INTRINSIC DEFECT STATES AND ELECTRON SPIN RESONANCE
IN THE Ge-S BULK GLASSES

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A review of electron paramagnetic resonance (ESR) of bulk glassy Ge-S system is presented. The longe-range periodicity in amorphous materials and glasses is disturbed by the fluctuations of bond angles, bond lengths and by composition as well. In a limit case an increase of the bond length can break chemical bonds between atoms of glass and so-called dangling bonds are formed. These are singly occupied an thus paramagnetic if stabilized by lowering of Hubbard's energy. The dangling bonds in chalcogenide glasses and their relation to the ESR spectra are still questionable. Dangling bonds however can interact with nearest atoms of glass and create another type of multiatomic defect centers which are still paramagnetic.

This review can also help to solve the problem why in the whole class of chalcogenide glasses the so-called dark ESR signal is found in Ge-S glasses only.

Defect states in chalcogenide glasses are known to have unique properties. Based on the idea of Anderson[1], Street and Mott[2] proposed a model that the defect states are the dangling bonds D°, and the lattice distortion effects are

strong enough for these states to exhibit a negative effective electron correlation energy U, resulting in charged centers D^+ and D^-. In chalcogenide glasses, a positively charged defect D^+ interacts with neighbouring lone-pair electrons, bonding with it by distorting their environment. The authors[3] proposed that the following reaction becomes exothermic by large lattice distortion effects

$$2D^\circ \rightleftharpoons D^+ + D^- \tag{1}$$

The neutral d° defect is ESR active because of the presence of one unpaired electron. The ESR signal in Ge-S glasses was observed first by Arai and Namikava in 1973 (Ref.[3]), Fig.1. They found that the signal changes with composition. In $Ge_{1-x}S_x$, for $x < 0.66$, the spectrum exhibits a single line, while a multicomponent line is observed for compositions with $x > 0.66$. The first problem was the assignment of the defects to the signals. But a basic problem which has not been solved up to now was, why in the group of chalcogenide glasses only Ge-S system exhibits the ESR signal. In order to answer these questions, several studies have been done, see below.
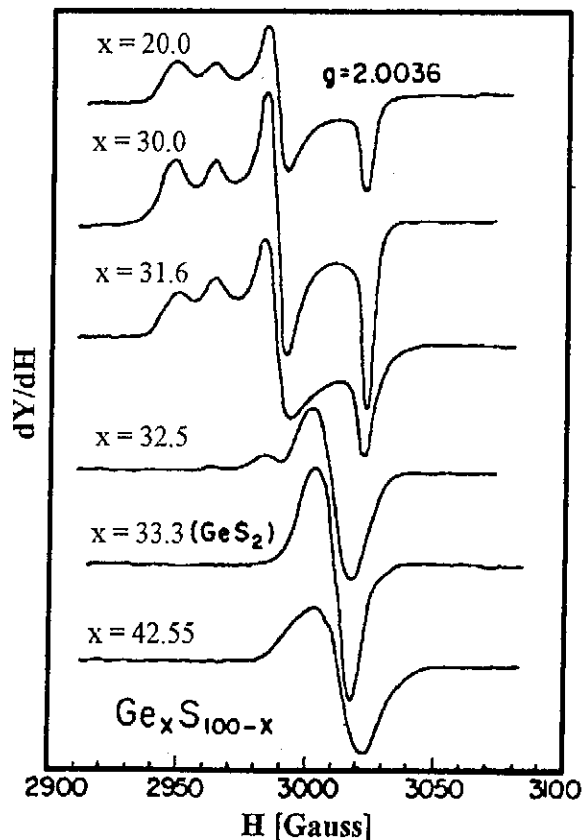

Fig.1 ESR spectra of Ge_xS_{1-x} glasses, firstly observed by Arai and Namikawa[3]

The authors[4] studied the effect of impurity-doping on the ESR spectra. Samples of $(Ge_{0.42}S_{0.58})_{100-x}$ X, X is Cu, Ag and I, were measured at room temperature by using X-band frequency. The authors observed two kinds of signal in undoped $Ge_{42}S_{58}$ glasses. One was asymmetric and of a nearly Gaussian shape with g = 2.0067 ± 0.0002 and a linewidth ΔH = 18 G, which is the same signal as that observed by Arai and Namikawa[3]. The other one was a new signal with Lorentzian shape, g = 2.0029 ± 0.0002 and ΔH = 4.5 G. The introduction of Cu or Ag into Ge-S glasses causes a g-shift to lower values and a sharp decrease of the defect center density. The introduction of iodine brings about a g-shift to higher values and a weak decrease of the defect center density. The g-shift was explained:

1. The ESR signal is composed of centers originating from dangling bonds of Ge and S, as well.
2. The g-value of the dangling bond of Ge is smaller than that of S.
3. Iodine prefers to combine with Ge in the glass, while Cu and Ag prefer to combine with S.

Under these assumptions, the introduction of Cu, Ag and iodine into the glass will destroy the S-dangling bonds and the Ge-dangling bonds, respectively. The authors[5] proposed a model of intrinsic paramagnetic defects in Ge-S glasses, and the ESR spectra were simulated, Fig. 2. On the basis of IR and Raman study[6-8] they concluded that these glasses are formed mainly by $[GeS_4]$ tetrahedra for GeS_2 stoichiometric composition, and by $[GeS_4]$ tetrahedra connected by $[S_n]$ chains inserted between the above-mentioned tetrahedra, in the glasses with overstoichiometry of sulphur. Defect centers are created by bonds breaking. The authors suggested:

for $[GeS_4]$ defect centers T_d symmetry .... A
for $[GeS_{4+n}]$ defect centers C_{3v} symmetry ...... B

They concluded that the A centers density depends on the sulphur concentration analogously to the relative population of $[GeS_4]$ tetrahedra given by Lucovsky[6].

