



HAL
open science

NETWORK DIMENSIONALITY OF AMORPHOUS GeS₂ : OPTICAL HIGH-PRESSURE EXPERIMENTS ON a-GeS₂, 2d-GeS₂, AND 3d-GeS₂

R. Zallen, B. Weinstein, M. Slade

► **To cite this version:**

R. Zallen, B. Weinstein, M. Slade. NETWORK DIMENSIONALITY OF AMORPHOUS GeS₂ : OPTICAL HIGH-PRESSURE EXPERIMENTS ON a-GeS₂, 2d-GeS₂, AND 3d-GeS₂. Journal de Physique Colloques, 1981, 42 (C4), pp.C4-241-C4-244. <10.1051/jphyscol:1981451>. <jpa-00220908>

HAL Id: jpa-00220908

<https://hal.science/jpa-00220908v1>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

NETWORK DIMENSIONALITY OF AMORPHOUS GeS_2 : OPTICAL HIGH-PRESSURE EXPERIMENTS ON a- GeS_2 , 2d- GeS_2 , AND 3d- GeS_2

R. Zallen, B.A. Weinstein and M.L. Sláde

Xerox Webster Research Center, Webster, NY 14580, U.S.A.

Abstract. We have carried out studies of the effect of pressure on the following properties of the amorphous form and the two crystalline forms of germanium disulfide: the absorption edge in the near-UV, the refractive index in the near-IR, and the Raman spectrum. The results support the view that GeS_2 glass is not a 3d-network glass akin to silica, but instead has lower network dimensionality.

Germanium disulfide, GeS_2 , exhibits three solid forms: an amorphous form (a- GeS_2) easily prepared from the melt, a layer-structure crystalline form (2d- GeS_2), and a quartzlike crystalline form (3d- GeS_2). The short-range order is the same (4,2 coordination) for all three solids, each of which is a large-bandgap semiconductor, but the long-range order is quite different for the two crystalline forms [1] and, of course, absent for the glass. The notation adopted here (2d-, 3d-) to distinguish between the two crystals refers to the macroscopic dimensionality of the covalent-bond network that characterizes the macromolecular units making up the material [2].

Since GeS_2 is chemically similar to SiO_2 , related to it by a one-row shift in the periodic table, the conventional wisdom for the structure of a- GeS_2 is to regard it as a 3d-network glass akin to fused silica. However, the existence of a form (2d- GeS_2) of lower network dimensionality, as well as recent suggestions by Phillips [3], call for a closer look at this question. In particular, Phillips' proposal for the structure of GeS_2 glass is essentially a 1d-network model based on ribbon-like structural elements derived by scission and edge reconstruction of the layers of 2d- GeS_2 . The difference between this polymeric "linguine model" and the continuous-random-network model is schematically indicated in figure 1.

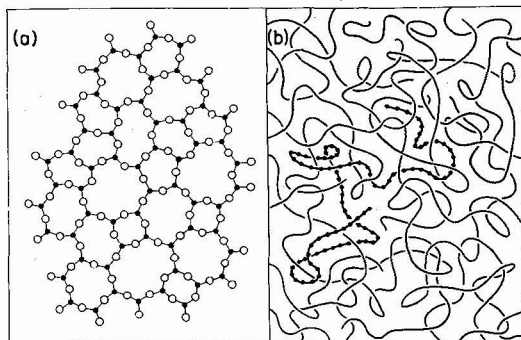


Fig. 1 : Two canonical models for amorphous solids containing covalent networks: (a) Zachariasen continuous random network (e.g., a-Ge, a- SiO_2), (b) Flory random-coil polymer model (e.g., a-Se, polystyrene).

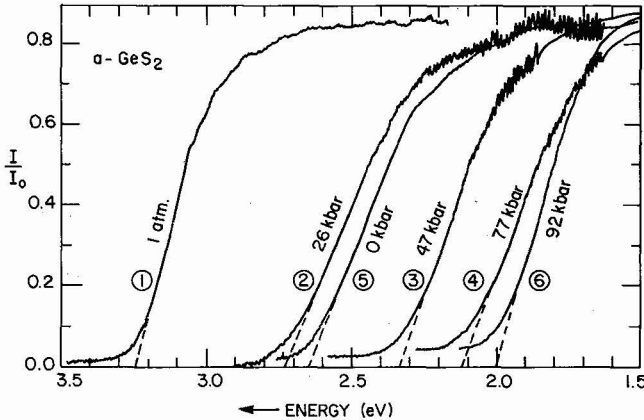


Fig. 2 : The effect of pressure on the room-temperature absorption edge of GeS_2 glass. Circled numbers place the scans in sequence.

