# EPR SPECTRA AND DEFECT STATES IN GLASSES OF THE $Ge_xS_{100-x}$ SYSTEM

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Received March 19th, 1981

*Dedicated to Professor J. Klikorka on the occasion of his 60th birthday.*

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Glasses of the $Ge_xS_{100-x}$ system were studied in the region of $30 \leqq x \leqq 45$. The concept of magnetically active defect centres was employed to account for the EPR spectra of pure samples as well as those doped with silver or iodine, prepared in different temperature conditions. In terms of this concept a consistent interpretation of the experimental data could be given for the composition region applied.

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In our previous works[1-3] we were concerned with the formation and nature of defect states in $Ge_xS_{100-x}$ glasses for the region $10 \leqq x \leqq 33{\cdot}3$. Based on the structure data[4-6] and the measured EPR spectra, a model of active defect centres has been suggested and the EPR spectra have been simulated[3]. In the present work, glasses with higher contents of germanium ($30 \leqq x \leqq 45$) are studied.

## EXPERIMENTAL

The glass samples were prepared by direct synthesis from the elements in evacuated quartz ampoules. Germanium for semiconductors ($\varrho = 50\,\Omega$ cm, 300 K) and sulphur of 6M purity were used; the latter was freed prior to use from trace carbon impurities by the Wartenberg method[7] and twice distilled in a quartz apparatus under pure argon.

Vitreous samples were obtained and no inclusions or crystals were traced under a microscope in the visible or infrared light. Their amorphous nature was also confirmed by X-ray diffraction analysis. The EPR spectra were measured in the X-band on Varian E4 and ERS 200-AdW Berlin spectrometers. The free spin concentrations were calculated for equal signal modulation width according to the relation $N = N_s I W^2 / I_s W_s^2$, where $N$ is the free spin concentration, $I$ is the peak-to-peak height, and $W$ is the half-band width. The subscript $s$ refers to the standard sample, which was represented by the DPPH radical or "strong pitch" supplied by the spectrometer manufacturer (Varian). The obtained $g$ factor values were corrected by employing an internal standard ($Mn^{2+}$) or the DPPH radical and the standard of Varian ($g = 2{\cdot}0028$).

## RESULTS

The EPR spectra of $Ge_xS_{100-x}$ glasses in the range $x > 33{\cdot}3$ display a single, slightly asymmetric signal (Fig. 1), approaching a Gaussian curve shape. As the concentration of germanium increases, the signal intensity decreases, the $g$ value shifts, and the half-band width $W$ varies to a small extent too (Fig. 2).

The shape and intensity of EPR spectra of vitreous solids are frequently affected also by the thermal history of the sample. With regard to this fact, the effect of the temperature of preparation was examined on two representatives of the glasses, *viz.* $GeS_2$ exhibiting an EPR signal constituted by a single band, and $Ge_{30}S_{70}$ possessing an EPR spectrum of a multiband nature (Figs 3 and 4, respectively). In the former case, the temperature of preparation affected both the shape and the intensity, whereas in the latter case only the intensity varied with temperature.

The shape of the EPR signal for the $Ge_{30}S_{70}$ glass remains virtually unaffected by doping with silver and changes slightly on doping with iodine (Fig. 5); the signal intensity decreases in either case.

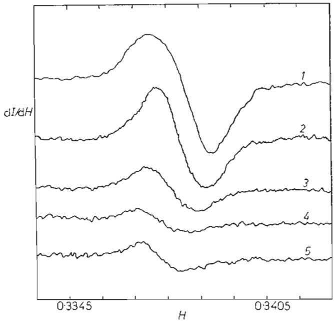


FIG. 1

EPR spectra of $Ge_xS_{100-x}$ glasses. *1* $Ge_{35}S_{65}$, *2* $Ge_{38}S_{62}$, *3* $Ge_{40}S_{60}$, *4* $Ge_{42}S_{58}$, *5* $Ge_{45}S_{55}$. The $dI/dH$ values are in relative units, the corresponding free spin concentrations are given in Fig. 2

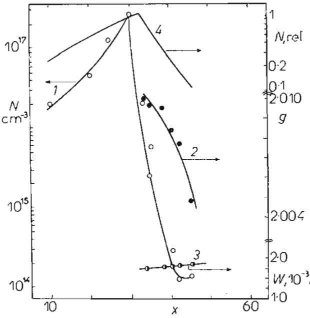
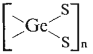