On the other hand Watanabe and Shimizu[9] attributed the single line ESR spectra of GeS_x (1 < x < 2) bulk glasses to a dangling bond on Ge, and the multi-line spectra for x > 2 to a dangling bond on sulphur. The ESR signal with three principal g-components one of which is very close to a free spin value can be explained on the basis of the so-called powder pattern spectra. For the present bulk sample, four effective g-values were observed: 2.002, 2.025, 2.040 and 2.050. The authors tentatively attribute the ESR spectrum observed to (-Ge-S.) and (-S-S.) paramagnetic defects.

The ESR signal of $Ge_{42}S_{48}$ glass is attributed to two types of Ge dangling bonds: ($-S_3Ge.$) and ($S_2Ge-Ge.$), Fig. 3. The reduction of densities of dangling bonds and the increase of the slope of the Urbach tail with Ag doping was explained by assuming that Ag is onefold coordinated and acts as a terminator of dangling bonds.
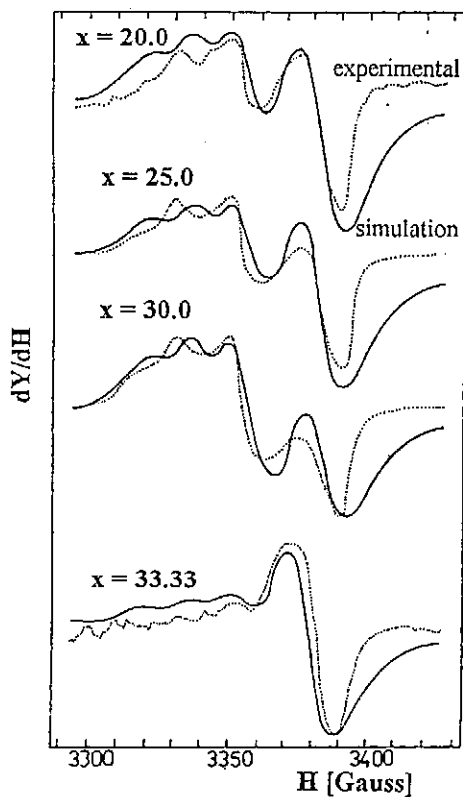
Fig. 2 Experimental (dashed lines) and computer-simulated (full-lines) ESR spectra, Ref.[5]. Computer simulation was made under assumption of delocalization of electron over the entire centrum
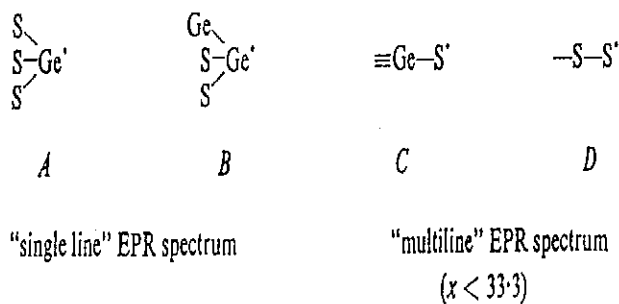

Fig. 3 ESR active defect centers in Ge-S glasses, Refs[4,9,10]

The authors[10] studied glasses of $Ge_{42}S_{58}$ and $Ge_{30}S_{70}$ compositions. They continued their former works[4,9,10] and explained the paramagnetic defects found

in Ge-S glasses by energy overlapping between one electron state of singly occupied dangling bonds and doubly occupied dangling bonds present in the glasses under study due to large randomness. The authors tried to solve the problem why Ge-S glasses are the only ones of chalcogenide glasses to exhibit dark ESR signal at room temperature, it means ESR spectra without any excitation. They suggested that this is due to a large randomness of Ge-S system in comparison with other chalcogenide glasses or to a large ionic character in Ge-S bond. The author[11] studied influence of impurities (Ag, Cu, Mn) on the ESR spectra of $Ge_{40}S_{60}$ glass, and concluded that the additions of Ag and Cu influence not only the intrinsic Gaussian signal of pure $Ge_{40}S_{60}$ glass, but cause a new, previously not observed Lorentzian signal. He attributed this signal to paramagnetic defect centers localized on the metal (Ag, Cu). On the basis of interpretation of measured ESR lines of Mn^{2+} ions he identified the Ge[4S] and Ge[2Ge2S] tetrahedra as structural units in the Ge-S glass-forming region with the concentration of Ge higher than 33.3 at.%. No octahedral coordination of Mn^{2+} ions (which can be expected from the short-range order in crystalline GeS) was observed. From the measured values of HFS constant[11] it was suggested, that the nearest neighbours Ge-S distances are shorter and the character of bonds in $Ge_{25}S_{75}$ glass is more covalent than in $Ge_{40}S_{60}$.

The authors[12] studied glasses of Ge_xS_{1-x} ($0.30 < x < 0.45$) compositions. A single line, slightly asymmetric signal, approaching a Gaussian shape was found. As the concentration of Ge increases, the signal intensity decreases, the g-value shifts and the half-width of band varies to a small extent as well. They connected this signal with ($-S_3Ge.$) defect center. The ESR spectral intensity of $Ge_{30}S_{70}$ glass changed with changing conditions of synthesis, but the line-shape remained unchanged. They found[12] that GeS_2 glass is homogeneous when quenched in cold water from temperature ranging from 970 up to 1000 °C and exhibits a single line ESR spectrum. The glass of the same composition quenched from 850 - 950 °C exhibits a multi-line ESR spectrum. This glass with multi-line ESR spectrum was found to be inhomogeneous, showing lighter and darker separated phases. The GeS_2 melt was probably partly dissociated forming two sparingly miscible liquids

$$2\,GeS_2 \rightleftharpoons GeS_{2+x} + GeS_{2-x} \tag{2}$$

The authors[12] studied the influence of doping of Ag, I and Cu ions into the Ge-S glasses, as well. Ag and Cu lower the g-values in contrast to iodine doping which increases g-value and whose effect on the defect concentration was not very distinct. Atoms of Ag or Cu impurities probably replace Ge atoms, iodine substitutes sulphur. By their incorporation, the nature of the chemical bonds in their neighbourhood is altered, the flexibility of the GeS_n chains increases and so the concentration of ($-S_3GeS.$) falls down. At the same time the Me/X ratio changes (Me is Ge+Cu or Ge+Ag, X is S or S+I). The value of g-factor depends on this ratio.

