulated conductivity. Measurements (a) and (c) are best made on lower resistivity materials, while measurements (b) and (d) and to some extent the photoconductivity measurements are best made on higher resistivity materials. Thus by choosing compositions which give intermediate resistivities, we expect to be able to make all or at least most of these measurements over the same temperature range on any given sample.

The information that we expect to derive from these measurements can be summarized as follows: from (b) - carrier drift mobilities, conductivity mobilities, trapping time constants and detrapping parameters as a function of temperature; from (d) - the position of the Fermi energy relative to the valence and conduction bands; from (a), (b), and (d) - carrier concentrations and activation energies, trap concentrations and depths, insight into the conduction mechanism; from (c) and (e) through (h) - trap distributions, recombination kinetics, response time, carrier scattering, conduction mechanism (holes or electrons, hopping or band conduction).

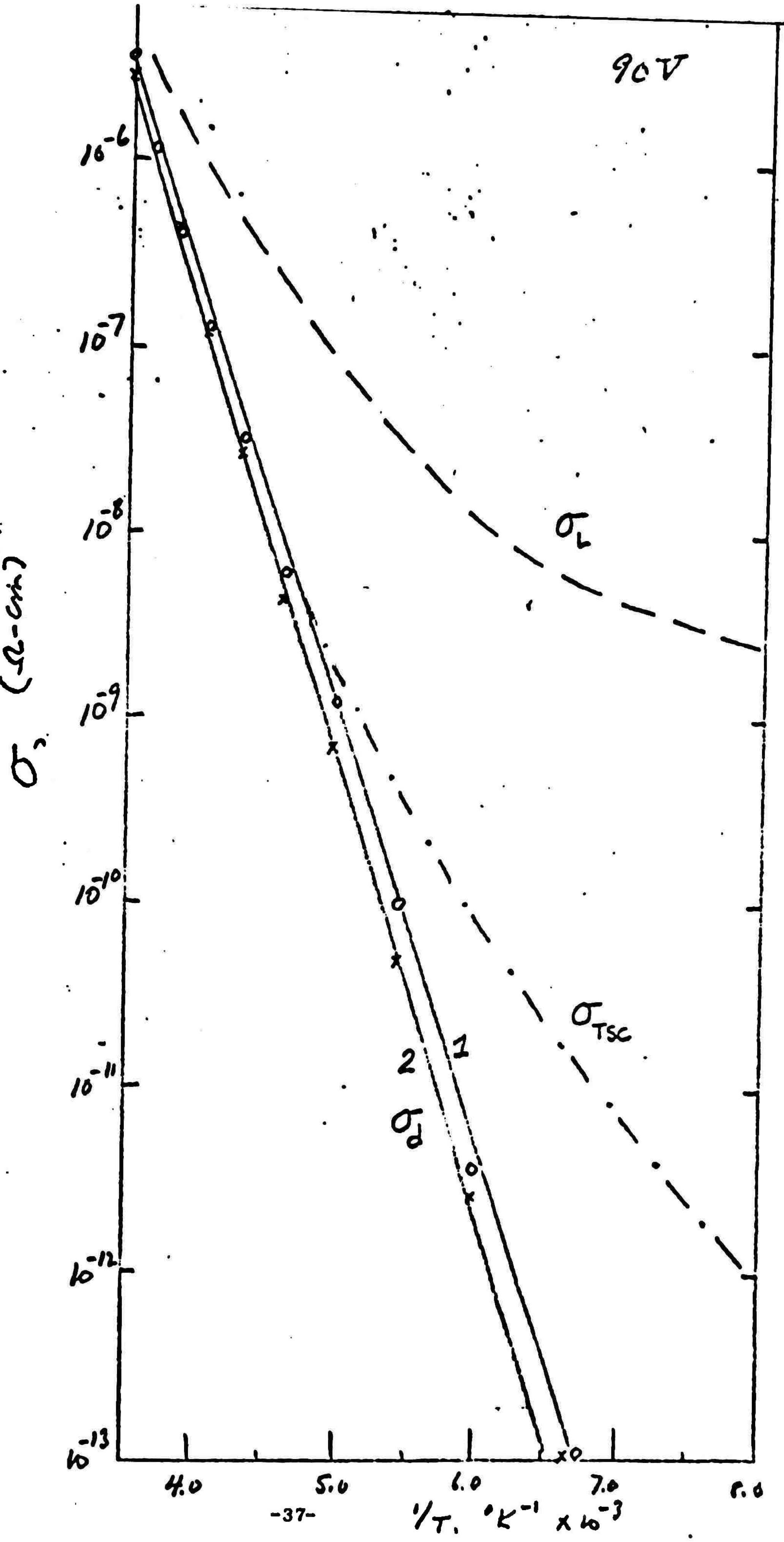
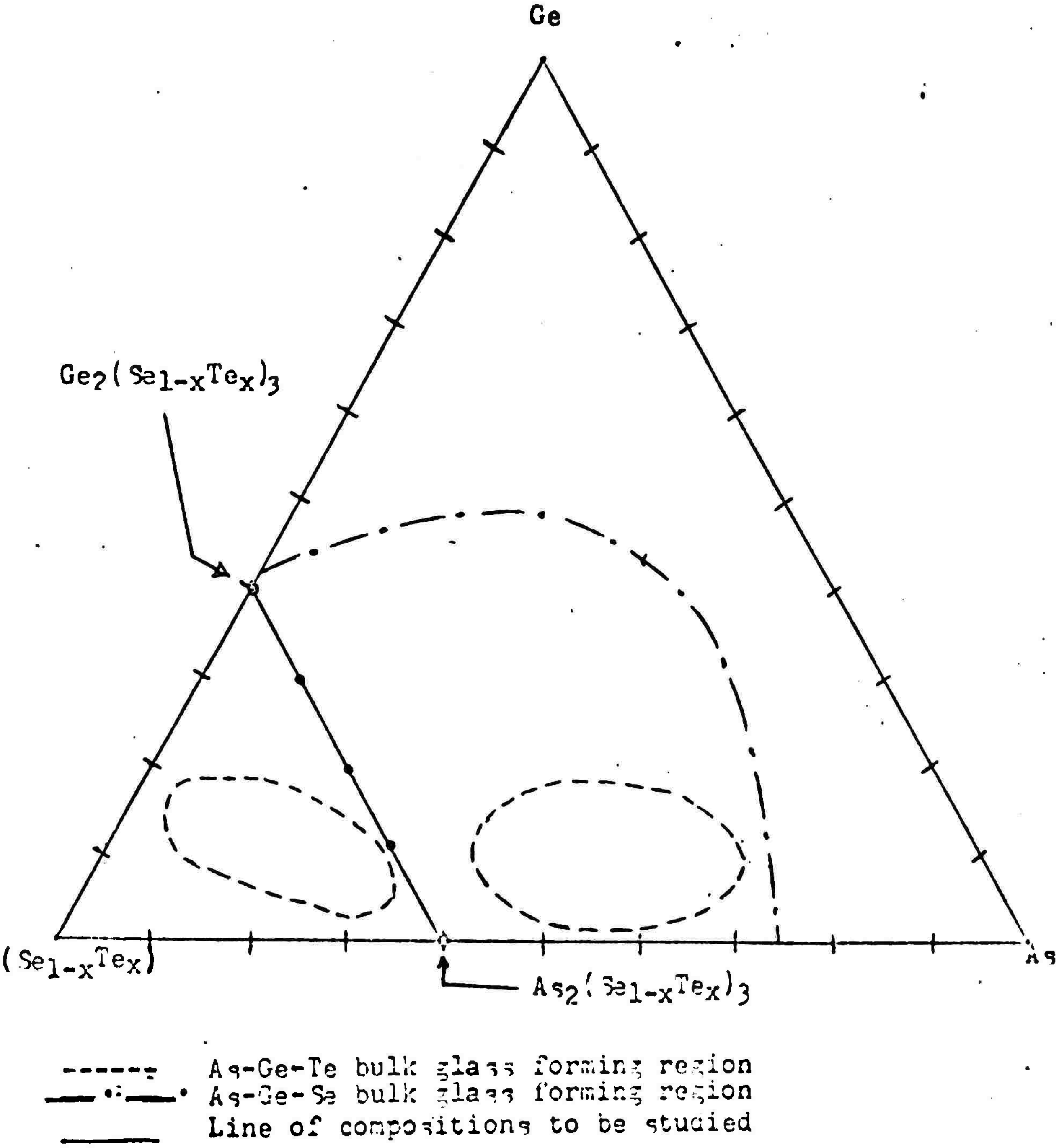

90V
σ, (Ω-cm)^-1
10^-6
10^-7
10^-8
10^-9
10^-10
10^-11
10^-12
10^-13
σ_L
σ_TSC
σ_d
1
2
4.0
5.0
6.0
7.0
8.0
1/T, °K^-1 x 10^-3

Figure XI-1



$x = 0$: As-Ge-Se
$x = 0.3$: As-Ge-$(Se_{0.7}Te_{0.3})$
$x = 0.7$: As-Ge-$(Se_{0.3}Te_{0.7})$
$x = 1.0$: As-Ge-Te

Figure XI-2