FIG. 2

Dependences of the free spin concentration *1*, $g$ factor value 2, and half-band width $W$ *3* of the EPR band attributed to DC I on the glass composition. The free spin concentrations for $x \leq 30$ were taken from ref.[3], the relative concentrations of the $[GeS_4]$ tetrahedra as the structure units in the $Ge_xS_{100-x}$ glasses 4, from ref.[4]

## DISCUSSION

In agreement with the structure data reported by Lucovsky and coworkers[4], the predominant structure motifs in glasses whose composition approaches $GeS_2$ are  tetrahedra, while in glasses with higher sulphur contents there are present also distorted tetrahedra of $GeS_{m/2}$ type ($m \geqq 5$). As the infrared and Raman spectra indicate, a majority of the germanium atoms is fourfold-coordinated, most sulphur atoms possess the coordination number two over the entire region of glass formation. For energy reasons, formation of heteroatomic bonds (Ge–S) is preferred to formation of homoatomic bonds (Ge–Ge and S–S). Thus in $Ge_xS_{100-x}$ glasses with $x = 33{\cdot}3$ most bonds will be Ge–S, while in glasses with $x < 33{\cdot}3$ and $x > 33{\cdot}3$, Ge–S and S–S bonds or Ge–S and Ge–Ge bonds, respectively, can be expected. In the last-mentioned glasses, the concentration of the $[GeS_4]$ tetrahedra diminishes with increasing $x$ and structure units of the type $[S_3{\equiv}Ge{-}Ge{\equiv}S_3]$ appear to an increasing extent; for $x > 40$, formations occur in which three or more germanium atoms are mutually bonded[4].

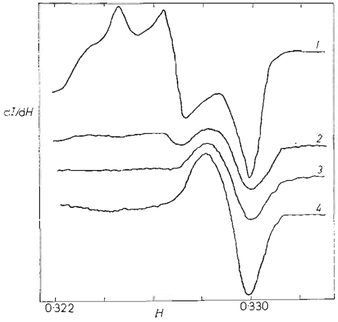


FIG. 3

EPR spectra of $Ge_{33{\cdot}33}S_{66{\cdot}7}$ glasses. The glasses were synthesized at 800°C for 12 h, then heated at 1 000°C for 3 h, and prior to quenching in water, heated for 3 h at the temperature: *1* 800°C, *2*, *3* 950°C, *4* 1 000°C. *1*–*3* inhomogeneous samples; *1*, *2* lighter phase richer in sulphur, *3* darker phase richer in germanium, *4* homogeneous sample

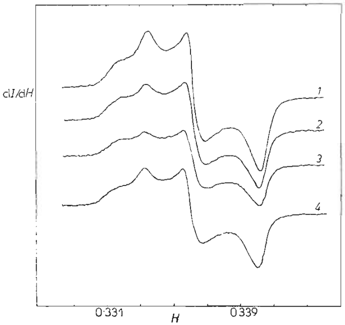


FIG. 4

EPR spectra of $Ge_{30}S_{70}$ glasses. Conditions of synthesis as for Fig. 3, the melt was heated to the temperature: *1* 750°C, *2* 800°C, *3* 850°C, *4* 900°C prior to quenching in water

Owing to higher fluctuations of the bond distances, bonds are broken and defect centres (DC) of the type I, II, and III are created (Fig. 6). According to our previous interpretation[3], the single line EPR spectrum is due to DC I defects (symmetry $\sim T_d$), the multiline spectrum, to DC III defects (symmetry $\sim C_{3v}$), while DC II defects were thought to be magnetically inactive in the region $x < 33{\cdot}3$. Obviously, these conclusions can be applied also to the elucidation of the EPR spectra of glasses richer in germanium ($x > 33{\cdot}3$). As the concentration of germanium increases, so does that of the Ge–Ge bonds. The energy of the Ge–Ge bond is lower than that of the Ge–S bond (in $GeS_2$, the bond energies are[8] $\varepsilon_{Ge-S} = 235{\cdot}7$ kJ mol$^{-1}$, $\varepsilon_{Ge-Ge} = 167{\cdot}5$ kJ mol$^{-1}$, $\varepsilon_{S-S} = 209{\cdot}3$ kJ mol$^{-1}$), and with the increasing germanium content the probability increases that the system disorder will be realized by the breakdown of the weakest bonds, *i.e.* the Ge–Ge bonds. Thus the probability of formation of DC II grows. If the DC II created were magnetically active, the intensity of the EPR signal could be expected to rise or a new signal to appear with increasing germanium content. This, however, disagrees with the experiment, where the EPR signal was observed to decrease with increasing germanium concentration (Fig. 2). (The increase in the free spin concentration in the $Ge_{45}S_{55}$ glass is inexpressive and can be ascribed to the experimental data scatter.)