The authors[13] studied temperature dependence of ESR signal in amorphous

Ge-S system for $Ge_{42}S_{58}$ glass and $Ge_{30}S_{70}$ glass and the effect of Ag doping. For glasses with composition close to $Ge_{42}S_{58}$ they found two kinds of paramagnetic defects whose densities at first increase and then decrease with increasing temperature, Fig. 4. From this anomalous temperature dependence they concluded that the network of the glasses contains dangling bonds on Ge having effective correlation energy U, which can change from positive to negative value depending on the environment relaxation around the dangling bond. They suggested that the Ge-defect was the T_3^0 defect (KAF notation), i.e. electrically neutral three-fold coordinated Ge. An electron transfer from one T_3^0 to another T_3^0 defect costs the effective electron-correlation energy U produces positive and negative three-fold coordinated defects, T_3^+ and T_3^-, both without unpaired electron. Among these defects, equilibrium would be attained through the interconversion reaction

$$2\,T_3^0 \rightleftharpoons T_3^+ + T_3^- \tag{3}$$

In this reaction:
  if U is positive, the state $2T_3^0$ is lower in energy,
  if U is negative, the state $T_3^+ + T_3^-$ becomes lower in energy.

Elliot[14] argued that the reaction (3) in tetrahedrally bonded amorphous semiconductors is endothermic ($U > 0$) in the framework of sp^3 hybridized bonding, but the reaction becomes exothermic ($U < 0$), if the centre dehybridizes from sp^3 to p-like bonding orbitals. Similar argument was also proposed by Adler[15]. In the Ge-S glasses, such a relaxation of defects would be more favourable than in the tetrahedrally bonded amorphous semiconductors because of additional degree of freedom of two-fold coordinated chalcogens.

Another possible reaction with negative U is

$$2\,T_3^0 \rightleftharpoons C_3^+ + T_3^- \tag{4}$$

C_3^+ means the chalcogen atom (three-fold coordinated, positively charged). The authors[13] did not say which of reactions (3) or (4) is more energetically favourable.

In the $Ge_{42}S_{58}$ glass with Ag doping the density of defects with positive U increases as compared to that in the undoped sample. These results suggest a decrease of randomness in the network by Ag doping. These suggestions are in good agreement with Refs[4,12].

The authors[16] studied $GeS_{2\pm x}$ ($x = 0.01$) glasses melted at 683, 789 and 895 °C. The ESR spectra of as-quenched glasses are characterized by a narrow symmetric ESR line ($g = 2.0037$, $\Delta H_{pp} = 3\,G$) - A-component and a broad asymmetric one ($g = 2.0113$, $\Delta H_{pp} = 17\,G$) - B-component. The A-component was attributed to a ($-Ge_3S.$) species, i.e. a hole located on non-bridging sulphur atom. It was argued that if the A-component is due to an electron state of Ge, g-value would be expected less than g-value of free electron (e.g., in GeO_2
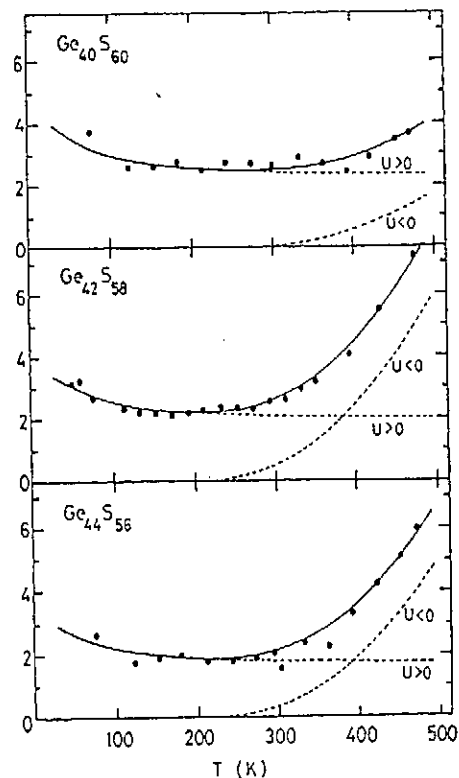
Fig. 4 Temperature dependence of the ESR centers density in bulk Ge-S glasses with different compositions. For details see Ref.[13]

glass so-called E' centrum has g-value $g_{x-y} = 1.9944$ and $g_z = 2.001$). The authors did not specify a configuration of S atom.

The research work described in Ref.[17] (started in the work[16]) studied frequency and temperature behaviour of ESR spectra of GeS_x glasses for $x = 1.25 - 2.01$. It was found:

A-component: a symmetric narow line
X-band $g_{eff} = 2.003$, $\Delta H_{pp} = 3\,G$
Q-band $g_{eff} = 2.003$, $\Delta H_{pp} = 4.8\,G$

B-component: an asymmetric broader resonance
X-band $g_{eff} = 2.0112$, $\Delta H_{pp} = 16.25\,G$
Q-band $g_{eff} = 2.0045$, $\Delta H_{pp} = 11\,G$

It was proposed[17], that the A- and B- components cannot be explained by unpaired electrons localized on sulphur or germanium dangling bonds[5,16]. An $S = 1/2$ paramagnetic state with anisotropic g-values will have a line width at

35 GHz four times grater than at 9.5 GHz (Ref.[18]). The line width with paramagnetic state $S > 1/2$, independent of the frequency of measurements provides that the line width is not appreciable affected by spin-lattice relaxation effects.

