

Electron-spin resonance of Mn^{2+} in Ge-rich bismuth-modified amorphous semiconductors $(Ge_42S_{58})_{99.5-x}Bi_xMn_{0.5}$

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Electron-spin resonance spectra of Ge-rich Bi-modified amorphous $(Ge_42S_{58})_{99.5-x}Bi_xMn_{0.5}$ (as prepared and annealed) have been observed by use of Mn^{2+} as a microprobe for the first time. The data on the g value and the line parameters in various samples studied show that the effects of addition of Bi to the Ge-rich composition Ge_42S_{58} and to the sulfur-rich composition $Ge_{20}S_{80}$ are quite different, indicating a dissimilar microscopic environment. The behavior of the resonance line at $g \approx 2$ in the composition $x=2$ is quite different from that in $x=0,4$ samples. Results are discussed in the light of the Phillips cluster model and constraint theory [J. C. Phillips, Phys. Rev. B **36**, 4265 (1987)].

Among the chalcogenide glassy semiconductors, the amorphous system Ge_xS_{1-x} occupies a unique position. Chalcogenide glassy semiconductors usually do not exhibit an electron-spin resonance (ESR) signal from defects under ambient conditions.¹ However, ESR signals from defects have been observed for the Ge_xS_{1-x} system. The absence of the ESR signal is associated with the fact that paired localized states appear in glassy semiconductors, due to the presence of charged defect centers C_3^+ , C_1^- , and the two electrons on the same defect site experience effective negative correlation energy.² The observation of ESR in $Ge_{1-x}S_x$ glasses has been associated with the presence of Ge and S dangling bonds which have unpaired electron spins.³ The nature of the signal has been found to change with composition. The chalcogenide-rich compositions $Ge_{20}S_{80-x}Bi_x$ has been found to show a $p \rightarrow n$ transition in the electronic conduction process at higher Bi concentrations ($x \geq 11$) (Ref. 4) and this feature has recently been explored in details.⁵⁻¹¹ It has also been reported¹² that these Bi-modified glasses do not show a measurable ESR signal. In the system having undetectable unpaired spin density, incorporation of transition-metal impurity atoms like Mn can be utilized to observe an ESR signal corresponding to the added transition-metal impurity. Analysis of such a signal can provide information about the lattice site and the environment in which the added paramagnetic center is situated. We reported recently^{7,8} the results of our study of ESR in chalcogen-rich $Ge_{20}S_{80-m-n}Bi_mMn_n$ glasses. It will be of relevance and considerable interest to study Ge-rich Bi-modified glasses with added Mn impurity $(Ge_42S_{58})_{100-x-y}Bi_xMn_y$ using the electron-spin resonance technique. Ge-rich glasses containing Bi do not show a $p \rightarrow n$ transition for $x \leq 4$. Therefore, such a study would be informative to learn more about the microscopic environment and mechanism in these glasses. We have undertaken such a study and our results are reported in this Communication.

The glassy compositions of the semiconducting materials $(Ge_42S_{58})_{100-x-y}Bi_xMn_y$ were prepared by the conventional melt-quenching technique starting with proper quantities of the high-purity elements (99.999%), and

characterized by differential thermal analysis and x-ray diffractometry as reported earlier.^{6,10} The electron-spin resonance spectrum of the materials was observed using a Jeol Jes-Fe 3X homodyne X-band spectrometer operating in the frequency range 8-9.6 GHz and using field modulation of 100 KHz. For annealing, the glassy sample was sealed in an evacuated quartz ampoule and was melted in the furnace and then the furnace was allowed to cool slowly to give polycrystalline compositions.

The measured ESR absorption spectra for compositions $x=0, y=0.5$; $x=2, y=0.5$; and $x=4, y=0.5$ (as prepared) are presented in Fig. 1. All the experimental parameters (power level, modulation frequency, amplifier gain, and temperature of measurement) were kept the same for all three compositions. The spectrum is normalized to 1-g sample weight for comparison of the shape, intensity, and area under the peak. Similar results were obtained on annealed compositions under similar experimental conditions.