So, in our opinion, the highly prevailing magnetically active centres in the Ge–S system glasses are the DC I ($x > 33{\cdot}3$) and DC I + DC III ($x < 33{\cdot}3$). This concept can account for the variations in the shape and nature of the EPR spectra with changing germanium content as well as for the effects of temperature and impurities on the defect concentration and nature in the $Ge_xS_{100-x}$ glasses.

Doping with iodine and silver results in a decrease in the EPR intensity and also affects the band shape and position (Fig. 5). We suggest that the iodine or silver

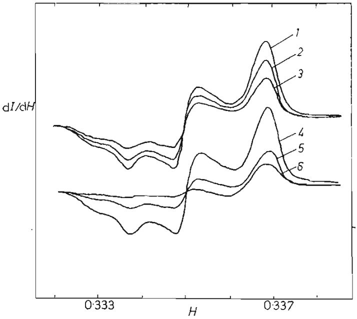
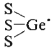


FIG. 5

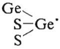
EPR spectra of $Ge_{30}S_{70}$ glasses doped with iodine and silver. 1 pure $Ge_{30}S_{70}$, 2 $Ge_{29{\cdot}7}S_{70}Ag_{0{\cdot}3}$, 3 $Ge_{29{\cdot}4}S_{70}Ag_{0{\cdot}6}$, 4 pure $Ge_{30}S_{70}$, 5 $Ge_{30}S_{69{\cdot}83}I_{0{\cdot}17}$, 6 $Ge_{30}S_{69{\cdot}66}I_{0{\cdot}34}$

atoms are capable of disturbing and terminating the $GeS_{m/2}$ chains or binding to the broken bonds. In both cases the probability of formation of defect centres is lowered. Moreover, the iodine incorporated can disturb the $S_n$ chains bonded in the DC III giving rise to diiodopolysulphanes. The $S_n$ chain shortening, leading to $S_nI_2$, is supposed[9] to be responsible for the substantial drop in the viscosity of molten sulphur effected by additions of small amounts of iodine. A similar mechanism is likely to operate in the $Ge_{30}S_{70}$ glasses, and so the effect is more pronounced in the spectral region that we attribute to the DC III (Fig. 5).

An EPR study of $Ge_{42}S_{58}$ glasses, pure as well as doped with copper, silver, and iodine, has indicated[10] that similarly as in the $Ge_{30}S_{70}$ glass studied by us, the impurities suppress the free spin concentration. Silver and copper doping lowered the *g* value, in contrast to iodine doping which increased this value and whose effect on the free spin concentration was not very marked. For an explanation, the existence was assumed of four types of magnetically active defect centres, two with an unpaired electron at the germanium atom, two with an unpaired electron at the sulphur atom[10]:



*A*



*B*

$\equiv Ge{-}S^{\cdot}$

*C*

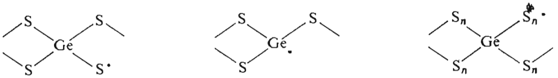
${-}S{-}S^{\cdot}$

*D*

"single line" EPR spectrum

"multiline" EPR spectrum
($x < 33{\cdot}3$)

Watanabe and coworkers[10] assumed that silver and copper atoms disturb the dangling bonds at sulphur and germanium, whereas iodine atoms do not influence the concentration of the broken bonds with the electron localized at sulphur, but do disturb the dangling bonds at germanium. In terms of this concept the authors offer