In the case of:

A component: $\Delta H_{pp}(35\ \text{GHz})/\Delta H_{pp}(9.5\ \text{GHz}) = 1.6$

B component: $\Delta H_{pp}(35\ \text{GHz})/\Delta H_{pp}(9.5\ \text{GHz}) = 0.68$

The A-component then was explained by an unpaired electron hopping between different germanium sites. B-component was attributed to a paramagnetic conduction electron.

The authors[19] studied defects of the chains ends in liquid S, As-S, Ge-S systems using the temperature dependence of ESR. From the temperature dependence of ESR spectra of sulphur they deduced three characteristics:

1. Appearance of an ESR singlet with $g = 2.02$ at temperatures higher than 160 °C (the S_8 ring molecules begin to break, forming long linear chains).
2. The line shape was almost Lorentzian and the width increased markedly with temperature. The life time of the radical decreases which occurs in turn by chemical exchange, spin-lattice or spin-spin relaxation.
3. The concentration of the radical species was very high especially at higher temperature (for example at 700 °C - 1.3×10^{21} spin/g).

It is interesting to note that the average chain length of about 20 atoms at this temperature was obtained by rheological experiments[20]. It is in close agreement with the spin concentration, if the chain ends are exclusively composed of a sulphur radical. This implies that at least several tens % of the chain ends are neutral defects. The authors supposed that ESR absorption in GeS_2 and Ge_2S_3 is due to Ge dangling bonds. Among all the stable isotopes of Ge has ^{73}Ge only nonzero nuclear spin ($I = 9/2$). One might expect to observe the HFS due to interaction between an unpaired electron localized on ^{73}Ge and Ge nuclear spin. The low natural abundance of ^{73}Ge (7.76%) could be compensated by gamma-irradiation at 77 K for enhancing the ESR absorption, Fig. 5. Simulations were carried out to confirm that these HFS absorption lines could be due to ^{73}Ge nuclear spin interaction. The agreement between the observed and calculated spectra was satisfactory when suggested the center is a E' centrum on germanium, Fig. 6.

It was found, that in the melts of sulphur, arsenic sulphides and germanium sulphides at high temperature, chain ends are composed exclusively of radical species, dangling bonds. The radical species disappear during the cooling process from a melt to glass in the case of S and As-S, whereas some fraction of neutral defects remain unchanged in Ge-S. Therefore, there must be a big difference between the rates of recombination of the radical species in
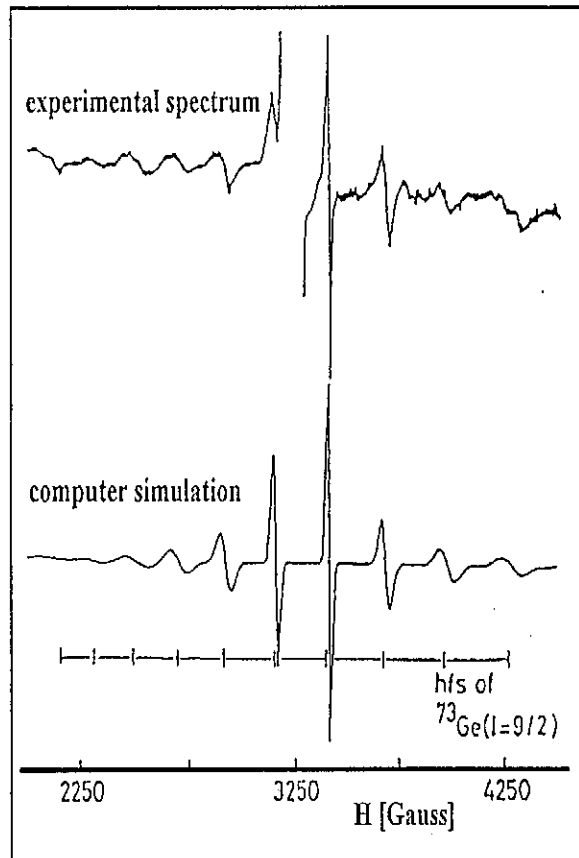
Fig. 5 ESR spectrum of γ-irradiated GeS_2 glass with well resolved HFS and its computer simulation, Ref.[19]

As-S and Ge-S; the rate in the former must be higher than that in the latter by several orders of magnitude. One of the chemical characteristics of S and As-S is that they are viewed as a molecular system in which two kinds of chemical bonds are present, intramolecular or covalent and intermolecular or van der Waals bonds. Upon melting of crystalline chalcogenides only the weak intermolecular bonds are broken, this resulting in a formation of a molecular liquid. In the case of GeS_2 melting is possible only by breaking of the intramolecular Ge-S bonds. The great rigidity of the melt suppresses atomic arrangements necessary for the recombination reaction.

The papers[19,21] suppose the existence of neutral defects in contrast to the authors[22] in their classical model of valence-alternation-pair (VAP-model). The most important assumption underlying this physical model is that the structural defects constituting the gap states must be negatively or positively charged.
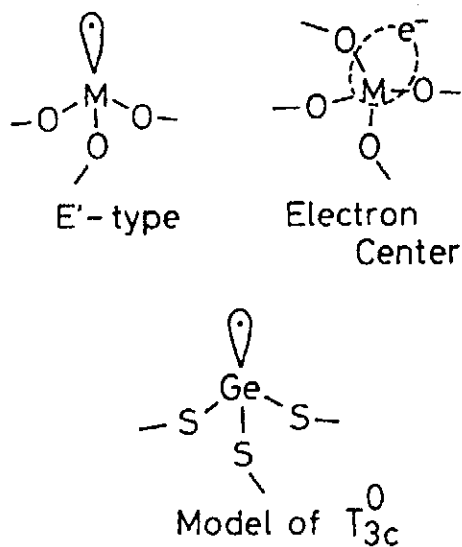
Fig. 6 Models of paramagnetic defects in oxide glasses and GeS_2 glass, Ref.[9]

In the S-rich Ge-S glasses it is considered[19,21] that the multi-line spectrum is composed of a superposition of absorptions due to S dangling bonds, (-S.) and (-S-S.). The difference between these two defects is apparent in the anisotropy of their g-tensors. Two of principal g-values, g_x and g_y, are similar for (-S.) and (-S-S.), whereas their g_z values are significantly different. In the Ge-rich glasses it was proposed that the absorption is due to Ge-dangling bonds. The origin of the ESR absorption in GeS_2 glass is connected with paramagnetic defect on germanium.