Bi-modified samples without the addition of Mn impur-

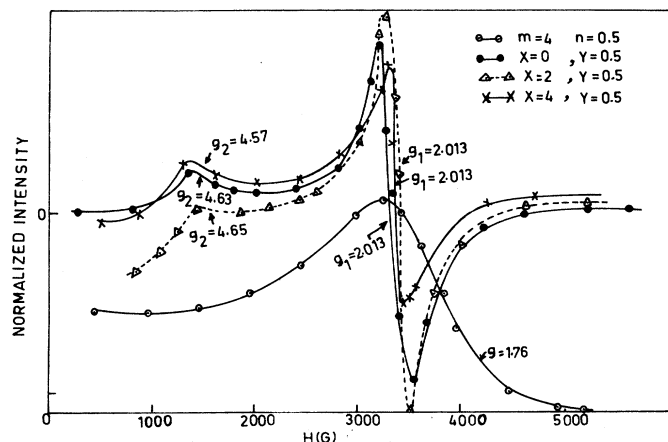


FIG. 1. The ESR spectra of $(Ge_42S_{58})_{100-x-y}Bi_xMn_y$ glasses of various compositions. The spectra are normalized to facilitate comparison of the relative intensity of the signal. The ESR spectra of $Ge_{20}S_{80-m-n}Bi_mMn_n$ ($m=4, n=0.5$) glass is also plotted for comparison.

ity did not show any measurable ESR signals which is in agreement with the observation of Elliott and Steel.¹² Various line parameters (H_{pp} the peak-to-peak width, $H_{1/2}$ the half-width, and I_{pp} the peak intensity) and g values of all the absorption lines included in Fig. 1 are presented in Table I. The corresponding data for the annealed compositions are also included in Table I. Since we have taken all the measurements under identical experimental conditions, the area under the peak in each case can be taken as proportional to the spin density and is represented by spin-density parameter D_s (Table I). The shape of the resonance line was also analyzed following the method of slopes of the derivative curve.¹³ The line in each case was found to be Lorentzian. The main features of the resonance spectrum are given below.

(i) In all the cases ($x=0,2,4$) a strong resonance line at $g \approx 2$ with a linewidth H_{pp} and half-width $H_{1/2}$ in the ranges 277–180 G and 249–150 G, respectively, was observed. The peak intensity I_{pp} for the absorption line at composition $x=2$ is very much higher than in the two other compositions in both as-prepared (virgin) and annealed samples. The spin-density parameter D_s also exhibits similar behavior. The g value of the line has been determined at the approximate zero-crossing value. There is no appreciable change in the g value of this line in various compositions.

(ii) A second broad and much weaker line appears around $g \approx 4.6$. The annealed samples did not show this

line. An amplified version of this part of the spectra for the three samples is presented in Fig. 2. The same part of spectrum for the sulfur-rich Bi-modified Mn-doped compositions $\text{Ge}_{20}\text{S}_{79.5-m}\text{Bi}_m\text{Mn}_{0.5}$ ($m=4,15$) taken from Ref. 7 is also plotted for comparison.

The resonance absorption spectrum of compositions $x=0,2,4$ is for the same experimental parameters to facilitate the comparison. There is not much change in the g value of this line with compositions. The corresponding absorption spectra of the $m=4$ and $m=15$ samples are altogether different. The composition $m=4$ shows no resonance absorption line in this region, whereas a weak and broad resonance absorption line appears at about $g \approx 3.85$ at composition $m=15$. These altogether dissimilar resonance effects in the sulfur-rich and Ge-rich Bi-modified Mn-doped semiconductors, indicate the presence of quite different types of microscopic fields in the two systems.

