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SYMPOSIUM ON THE STRUCTURE OF NON-CRYSTALLINE MATERIALS
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15 February 1977

\*NRL (On sabbatical leave at Heriot-Watt University, Edinburg)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In this symposium, which attracted contributions from both the amorphous semiconductors and the glass sciences communities, recent results were presented concerning the structure of non-crystalline solids as deduced from several different experimental techniques. These techniques include x-ray diffraction, extended x-ray absorption fine structure (EXAFS), infra-red and Raman spectroscopy, low temperature specific heat, and electron spin resonance (ESR). The symposium featured discussions of recent EXAFS measurements and		

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methods of data reduction, of defects in semiconducting and oxide glasses,  
and of structural modelling techniques including continuous random network  
models.



## SYMPOSIUM ON THE STRUCTURE OF NON-CRYSTALLINE MATERIALS

This Symposium, which was held at the University of Cambridge, was an attempt to bring together two disparate scientific communities both of which are interested in structural properties of non-crystalline solids--the amorphous semiconductors community (composed predominantly of solid state physicists) and some electrical engineers and the more heterogeneous glass-science community (composed of materials scientists, electrical engineers, chemists, ceramists and physicists). The attempt largely failed, in my opinion, in part because not enough time was spent on tutorial talks and too much was used by the presentation of detailed and specialized information. I don't know how this dilemma could have been avoided because in these times of tight travel budgets most participants needed a paper accepted at the meeting in order to attend. In fact, several papers which were scheduled to be presented were not given because the author could not be present.

The meeting covered four days (20-23 September, 1976) and contained 12 sessions on topics which included scattering measurements, structural modeling, short- and intermediate-range order, defects, electrons and phonons, relaxation processes, and amorphous metals. Five of the sessions were opened with plenary talks which were intended to introduce the major topics of the conference but which tended, in general, to be too specific and detailed. My review of this meeting will concentrate on those topics which I judged were either new or contained significant advances over previous conferences. Because of the dissimilar backgrounds of the participants which I have already mentioned, my choice may be open to some well-founded criticisms.

In his opening remarks, Dr. P.H. Gaskell (Pilkington Brothers Ltd.) expressed the optimistic wish that the conference would result in a "quantum jump" in the knowledge of the structure of amorphous solids. This optimism was quickly dispelled by the assertion by Professor J.D. MacKenzie (Univ. of California, Los Angeles) that little significant progress in understanding the structure of amorphous solids has been achieved since the original pioneering work of this despite the frequent claims of crystallographers of new important breakthroughs.

It was perhaps fitting that the latest "breakthrough" was the opening topic of the conference--extended x-ray absorption fine structure (EXAFS). The first plenary talk was given by Professor A. Bienenstock (Stanford Univ.) who first reviewed the role of the radial distribution function in determining structure and then discussed EXAFS studies of amorphous materials. This plenary presentation was one of the few which really succeeded in both reviewing the subject and setting the tone for the rest of the session. Bienenstock

used amorphous arsenic as an example to describe x-ray scattering techniques as applied to amorphous solids. He made a plea for publication of the derived radial distribution function (RDF) below 2 Å in order that one may judge the accuracy of a given RDF. Bienenstock went on to describe the most commonly encountered difficulty with the interpretation of x-ray scattering data in amorphous solids--the dependence of any interpretation on an assumed structural model. In particular he mentioned the Ge-Se system where the first peak in the x-ray RDF can be interpreted as due to Se-Se, Se-Ge or Ge-Ge pairs. Neutron scattering can, in principle, distinguish between pair distribution functions, and thus between like and unlike neighbors, but there are not many good nuclei with which to work. On the other hand, EXAFS spectra, which are due to the interference of back-scattered waves from like nearest neighbors only, can in principle be employed to study only the like neighbors surrounding any atom.

The difficulty in applying this technique to amorphous materials is, of course, the mathematical complexity of deconvoluting the observed fine structure oscillations to obtain a meaningful RDF. Much of the remainder of the presentations on EXAFS concerned various attempts to get around these mathematical difficulties.