The authors[23] studied in detail Ge_xS_{1-x} glasses by ESR method, Fig. 7. They have subdivided the glass forming region $0.10 \leq x \leq 0.44$ into three intervals:

a) $0.10 \leq x \leq 0.335$
b) $0.335 < x \leq 0.39$
c) $0.39 < x \leq 0.44$

Each of these intervals has many specific features and can be divided, accordingly, into smaller intervals.

1. In the first region $x \leq 0.325$ the ESR signal with g-tensor components g_1', g_2', g_3', Fig. 7, is produced by defects in the *cis*-configuration of sulphur atoms which is typical of the broken sulphur rings. The ESR signal with g_1, g_2, g_3 components is generated by the defects in *trans*-configuration of sulphur which arise at the breaking of sulphur chains. The ratio of the paramagnetic centers in *cis*- and *trans*-configurations of sulphur remain constant up to $x = 0.30$. This means that the relative
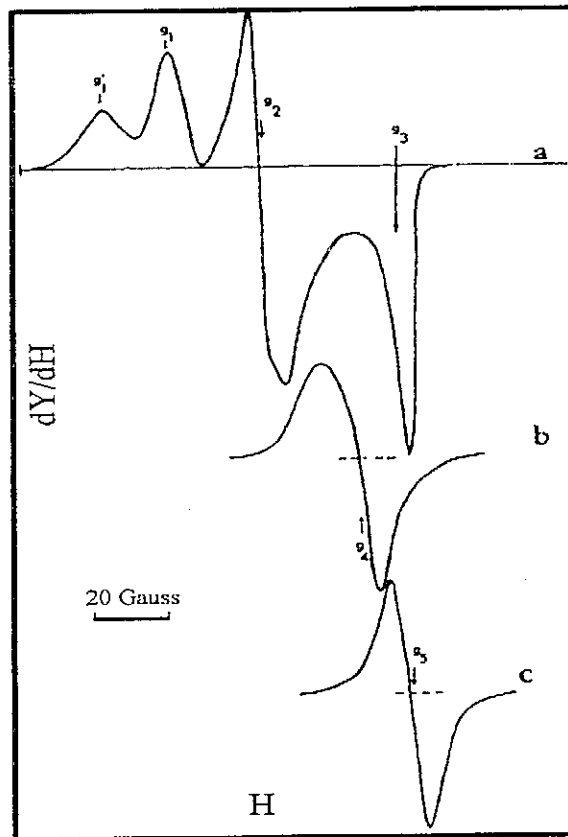
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Fig. 7 Typical ESR spectra for Ge_xS_{1-x} glasses taken from Ref.[23], see text for details

number of ring and chain paramagnetic centers is a constant quantity.

2. The second part of the glass-forming region is characterized by slightly asymmetric line with the parameters: $g_{av} = g_4 = (2.0096 \pm 0.0005)$. This signal was assigned to $(-S_3Ge.)$ defect.

3. The third part of the glass-forming region showed an ESR signal with $g_{av} = (2.004 \pm 0.0005)$.

The authors[23] studied these paramagnetic defects in all these regions under γ - irradiation and temperature dependence of concentration of these centers, as well.

The authors[24-34] studied ESR spectra of Ge-S glasses. They started from the short range order model (SRO) (Ref.[24], Fig. 8, giving the relative population of the structure units in the sulphur-rich Ge-S glasses. The units proposed were: (-S-S-S-), (-Ge-S-S-) and (-Ge-S-Ge-) . They tried to answer the following
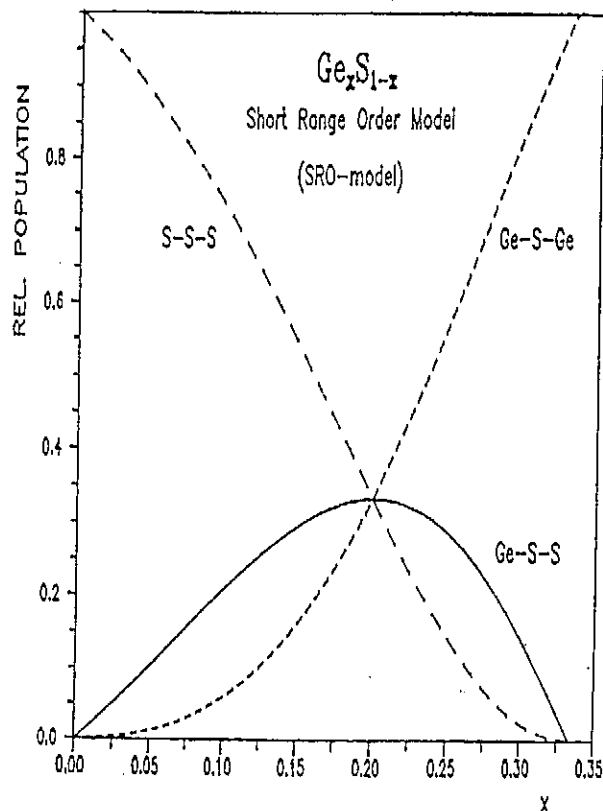
Fig. 8 Short range order model of Ge-S glasses with sulphur overstoichiometry, Ref.[24]

questions:

1. Why the dark-ESR (not induced) signal is in Ge-S glasses only and is not present in the glasses from the whole family of chalcogenide glasses.
2. Why the paramagnetic centers in Ge-S glasses are very stable not only at room temperature but even at higher temperatures.
3. Why the dependence of concentration of paramagnetic centers is not monotonous with increasing of sulphur content (and thus decreasing Ge content).
4. Why stable paramagnetic centers do not exist in amorphous sulphur.