Optical experiments at high pressure can provide a means of probing network dimensionality [4,5]. We have carried out, using the ruby-calibrated diamond-anvil-cell technique, studies of the effect of hydrostatic pressure on the following room-temperature properties of all three solid forms of GeS_2 : the absorption edge in the near-UV, the refractive index in the near-IR, and the Raman-scattering spectrum.

Figure 2 shows the effect of pressure on the absorption edge of the glass. Optical transmission is shown plotted against photon energy, at several pressures, for a sample about 2×10^{-3} cm thick (interference fringes produce the oscillations at long wavelength). The optical bandgap redshifts rapidly, decreasing from 3.2 eV at $P=0$ to 1.9 eV at 100 kbar; this may be the largest spectral range over which a bandgap has been "tuned" by an applied field. Unlike the results for the crystals, hysteresis was observed in the pressure behavior of the glass. The pressure dependences of optical bandgaps of all three solids are compared in figure 3. For each, the bandgap closes under pressure; the rate of redshift is swiftest for $\alpha\text{-GeS}_2$ and slowest for 3d-GeS_2 , with 2d-GeS_2 in between.

These results apply to the electronic threshold, the energy gap between the top of the valence band and the bottom of the conduction band. More relevant with respect to the issue of network dimensionality is the *average* gap separating the bands. Information about the effect of pressure on the average gap can be obtained by observing the infrared refractive index, which was done in our optical transmission experiments by monitoring the spacing of the interference fringes in the transparent regime. The results are shown in figure 4. The refractive index is seen to increase rapidly with pressure for $\alpha\text{-GeS}_2$ and 2d-GeS_2 , implying a large pressure-induced decrease in the appropriate average gap (*different* from the bonding-antibonding gap, as will be discussed elsewhere). For 3d-GeS_2 , only a small effect is seen.

In the 3d-network semiconductors of the germanium family, ultraviolet reflectivity studies show that the average gap increases with pressure [6]; the reason is that pressure shortens the covalent bond and increases the bonding-antibonding splitting responsible for the average gap. The bandgap in Ge-family solids usually follows the average gap and blue-shifts under pressure. Chalcogen-based semiconductors such as 1d-Se (chain-structure Se) and $2\text{d-As}_2\text{S}_3$ are essentially molecular solids with van der Waals interactions coupling the covalent-network molecular units. The bandgap in such chalcogenides is observed to *decrease* under pressure because of pressure-enhanced intermolecular-interaction band broadening [5], while relatively little is known about the pressure behavior of the UV reflectivity in these materials.

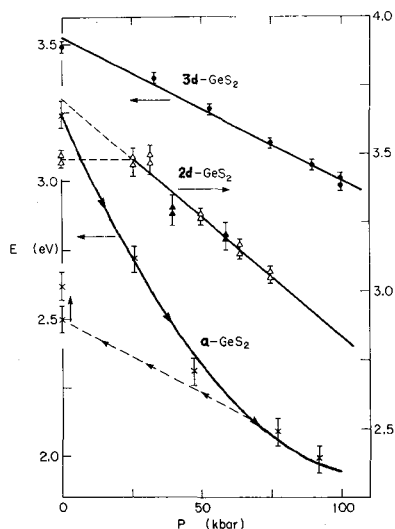


Fig. 3 : The pressure dependence of the positions of the absorption edges of the three solids.

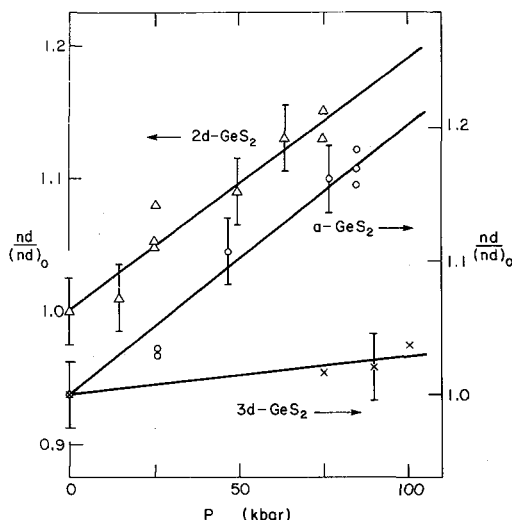


Fig. 4 : The pressure dependence of the infrared refractive index for each material. d denotes sample thickness.