In a contributed paper J.B. Pendry and S.J. Gurman (SRC, Daresbury) described the fundamentals of performing a fast Fourier transform (FFT) as applied specifically to EXAFS spectra. Two of the problems encountered include calculating atomic core potentials and estimating the attenuation on scattering due to plasmons. Pendry and Gurman discussed a "hybrid" method of progressively subtracting out first, second, and so on, coordination spheres one at a time from the EXAFS spectra in order to extract the structural information.

R.F. Pettifer *et al* (Univ. of Warwick) presented their interpretation of EXAFS spectra which they observed in two crystalline and one amorphous form of  $As_2Te_3$ . Because the As EXAFS in the glassy phase extends to much higher energies than those observed in the crystalline phases, these authors conclude that there is a much more homogeneous first nearest-neighbor As shell in the glass. The fit of a model calculation to the EXAFS spectrum in the glass was used to conclude that As-As bonds do not often occur and that the As atoms are probably three-fold coordinated and the Se atoms two-fold coordinated. Thus the glass has quite a different local structural order than either of the two known crystalline modifications, where four-fold coordinated As and three-fold coordinated Te occur. I note that several other authors (among them J. Cornet of the Laboratory of Electronics and Applied Physics, Limeil-Brevannes,) at this conference have previously reached the same conclusions, on what seems to me to be just as solid evidence--from ordinary x-ray scattering and vibrational absorption data.

A slightly different approach to extracting structural information from EXAFS spectra was presented by T.M. Hayes *et al* (Xerox, Palo Alto Research Center and Stanford Univ.) These authors extracted the first shell and then broadened and shifted this peak to simulate the second, third, and higher shells. All the contributions were then added together to obtain an approximation to the experimentally observed spectrum. Results were shown for amorphous Ge, Se and C by use of this technique. In amorphous Ge, Hayes *et al* obtain a broadening in the second coordination shell of at least 0.2 Å. In Se these authors find that the first nearest-neighbor bond is 0.03 - 0.04 Å less than in crystalline trigonal Se, although not surprisingly, the number of nearest neighbors is the same in both forms.

EXAFS studies of glasses in the system Cu-As-Se were discussed by S. Hunter and A. Bienenstock (Stanford University). Ordinary x-ray diffraction attempts to deduce the structure of these glasses have been inconclusive, but unfortunately so are the EXAFS results to date. The interpretation favored by Hunter and Bienenstock is that As atoms remain three-fold coordinated in this glass system, but Se atoms go from two- to four-fold coordinated (no chalcogenide lone pair orbitals remaining) for more than 25% Cu.

The sessions on EXAFS were interesting, informative and promising. However, the extent to which EXAFS will provide a "quantum jump" in our understanding of the structures of amorphous solids and not merely the latest in a long line of initially promising, but ultimately disappointing advances remains to be seen.

If nothing else, this meeting provided fresh evidence that the interpretation of x-ray scattering data for even the simplest of glasses is still a controversial subject. A.R. Cooper and F.M. Dunlevey (Case Western Reserve University) described x-ray scattering measurements on quenched and pressure-compacted B<sub>2</sub>O<sub>3</sub>. Cooper suggested that the RDFs observed for B<sub>2</sub>O<sub>3</sub> glass do not support the recent interpretation of R.L. Mozzi and B.E. Warren (*J. Appl. Crystallogr.* 3, 251, (1970)) that the glass consists of boroxal rings. In fact, from identical experimental data, Cooper comes to the opposite conclusion that there are fewer than 10% of the BO<sub>3</sub> triangles arranged in boroxal rings in B<sub>2</sub>O<sub>3</sub> glass. The compacted B<sub>2</sub>O<sub>3</sub> showed no changes in the positions of the first two peaks in the RDF from the uncompact glass. This behavior suggests that the BO<sub>3</sub> triangular units are not compressed but that the linkage between units is distorted upon compaction.

Professor N.F. Mott (University of Cambridge) presented the plenary invited talk on defects in glasses. The introduction

of this presentation overlapped with the one he gave at the Semiconductors Conference in Rome (c.f. ONRL-C- 77 on XIII International Conference on the Physics of Semiconductors). Mott assumed a random network model, where the only electronic states in the gap are due to point defects, and described the evidence for defect states from the glow-discharge amorphous silicon measurements of W. Spear and P.G. LeComber (University of Dundee) and of J. Stuke and co-workers (University of Marburg). He again briefly described the kinks expected in plots of Hall mobility, conductivity or photocurrent as functions of  $1/T$ .