In order to understand the above observed features of the ESR spectra, it is necessary to discuss the known facts of resonance absorption in Mn-doped glasses. The ESR spectra of Mn^{2+} ions in amorphous chalcogenide semiconductors usually exhibit absorption lines centered at $g=4.3$ and 2.0.^{14,15} These absorption lines may or may not exhibit resolved hyperfine structure.¹⁵ Particularly, at higher Mn^{2+} concentration (> 0.01 at.%) strong dipole-dipole interaction broadens the hf structure and it is smeared out. It has usually been accepted that the line with $g=4.3$ is characteristic of the Mn^{2+} ions incorporated into the

TABLE I. Line parameters of the resonance line. H_{pp} (the peak-to-peak width), $H_{1/2}$ (the half-width), and I_{pp} (the peak intensity). g_1, g_2 are g values of two resonance lines in Ge-S-Bi-Mn glass, respectively. D_s is the spin-density parameter as defined in the text. The estimated uncertainty in g values of broad lines (around $g \approx 4$) is ± 0.05 . $\sigma(300)$ is the electrical conductivity at 300 K.

Sample	g	H_{pp} (G)	$H_{1/2}$ (G)	I_{pp} (arbitrary units)	D_s	$\sigma(300)$ ($\Omega^{-1} \text{cm}^{-1}$)
$(\text{Ge}_{42}\text{S}_{58})_{100-x-y}\text{Bi}_x\text{Mn}_y$ (as prepared)						
$x=0, y=0.5$	$g_1=2.013$ $g_2=4.63$	277.7	249.9	2.6	4.6	1.2×10^{-10}
$x=2, y=0.5$	$g_1=2.013$ $g_2=4.65$	222.2	195.0	13.5	19.0	5.0×10^{-10}
$x=4, y=0.5$	$g_1=2.013$ $g_2=4.57$	180.5	166.5	3.6	4.15	6.6×10^{-11}
$(\text{Ge}_{42}\text{S}_{58})_{100-x-y}\text{Bi}_x\text{Mn}_y$ (annealed)						
$x=0, y=0.5$	$g=2.013$	166.6	124.9	13.3	11.5	
$x=2, y=0.5$	$g=2.013$	138.9	124.9	52.5	35.0	
$x=4, y=0.5$	$g=2.013$	152.7	138.8	12.2	10.0	
$\text{Ge}_{20}\text{S}_{79.5-m}\text{Bi}_m\text{Mn}_{0.5}$ (as prepared)						
$m=4$	$g=1.76$	1850	1290	9.1		1.8×10^{-10}
$m=15$	$g_1=1.85$ $g_2=3.85$	1420	700	8.5		2.2×10^{-11}

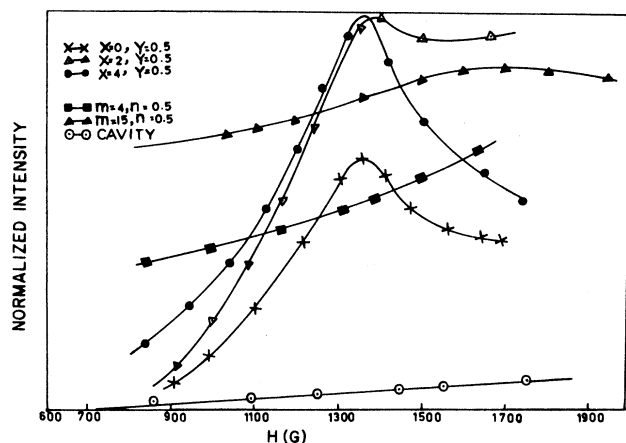
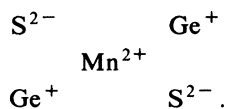


FIG. 2. The amplified version of the ESR spectra of $Ge_{20}S_{80-m-n}Bi_mMn_n$ and $(Ge_{42}S_{58})_{100-x-y}Bi_xMn_y$ glasses in the region $g \approx 4$.

glass network and the line with $g=2$ is caused by the Mn^{2+} ions forming phase-separated Mn-chalcogenide particles or microcrystalline inclusions. It is pointed out that in the covalently bonded amorphous semiconductors the value of electrical conductivity is usually very small and few carriers are thermally excited into the conduction band¹⁶ [measured values of room-temperature electrical conductivity $\sigma(300)$ for the as-prepared glasses under reference are given in Table I]. As such, the conduction electron-spin resonance signal is negligibly small.¹⁶ Therefore, the absorption line at $g=2$ cannot be associated with the conduction electron-spin resonance. Durny¹⁴ has proposed the following model for the location of Mn^{2+} ions in Mn-doped $Ge_{40}S_{60}$ and $Ge_{25}S_{75}$ glasses