In the work[25] the authors studied polycrystalline $\alpha - GeS_2$ and $\beta - GeS_2$ modifications by ESR spectroscopy, Fig. 9.

Compared with $v - GeS_2$ they assumed, that the structure of $v - GeS_2$ in medium range order is probably very close to the structure of high-temperature modification (α-modification) of crystalline GeS_2. They deduce that the structure of glassy GeS_2 is composed of the fragments of 2D structure of $\alpha - GeS_2$ rather than of 3D cross-linked "network" of $\beta - GeS_2$ type.

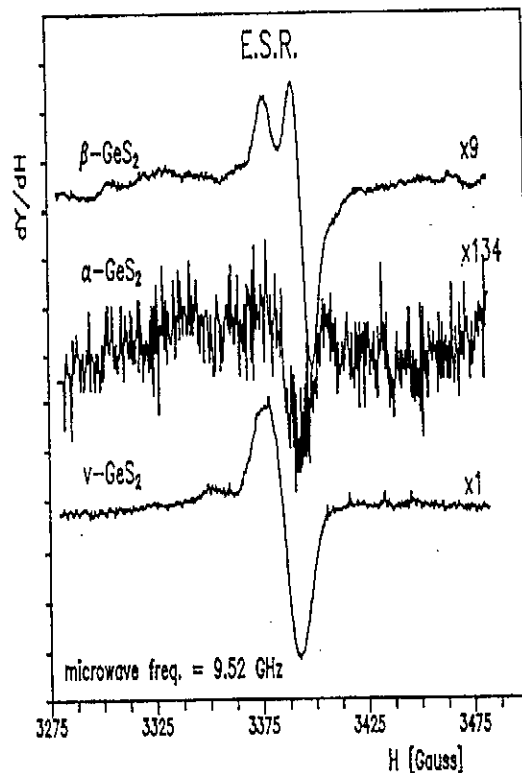The author[26] studied vanadium doped Ge-S glasses, Fig. 10. Based on the

Fig. 9 Comparison of ESR spectra of α- and β-modifications of polycrystalline GeS$_2$ and vitreous GeS$_2$, Ref.[25]

analysis of ESR spectra the author suggested, that vanadium in oxidation state +IV with sixfold coordination is built up in the glassy matrix of Ge-S. Experimental results are interpreted on the basis of chemical ordering model which prefers heteropolar Ge-S bonds. It is supposed that vanadium is bonded mainly to sulphur of Ge-S-S-Ge structural units.

The authors[27] suggested, that the ESR active centers in the sulphur-rich Ge-S glasses are intrinsic DC with unpaired electrons of the type (Ge-S.) and (Ge-S-S.). These centers are formed by breaking of the S-S or S-Ge bonds on the edges of 2D S-rich clusters. The doping of vanadium into stoichiometric GeS$_2$ glass gives rise to a new ESR spectrum which can be assigned to V^{4+}, or more probably VS^{2+} ion. The doping of vanadium into Ge-S glasses from S-rich region lowers the intrinsic ESR signal only, but does not create a new signal.

In the papers[28-32] the authors studied the structure and defect states by IR, temperature dependence of d.c. conductivity, luminescence, LESR and ODMR. Based on the results of these studies a new non-dangling bond model of paramagnetic defects in Ge-S glasses was created[36].

Several models of paramagnetic defect centers (DC) were proposed, for
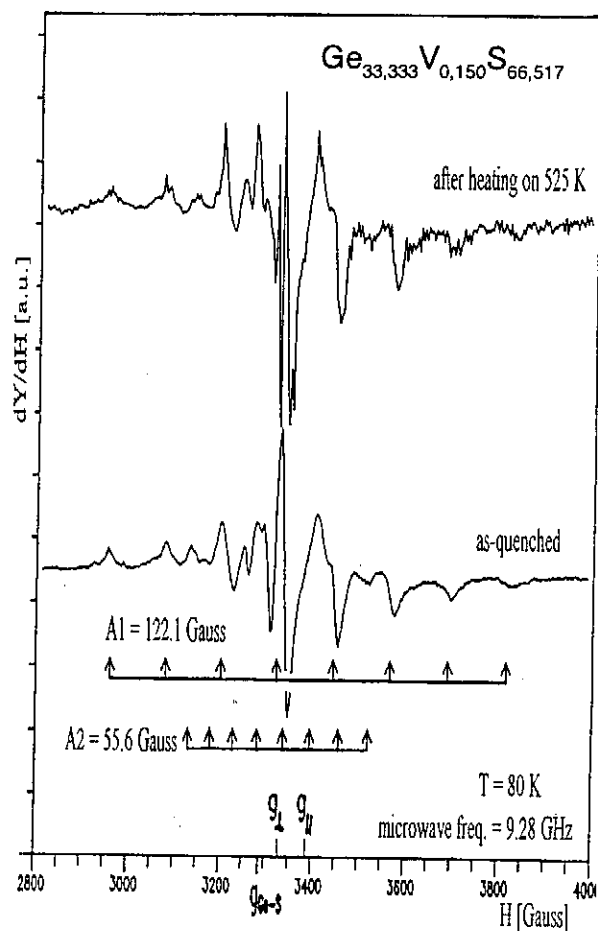
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Fig. 10   Typical ESR spectrum of Ge-V-S glass, Ref.[26]

example by Černý and Frumar[5], Watanabe et al.[21], Zhilinskaya et al.[23], but non of the above-mentioned models is able to explain consistently the important features of DCs in Ge-S glasses, among others the compositional dependence of DC's density as well as their good thermal stability in the Ge-S glasses. These models mentioned-above cannot give a convincing answer to the fundamental question: Why the stable dark ESR spectra can be found *in Ge-S glasses only*?