DC I

DC II

DC III

FIG. 6

Suggested defect centres in $Ge_xS_{100-x}$ glasses. The unpaired electron is shown as a dot. This electron is probably delocalized over the entire centre. The indices at the sulphur atoms in DC III can acquire various values $n \geqq 1$, of which at least one $n > 1$

an explanation of the opposite sense of the $g$ value shifts on doping the $Ge_{42}S_{58}$ glass with iodine and with silver or copper. For reasons discussed above, we suggest that the Watanabe's A centre (corresponding to our DC II, refs[1-3]) is magnetically inactive or at least its concentration is exceedingly low and plays no appreciable part. This is borne out by the fact that in the $Ge_{42}S_{58}$ glass, in which there is a relatively high Ge–Ge bond concentration and consequently a high probability of DC II formation, the centres possessing the unpaired electrons at the sulphur atoms are more abundant[10] than those with the lone electrons at germanium.

Atoms of silver or copper impurities obviously replace germanium atoms, iodine substitutes sulphur. By their incorporation the nature of the chemical bonds in their neighbourhood is altered, the flexibility of the $GeS_m$ chains increases, and so the DC I concentration drops. At the same time, the Me/X ratio changes (Me is Ge + + Cu or Ge + Ag, X is S or S + I). The $g$ factor value depends on this ratio to an extent (Fig. 2). This is why the $g$ value is altered in different ways by the presence of I and Cu. Thus in the region $x > 33{\cdot}3$ a single defect centre, *viz.* DC I, can be attributed to the experimental EPR spectra. This view is also supported by the fact that the shift in the $g$ value of the EPR band is not accompanied by a change in the half band width, as would be expected for an overlap of two bands due to two defect types. The actual defect concentration in the glasses exceeds the free spin concentration[11]; thus a fraction of the electrons form the broken bonds is paired, as evidenced by photoinduced EPR measurements. The photoinduced increase in the EPR intensity is higher[11] for samples richer in germanium, which is consistent with out concept. Also the observed free spin concentration is lower than the concentration of the $[GeS_4]$ tetrahedra as determined by Lucovsky and coworkers[4]. For instance, in the $GeS_2$ glass there is one broken bond with an unpaired electron per approximately $10^4$ $[GeS_4]$ tetrahedra. The free spin concentration varies with the content of germanium faster than the concentration of the $[GeS_4]$ tetrahedra (Fig. 2). In the region richer in sulphur ($x < 33{\cdot}3$) the disorder in the system can result from the breakdown of the weaker S–S bonds; in the region richer in germanium ($x > 33{\cdot}3$) the weakest bonds of the system, Ge—Ge, are broken more easily and the free spin concentration drop relative to the $[GeS_4]$ tetrahedra concentration is here even more rapid (Fig. 2) than in glasses richer in sulphur.

In dependence on the way of preparation (Fig. 4), only the EPR spectral intensity varies for the $Ge_{30}S_{70}$ glasses, whereas in the case of vitreous $GeS_2$ both the intensity and the shape can vary. Homogeneous $GeS_2$ glasses cooled by quenching in water from temperatures of 970 – 1 000°C exhibit single line spectra, as observed by us previously[1-3]. For the same quenching from temperatures 850 – 950°C a multiline structure can be traced or even can predominate. Glasses displaying multiline spectra, however, are inhomogeneous, showing lighter and darker (of more pronounced red colour) regions. The content of germanium in the two phases is different, its fraction in the darker phase being $x > 33{\cdot}3$, in the lighter phase, lower. At temperatures 850−950°C the $GeS_2$ melt is in part dissociated through the reaction

$$2\,GeS_2 \rightleftarrows GeS_{2+x} + GeS_{2-x} \qquad (A)$$

which is accompanied by the formation of two sparingly miscible liquids. In the lighter part, richer in sulphur, the DC III prevail, in the darker part as well as in pure $GeS_2$, the DC I predominate. The resultant spectrum then represents their combination. The total change in the defect centre concentration is in both cases ($Ge_{30}S_{70}$ and $GeS_2$) affected by the temperature shift of the equilibrium between the broken and the intact bonds as well as by the temperature dependence of the reaction

$$2\,D^\circ \rightleftarrows D^+ + D^- , \qquad (B)$$

according to which the electronic states with unpaired electrons ($D^\circ$) are brought into the polar states with paired electrons.

To sum it up, the most probable defect centres in glasses rich in Ge ($x \geqq 33{\cdot}3$) are the DC I; this is consistent with the results of the papers[3] as well as[10-13].

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Translated by P. Adámek.