According to this model the Mn^{2+} ion is located in a strong electric field of two S^{2-} ions and the Ge^{2+} ions are placed on the corners of a tetrahedron, thus forming a spatial complex. In such a situation, a distorted crystal-line field around the Mn^{2+} may be expected because of the difference in the ionic radii between Mn^{2+} and Ge^{2+} . Such a complex would develop a field component of rhombic symmetry giving rise to the resonance line at $g=4.3$ which is in agreement with the spin Hamiltonian of rhombic symmetry.¹⁴ Thus, Mn^{2+} occupies sites similar to Ge. Further, the origin of the $g=2$ lines has been associated with the Mn^{2+} sites in a cubic field with axial perturbation. In general, assuming the Zeeman energy is much less than that of zero-field splitting, it has been shown¹⁷ that there can only be three isotropic g values of 2.0, $\frac{10}{3}$, and $\frac{30}{7}$ for $3d^5$ ions (like Mn^{2+}) in a glass. The point group symmetries corresponding to each g value are as follows: (a) cubic symmetry $g = \frac{10}{3}$, (b) tetragonal symmetry $g = 2, \frac{10}{3}$, and $\frac{30}{7}$, (c) trigonal or hexagonal symmetry $g = \frac{10}{3}$, and (d) monoclinic and orthorhombic symmetry $g = \frac{10}{3}, \frac{30}{7}$.

In view of the above features of Mn^{2+} in Ge-S glass, the resonance absorption line appearing with g value ≈ 4.6 in all three compositions ($x=0,2,4; y=0.5$ in each case) should correspond to the Mn^{2+} occupying sites similar to Ge in an environment with approximately orthorhombic symmetry. Presence of strong dipolar broadening and scattered g values, may make the line broad.^{14,16} There seems to be little effect of addition of Bi on the sites responsible for this resonance absorption. This indicates the presence of almost similar crystal fields surrounding Mn sites in the glass with and without Bi. The behavior of a similar resonance line in sulfur-rich Bi-modified composition is very much different. This striking difference between the behavior of resonance absorption in sulfur-rich $Ge_{20}S_{80-m-n}Bi_mMn_n$ and Ge-rich $(Ge_{42}S_{58})_{100-x-y}Bi_xMn_y$ compositions is of interest in this study. Evidently, the microscopic environment and hence the local crystalline fields are not similar in the two situations. Our earlier investigations by differential thermal analysis,¹⁰ and the measurement of electrical transport under high quasihydrostatic pressure⁶ in sulfur-rich and Ge-rich Ge-S-Bi glasses has established the structural differences between these two types of glasses.