Based on the results of[33], the authors[34] studied the ESR spectra of Ge-S glasses from the whole glassforming region at $N_2(I)$ temperature as well as the LESR spectrum of amorphous sulphur (Ar^+ laser illumination, $\lambda = 454$ nm, i.e. 2.73 eV).

The ESR spectra of Ge_xS_{1-x} glasses can be divided into two groups, as we mentioned above.

1. multi-line spectra of the glasses, $x < 0.333$

2. single-line spectra of the glasses, $x \geq 0.333$

In the multi-line ESR spectra there is a slightly asymmetric band with $g \sim 2.010 - 2.014$ superimposed over well-known multi-line part of ESR spectra found in previous studies. The relatively highest intensity of this asymmetric band ($g \sim 2.010 - 2.014$) as compared with the intensity of multi-line part was found in the multi-line ESR spectrum of as-quenched glass $Ge_{0.15}S_{0.85}$. The g-factor of asymmetric band is typical of the asymmetric single-line ESR spectrum of Ge_xS_{1-x} glasses with $x > 0.333$. The DC responsible for this signal is, therefore, present in the glasses from the whole Ge-S glassforming region and *not only* in the glasses with $x > 0.333$, as it was supposed, e.g. in Refs[13,21].

The integral area of the ESR bands is proportional to the density of ESR-active defects, Fig. 11. Compositional dependence of DCs' density possesses a broad maximum for glasses with composition near to $x = 0.25$. For samples with overstoichiometry of Ge or S the DCs' density decreases when the content of Ge or S increases. This fact is in *strong contradiction* with DCs' based on the idea of dangling bonds on sulphur (-S. and -S-S.), proposed earlier, e.g. in Refs[5,9].

In the single-line part of ESR spectrum the maximum is near $x = 0.35$ and it is not as high as for multi-line spectrum. The intensity of ESR signal also decreases with the increase of Ge.
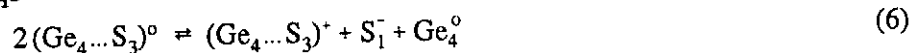
The way of localisation of unpaired electron on the DCs affects the ESR g-tensor components. The value of i-th component of the g-tensor can be described by

$$g = g_e + \Delta g_i \qquad (5)$$

where $g_e = 2.00232$ free electron g-value). For the so-called electron ESR active centrum $\Delta g_i < 0$ and $\Delta g_i > 0$ for the so-called hole centrum, in usual cases.

The defect centres created in glasses during the material preparation (synthesis in the melt) and then frozen in the glass exhibit $\Delta g_i > 0$ in all known cases. In the glasses formed, the equilibrium of uncharged defects is reached, according to Eq. (1).

If the uncharged defect holds threefold coordinated sulphur and normally bonded sulphur or Ge (D^0 defect), then the positively charged defects have to be $(Ge_4...S_3)^+$ or $(S_2...S_3)^+$, Fig. 12. From the chemical point of view it seems unprobable to consider the *negatively* charged Ge surrounded by more electronegative S atoms. Therefore, the negatively charged defect has to be S_1^- in equilibrium, for both type of two-atomic defects mentioned above, according to Eqs
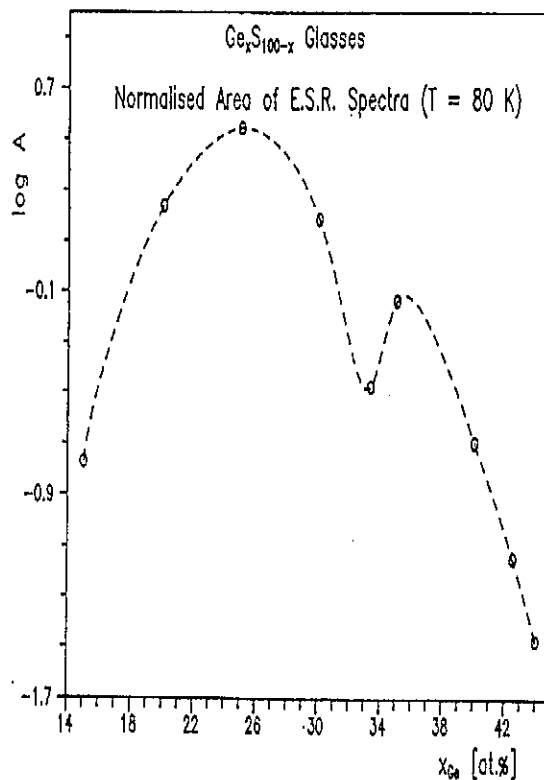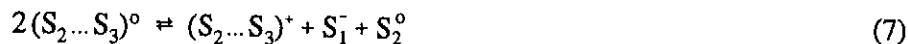
$$2(Ge_4...S_3)^0 \rightleftharpoons (Ge_4...S_3)^+ + S_1^- + Ge_4^0 \qquad (6)$$

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$$2\,(S_2 ... S_3)^{\circ} \rightleftharpoons (S_2 ... S_3)^{+} + S_1^{-} + S_2^{\circ} \tag{7}$$

Fig. 11 Compositional dependence of density of paramagnetic centra of Ge-S glasses, Refs. [28,33,34]

In the new non-dangling bond model the interaction of a dangling bond of sulphur or germanium (homolytically broken bonds) with nonbonding lone-pair orbital of S creates a new, electrically neutral two-atomic DC with triply bonded sulphur, having an unpaired electron in the antibonding MO^{*}. The empty MO^{*} orbital of positively charged DC, which is in equilibrium with uncharged one, Eqs (6) and (7), forms a deep level in the energy gap of Ge-S glasses, closer to the conduction band. The chemical equilibrium of DCs mentioned above is sensitive to the chemical composition of studied glasses.