It is clear from figure 4 that a-GeS₂ closely resembles 2d-GeS₂ with respect to the pressure dependence of the refractive index, with both materials distinctly different from 3d-GeS₂ in this regard. This is evidence in support of a molecular structure (covalent network dimensionality <3) for the glass. The bandgap behavior of figure 3 is also consistent with this viewpoint, although the result would have been cleaner had the 3d-network form shown a shift of opposite sign (blue shift under pressure, as in most Ge-family semiconductors). The weak red shift of the 3d-GeS₂ edge may be associated with the bubble-like hollows peculiar to this structure [3] and the nonbonding character of the valence band. At 100 kbar, 3d-GeS₂ undergoes a phase transition to a new (unknown) form that can be retained at atmospheric pressure.

The influence of pressure on the first-order Raman spectrum of the glass is indicated in figure 5. The main effect of pressure is to broaden and to shift the dominant Ge-S stretching band to higher frequency. Several other sharp features in the glass spectrum also broaden with pressure.

Each of the crystalline forms exhibit about 35 sharp Raman lines, consistent with their unit cell complexities. Both crystals have strong lines in regions in which the glass has its main bands. Pressure increases the observed phonon frequencies. The overall behavior of the pressure sensitivities of mode frequencies in 2d-GeS₂ follows a scaling law found earlier for molecular solids [4], while 3d-GeS₂ shows a more subtle behavior. The effect of pressure on the complex phonon spectra of the crystals will be described more fully elsewhere.

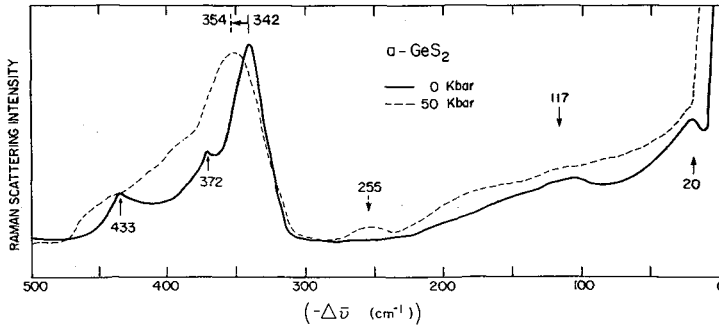


Fig. 5 : The effect of pressure on the Raman spectrum of α -GeS₂.

To summarize, the effect of pressure on several optical properties has been studied for the three forms of germanium disulfide. The results provide evidence that α -GeS₂ is *not* a 3d-network glass akin to α -SiO₂ but instead has lower network dimensionality, a conclusion consistent with a *class* of molecular-solid models which *includes* the Phillips linguistic model. The authors wish to thank J.C. Mikkelsen (Xerox Palo Alto Res. Ctr.) and Z. Popovic (Belgrade University) for kindly providing several GeS₂ samples.

References

- [1] DITTMAR, G. and SCHAFFER, H., Acta Cryst. **B31** (1975) 2060; **B32** (1976) 1188.
- [2] ZALLEN, R., in *Proc. Twelfth Int. Conf. on the Physics of Semiconductors*, edited by M.H. Pilkuhn (Teubner, Stuttgart, 1974), p. 621.
- [3] PHILLIPS, J.C., *J. Non-Crystalline Solids* **43** (1981) 37.
- [4] ZALLEN, R. and SLADE, M.L., Phys. Rev. B **18** (1978) 5775.
- [5] BESSON, J.M., CERNOGORA, J., and ZALLEN R., Phys. Rev. B **22** (1980) 3866; WEINSTEIN, B.A., ZALLEN, R., and SLADE, M.L., *J. Non-Crystalline Solids* **35** & **36** (1980) 1255.
- [6] ZALLEN, R. and PAUL, W., Phys. Rev. **155** (1967) 703.