At this conference Mott focused his attention on the chalcogenide glasses and  $\text{SiO}_2$ , while at Rome he presented a more extended introduction and then emphasized the tetrahedrally coordinated amorphous films. The new application of the charge-dangling-bond model which Mott presented in this talk concerned an explanation of the extreme effect on the Cu or Mn into  $\text{As}_2\text{Se}_3$ . Mott cited experimental evidence that both Cu and Mn content ( $\approx 25\%$ ) and are thus negatively charged. He suggested that the positively charged "dangling bonds" ( $D^+$  states) form dipos with the negatively charged impurities, and one thus expects an increase in the number of  $D^+$  defects and a decrease in the number of negatively charged  $D^-$  defects. This trend explains why both conductivity increases greatly and the activation energy drops by  $\sim 1/3$  as Mn and Cu are added. The changes in the conduction properties of Se upon the addition of O can be explained in the same manner, as Mott described in detail in his presentation at Rome.

In the final portion of his talk, Mott discussed  $\text{SiO}_2$  and the oxide glasses in which he expects that, unlike his analysis of the chalcogenides, self-trapped excitons are important in determining the conduction properties. The transport measurements of R.C. Hughes (*Appl. Phys. Lett.* 26, 436, (1975) and (1976) to be published) and the optical work reported by G.H. Sigel (*J. Non-Crystal. Solids* 13, 372, (1973/74)) were cited in support of the existence of excitons in  $\text{SiO}_2$ . Mott did however concede that the existence of a self-trapped exciton in  $\text{SiO}_2$  was still a controversial point.

In a short discussion of alkali-doped (4%) silicate glasses, which concluded his presentation, Mott described what he perceived to be the differences between non-bridging or singly bonded Se and O in chalcogenide and oxide glasses. The Se defects in the chalcogenide glasses consist of doubly occupied (negatively charged) and unoccupied (positively charged) "dangling bonds," which Mott denotes by  $D^-$  and  $D^+$ , respectively. In the oxide glasses the analogous

defects are in his view probably positively charged oxygen vacancies (which can form paramagnetic E' centers) compensated by negatively charged non-bridging oxygens ( $D^-$  in Mott's notation).

Following Mott's presentation, D.L. Griscom (Naval Research Laboratory) commented that W.B. Fowler (Lehigh University) had predicted that self-trapped excitons are not formed in glassy  $SiO_2$ . Mott acknowledged that several authors had suggested that the first peak in the optical absorption spectrum was not due to an exciton (S.T. Pantelides and W.A. Harrison, *Phys. Rev.* B13, 2667 (1976); T.H. DiStefano and D.E. Eastman, *Solid State Commun.* 9, 2259 (1971); P.M. Schneider and W.B. Fowler, *Phys. Rev. Lett.* 36, 425 (1976)), but he reiterated his belief to the contrary.

In contributed papers S.G. Bishop *et al.* (Naval Research Laboratory) described the optically induced paramagnetic centers in chalcogenide glasses and D.L. Griscom *et al.* reviewed radiation-induced paramagnetic defects in  $SiO_2$  and borosilicate glasses. Bishop discussed the influence of local structural order on the observed densities of optically induced ESR centers  $N_S$ , and suggested that the density of the specific structural anomaly which determines  $N_S$  is reduced upon the introduction of tetrahedrally coordinated Ge into the chalcogenide glasses. Griscom enumerated the specific defects in  $SiO_2$  and borosilicate glasses which can be studied using ESR techniques. He also discussed the determination from ESR results of local structural distortions at defect sites which result from the vitreous disorder. R.K. MacCrone *et al.* (Rensselaer Polytechnic Inst.) reviewed their NMR, ESR and Mössbauer studies of  $Fe^{57}$  in oxide glasses.