The non-dangling model can elucidate the fact that the intrinsic DCs can be found only in Ge-S glasses without excitation. The energy gaps of other sulphur-based chalcogenide glasses are higher or comparable to the $E_g^{opt}(300) = 2.5$ eV of amorphous sulphur (e.g. 2.68 eV for $As_{0.2}S_{0.8}$ 2.57 eV for $As_{0.3}S_{0.7}$, 1.75 - 2.57 eV for Ge-Sb-S glasses). Thus the antibonding levels
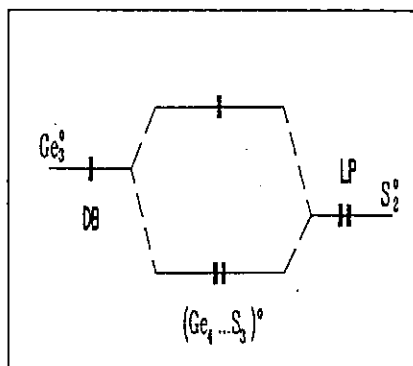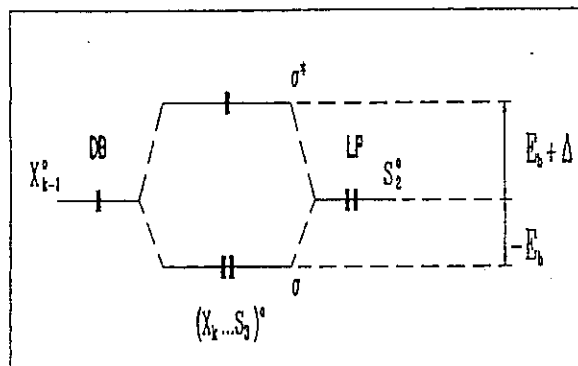
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Fig. 12 Simplified molecular orbital diagrams of defect centers proposed in the non-bonding defect centers model, Refs.[33,34]. For more details see text

of positively charged DCs probably lie in the vicinity of conduction band or inside them and cannot be converted to ESR active ones by electron capturing.

The photoinduced ESR spectrum of glassy sulphur, Fig. 13, was found to be identical in line-shape and g-tensors components with the multi-line spectrum from the S-rich region of Ge-S glasses. It is concluded that the DCs responsible for multi-line spectrum of Ge-S glasses are, therefore, associated with S atoms only. The unpaired electron states are stabilized by interaction with lone-pair states of two-fold coordinated sulphur. Depending on configuration of S_n chains (*cis-* or *trans-*), two types of paramagnetic defects $((S_2...trans\text{-}S_3)^\circ$ or $(S_2...cis\text{-}S_3)^\circ)$ are formed in S-rich region of Ge-S glassy system. *The unpaired electron is localized in the antibonding molecular orbital of DC which creates deep one-hole level in energy gap of the Ge-S glasses.* The composition change alters the value of E_g^{opt} by the way of changing the ratio of Ge-S and S-S antibonding levels and, hence, the distance of two-hole levels, which is constant in energy, from bottom of conduction band as well as deeper in the gap localized one-hole antibonding level. As a consequence, some and/or all of
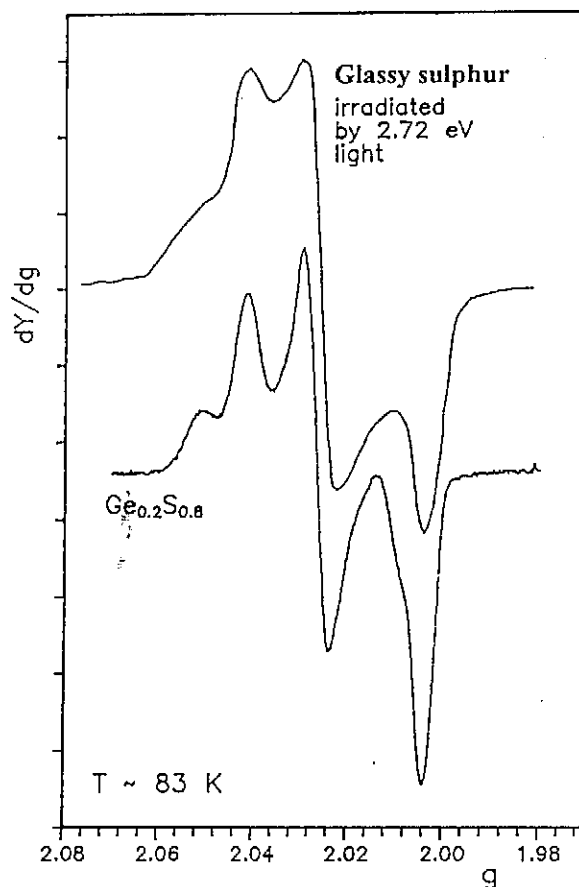
Fig. 13 LESR spectrum of amorphous sulphur and dark multi-line ESR spectrum, typical for Ge-S glasses with overstoichiometry of sulphur, Ref.[34]

empty (two-hole) antibonding orbitals of DCs are immersed in the conduction band and the density of paramagnetic DC lowers with increasing of sulphur or germanium content. It is important to stress, that the energy of non-bonding lone-pair states creating the top of the so-called valence band remains unchanged as well as levels of DCs localized in the gap under discussion.

Conclusion

Contrary to all the other models proposed up to now, e.g. in Refs[5,21,23], the compositional dependence of ESR signal intensity can be easily qualitatively explained, the thermal stability of defect centers in the Ge-S glasses elucidated and the absence of ESR signal in other chalcogenide glasses can be explained by the new non-dangling bond model[33,34]. Based on this model, a new approach

to some other problems, e.g. photoluminescence and ODMR in chalcogenide based glasses, can be solved, see e.g. Ref.[28].

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