Mechanism for Doping in Bi Chalcogenide Glasses

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The structural environment of Bi incorporated in Ge chalcogenide glasses has been found from extended x-ray absorption fine-structure data to consist of threefold coordination. An increase by a factor of 2 in the Debye-Waller factor occurs as the carrier type changes from p to n. A mechanism involving the suppression of positively charged structural defects, and the consequent unpinning of the Fermi level, by the formation of partially ionic Bi-chalcogen bonds is proposed to account for the doping effect.

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Chalcogenide glasses are remarkably resistant to electrical doping by the incorporation of dopant atoms; the Fermi level is pinned effectively by the presence of charged defect centers[1,2] and holes are the predominant charge carrier. The discovery[3,4] that the addition of Bi to certain chalcogenide glasses changed the conductivity type from p to n was therefore extremely surprising. Bi appears to be unique in this regard; the addition of other Group V elements, such as P, As, or Sb, does not alter the dominant carrier type.

Several mechanisms have been proposed to account for the doping behavior of Bi: Most propose that the effect of the Bi is to upset the equilibrium between oppositely charged native (chalcogen) defect centers, D^+, D^-, by being incorporated in a charged state, thereby allowing the Fermi level to become unpinned. Thus, mechanisms involving *positively* charged Bi having threefold[5] and fourfold[6,7] coordinations and *negatively* charged Bi having twofold[8,9] and sixfold[6,10] coordinations have variously been proposed. In addition, a model assuming percolative transport between microcrystalline Bi_2X_3 ($X = S,Se$) inclusions in a glassy Ge-chalcogenide matrix has also been suggested.[11] Therefore, the use of a chemically specific structural probe, capable of determining the local coordination of Bi in these glasses, should shed considerable light on the doping mechanism responsible.

In order to try to resolve this problem we have undertaken extended x-ray absorption fine-structure (EXAFS) measurements on a series of Bi-doped Ge-S and Ge-Se glasses. It has been observed[11,12] that the p-n transition in the glassy alloys $Bi_xGe_{20}C_{80-x}$ ($C = S,Se$) occurs in the range $x \simeq 6$–9. Therefore, EXAFS measurements were performed on a number of samples having compositions in the range $3 < x < 10$, i.e., spanning the p-n transition. The bulk glass samples were finely powdered and pressed between Sellotape to fabricate specimens suitable for x-ray absorption spectroscopy. Transmission EXAFS spectra were taken at ambient temperature beyond the Bi L_{III} and Ge and Se K edges on the wiggler line at the Daresbury synchrotron radiation source. Severe absorption due to Se precluded quantitative EXAFS measurements beyond the Bi L_{III} edge for the Bi-Ge-Se glasses. Details of sample preparation and experimental procedure are given elsewhere.[13] The EXAFS spectra were analyzed by fitting in reciprocal space the back-transformed, Fourier filtered, and background-subtracted data by use of standard Daresbury routines based on the curved-wave approximation for the EXAFS amplitude.[14] Phase shifts for the elements in question were calculated,[15] and then used to fit the EXAFS spectrum of a "standard" compound (crystalline Bi_2Si_3); the resulting radii and coordination numbers of each coordination shell were compared with crystallographic data[16] as a check on the accuracy of the calculated phase shifts. Since all available crystalline Bi sulfosalts possess a considerably greater degree of disorder in the primary Bi-S coordination shell than is found in the Bi-doped glasses, they are not suitable as standards from which to obtain *measured* phase shifts which would be transferable to the case of the glasses.

The principal result of our study can be seen by reference to Fig. 1, where the EXAFS amplitudes, $\chi(k)$, and their Fourier transforms, $P(r)$, for Bi-Ge-S glasses with $x = 3$ and 10 are compared. It can be seen that the amplitude of $\chi(k)$, and concomitantly also that of $P(r)$, *decreases* by about 40% on increase of the Bi concentration from 3 to 10 at.%. Similar results to those for the 10-at.% Bi sample were observed for all Bi concentrations in excess of 6 at.%. This suggests that the p-n transition is caused and/or accompanied by a significant change in the local structural order surrounding the Bi impurity atoms. A curve-fitting analysis of the Bi L_{III} EXAFS data (see Fig. 2) has in-

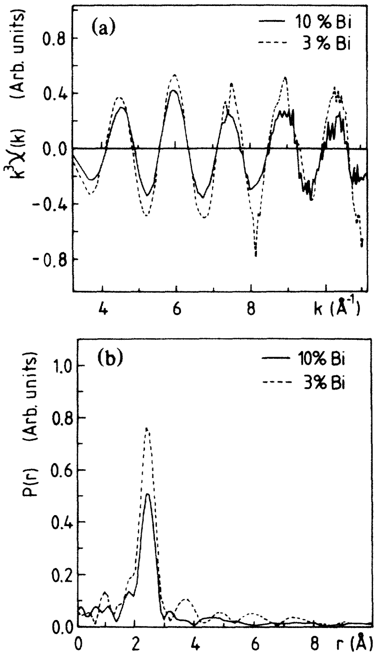

FIG. 1. EXAFS spectra taken above the Bi L_{III} edge for glassy $Bi_xGe_{20}S_{80-x}$ samples with $x=3$ and 10: (a) k^3-weighted EXAFS amplitude (Fourier filtered) and (b) Fourier transform.