Phillips¹⁸ has recently proposed the application of his cluster model and constraint theory to Bi-modified Ge-M-Bi ($M=S,Se$) glasses and has also reinterpreted the experimental results of Elliott and Steel¹² taken by extended x-ray absorption fine structure. We apply these concepts to discuss the present experimental data. Germanium sulfide glasses Ge_xS_{1-x} can be described as small chemically ordered clusters embedded in a continuous network.¹⁸ The sulfur-rich composition $Ge_{20}S_{80}$ contains predominantly $Ge(S_{1/2})_4$ tetrahedral units and S_n chains. As the Ge content of the alloy Ge_xS_{1-x} is increased, the S_n chains start disappearing and are replaced by Ge_2S_3 chains with a polymerized ethaneline structure having the $Ge_2(S_{1/2})_6$ unit. The composition $Ge_{20}S_{80}$ is taken to be at a stiffness threshold¹⁸ and the Ge-rich composition $Ge_{42}S_{58}$ is away from such a stiffening point. This is perhaps the reason that the glassy alloys $(Ge_{42}S_{58})_{100-x}Bi_x$ cannot be prepared for $x > 4$ following usual melt quenching technique and $p \rightarrow n$ transition is also not exhibited by this system. The addition of Bi impurity to $Ge_{42}S_{58}$ and $Ge_{20}S_{80}$ produces the different types of systems. Following Phillips,¹⁸ the system $Ge_{20}S_{80-m}Bi_m$ is taken to have a diphasic structure with microclusters Bi_2S_3 (30–40° A size) embedded in the background matrix of GeS_2 and S_n . At lower Bi concentration ($x < 6$) Bi_2S_3 clusters dissolve in the background matrix and at higher Bi concentration ($x > 6$) the microclusters are unable to dissolve due to increased rigidity of the background matrix. This leads to a phase separation at the microscopic level. The appearance of a resonance line at $g=3.6$ in composition $m=11,15$ (Ref. 7) should have a link with this increased rigidity of the background matrix and the microscopic phase separation. We think that these microstructural features should have considerable influence on the local environment and the crystal field which Mn^{2+} impurity experiences in the Bi-modified Ge-rich and sulfur-rich network, respectively. Appearance of resonance line with $g \approx 4.6$ in all the Ge-rich compositions ($x=0,2,4$) sup-

ports the view that Mn^{2+} impurity occupies sites similar to Ge as proposed to Durny¹⁴ and experiences crystal field of almost orthorhombic symmetry. Since the basic network $Ge_{42}S_{58}$ is away from the stiffness threshold and the addition of Bi to it does not create a very different microscopic structure, the paramagnetic properties are not expected to be very affected. On the other hand, the situation in S-rich compositions is bound to be different because of the different microscopic features. Absence of the resonance line at $g \approx 4$ in $m=4$ composition and the appearance of a broad absorption line with $g \approx 3.8$ in $m=11, 15$ compositions indicates a modified local environment in sulfur-rich glasses. Further, absence of the $g \approx 4$ line in the $m=4$ composition also suggests that the distortion produced by Mn^{2+} in the host network is presumably compensated by the glass structure.

In the $x=0, 2, 4$ composition (as prepared) the resonance absorption line at $g \approx 2$ appears with the distinct Lorentzian character. Features of this line in Ge-rich and sulfur-rich compositions are very different. A comparison of Fig. 2 in Ref. 7 and Fig. 1 of the present paper should be made. A plot of the resonance in the $m=4$ composition is also drawn in the present Fig. 1. The line shape of this line in $m=4, 11, 15$ compositions is found to be more Dysonian rather than Gaussian or Lorentzian. The broad and asymmetric shape of this line ($g \approx 2$) may be due to the presence of strong dipolar broadening and scattered g values.¹⁶ These perturbations may make the line shape somewhat like Dysonian. This difference also confirms the dissimilar local microscopic environment in Ge-rich and S-rich alloys. Much higher intensity of this resonance

line in $x=2$ composition in both as-prepared and annealed samples is to be noted. The increase in the spin-density function D_s in the Ge-rich glasses on annealing could be associated with the decomposition of complex glassy clusters into crystalline Bi_2S_3 and GeS_2 . This creation of simpler crystalline units could produce more free spins which take part in the resonance absorption.

In view of the above analysis it seems that the concepts of constraint theory and microscopic inhomogeneity proposed by Phillips¹⁸ is quite appropriate for the Bi-modified semiconductors. Similar conclusions have also been arrived at in our recent study of ac conductivity and dielectric relaxation in this class of amorphous semiconductors.¹¹ Further experiments are in progress.

In summary we have observed the ESR spectra of Ge-rich $(Ge_{42}S_{58})_{99.5-x}Bi_xMn_{0.5}$ glasses at room temperature for the first time. The microscopic environment in compositions without Bi seem to be not much different from each other. The behavior of the resonance line with $g \approx 2$, in $x=2$ composition is found to be quite different from that in $x=0, 4$ compositions. The resonance absorption spectrum of Mn^{2+} in Ge-rich and S-rich Bi-modified glasses is found to be dissimilar.

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