Three papers at the conference were concerned with random-network models of amorphous solids. P.H. Gaskell *et al.* (Pilkington Brothers Ltd.) described a computer-generated model for amorphous tetrahedral materials which employed a crystallite-like packing arrangement of atomic modules each containing greater than 10 atoms. Gaskell showed agreement with experimentally determined radial distribution functions (RDFs) which was comparable to that obtained using continuous random-network (CRN) models. This presentation was a graphical illustration, to me at least, of the reasons for the lack of progress over the last forty years in determining the structure of glasses - the techniques which give unique structural answers for periodic solids do not provide the basis for a unique structural interpretation in the absence of long-range periodic order.

A 155-atom relaxed CRN model of amorphous Ge which fits the experimental RDF well was described in a paper of M. Popescu

and R. Grigorovici (Institute of Physics, Bucharest) which was competently read by S. Elliot (University of Cambridge) in the absence of the authors. This computer calculation predicted quantitative differences in the elastic constants between amorphous and crystalline Ge. The paper provoked several interesting questions which only the authors could have answered. It is a shame that a full appreciation of this paper was stifled by Romania's foreign travel restrictions.

A three-fold coordinated, 533-atom CRN model was discussed by E.A. Davis *et al* (University of Cambridge). This physical model, which was originally constructed to simulate the structure of amorphous As, has had its atomic coordinates refined and relaxed in energy using a computer. Davis described fits to the RDF's of amorphous As, Sb and P using various versions of the refined and relaxed model. Dihedral angle distributions and ring-size statistics were presented for the three amorphous structures. Davis attributed a peak in the experimental RDFs of amorphous As and  $\text{As}_2\text{Se}_3$  at  $1 \text{ \AA}^{-1}$  to interlayer effects.

Infrared and Raman measurements on glasses were the topics of several contributed papers. G. Lucovsky *et al* (Xerox Palo Alto Research Center) described their interesting, although not surprising, structural interpretations of the infrared and Raman spectra from bulk glasses in the  $\text{Ge}_x\text{S}_{1-x}$ ,  $\text{As}_x\text{S}_{1-x}$  systems and in the corresponding selenide systems. Their results indicate complete chemical ordering (only Ge-S and As-S bonds) at the  $\text{GeS}_2$  and  $\text{As}_2\text{S}_3$  compositions and no As-As or Ge-Ge bonds for the chalcogen-rich compositions. In the Ge- or As-rich regions of composition atomic clusters which contain Ge-Ge and As-As bonds do occur. Similar results for the As-S system were also presented by P.S. Ewan *et al* (University of Edingburgh).

Interpretations of the Raman spectra of  $\text{SiO}_2$ ,  $\text{GeO}_2$  and  $\text{BeF}_2$  were discussed by F.L. Galeener (Xerox Palo Alto Research Center) who suggested that scattering from "longitudinal modes" accounts for nearly half of the lines in the observed spectra. Raman measurements in amorphous polystyrene at low frequencies ( $< 150 \text{ cm}^{-1}$ ) were presented by S.J. Spels and I.W. Shepherd (University of Manchester). Calculations of the vibrational spectra of amorphous As and Se were described by P.E. Meek (University of Cambridge).

Some of the most interesting new results at this meeting were the low-temperature specific heat measurements on amorphous As and germanium chalcogenide glasses which were presented by W.A. Phillips (University of Cambridge). He described a peak in the heat capacity of  $\text{Ge}_x\text{S}_{1-x}$  glasses which becomes more pronounced,

greater in magnitude, and lower in temperature (frequency) as the sulfur content is increased. These significant departures from simple Debye behavior occur in crystalline solids also where they are extremely sensitive to small changes in local structural order. For example, Cristobalite and quartz differ only in the positions of the third nearest neighbors and yet the low-temperature peaks in  $C_V$  are quite different in these two crystals. Thus one cannot conclude much about the changes in local structural order of glasses from changes in the peaks of the low-temperature specific heat except that the changes are due to slight variations in the bonding force constants (i.e., the stiffness of the glass) with composition.

Phillips also presented some unexpected results in the very-low-temperature specific heat of amorphous As where, unlike all other bulk amorphous solids measured to date, no linear term in T is observed. It was suggested that the disappearance of the linear term results from the lack of any two-fold coordinated atoms in amorphous As. If this suggestion turns out to be correct, then it places an important qualification on the topology necessary for the existence of tunnelling modes in amorphous solids.

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