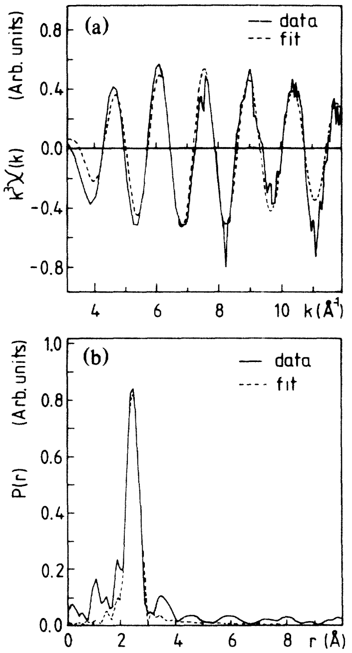

FIG. 2. Results of fitting the EXAFS data for glassy $Bi_3Ge_{20}S_{77}$. Fit to (a) EXAFS amplitude and (b) Fourier transform. In both cases the solid curves refer to the (unfiltered) data and the dashed lines are the fits.

dicated[13] that the Bi atoms are coordinated by three S atoms, independent of the Bi content, and that the difference in the EXAFS spectra between low and high Bi concentrations, e.g., as shown in Fig. 1, is due to a factor of 2 increase in the Debye-Waller factor, $A=2\sigma^2$ [where σ is the rms fluctuation of the interatomic distance projected along the line connecting the absorbing (Bi) atom and the atom responsible for the backscattering]. Confirmation of this finding comes from plotting for the two Bi compositions the ratio of the EXAFS amplitudes (at extrema in the spectra) logarithmically versus k^2. In the single-scattering, plane-wave approximation, this plot should yield a straight line whose slope is equal to the difference in Debye-Waller factors, $2\sigma^2$, with the $k=0$ intercept equal to the logarithm of the ratio of the first-shell coordination numbers for the two materials. Such a plot of the EXAFS data for the $x=3$ and 10 at.% Bi samples can be fitted by a straight line with a nonzero gradient[13]; the slope gives a value for the difference in Debye-Waller factors of 0.006 Å, in good agreement with that obtained by curve fitting of the EXAFS data, 0.007 Å (see Table I). In addition, the Bi—S bond length increases by ~0.02 Å with increasing Bi content, although the value of this difference is on the limit of experimental uncertainty associated with variations in x-ray absorption-edge threshold energies, etc. The results are summarized in Table I; the errors quoted therein reflect the uncertainties resulting from the use of calculated, rather than measured, phase shifts, as well as, to a lesser extent, those associated with the fitting of the data.

Within the sensitivity of the EXAFS technique, the measured spectra [Fig. 1(a)] show no evidence [e.g., beating in $\chi(k)$ or peaks at higher r in $P(r)$] for the presence of an appreciable contribution ($\gtrsim 10\%$) of an additional atomic species to the first coordination shell having a significantly different bond length from that of Bi—S, such as Bi-Bi nearest neighbors (indicating a homogeneous distribution of Bi), or Bi—Ge bonds (as suggested on the basis of Raman evidence[17]). This indicates that the Bi atoms are "dissolved" preferentially in the chalcogen-rich regions of the structure, a result which is in accord with bond-energy considerations.[10] Moreover, there is no similarity between the EXAFS spectra for high- or low-content Bi-doped glasses and the corresponding crystalline compound Bi_2C_3 ($C=S,Se$)—see Fig. 3. This

TABLE I. Structural parameters obtained from fit to EXAFS of $Bi_xGe_{20}S_{80-x}$ glasses. N_1, R_1, and A_1 are the first-shell coordination number, the bond length, and twice the Debye-Waller factor ($2\sigma^2$), respectively.

x	N_1	R_1 (Å)	A_1 (Å^2)
3	3 ±0.5	2.54 ±0.02	0.007 ±0.001
10	3 ±0.5	2.56 ±0.02	0.014 ±0.001

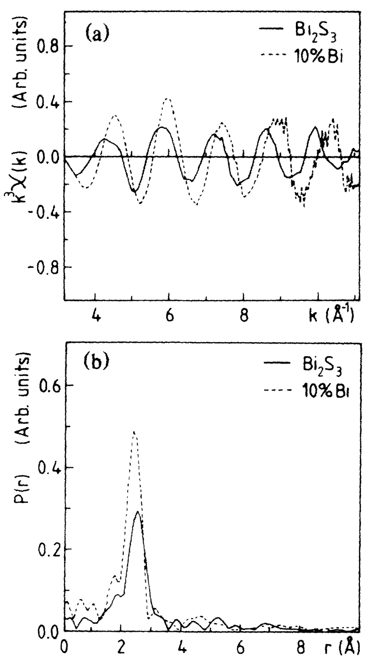

FIG. 3. Comparison of (a) the EXAFS amplitudes and (b) the Fourier transforms for glassy $Bi_{10}Ge_{20}S_{70}$ and crystalline Bi_2S_3.

is strong evidence against the existence in any significant proportion of microcrystalline (or smaller) regions having a structure similar to (crystalline) Bi_2S_3 or Bi_2Se_3. Furthermore, the percolation model[11] for the influence of Bi on electrical properties would predict a continuously increasing proportion to the (crystalline) Bi-rich phase, with increasing Bi content, always having the *same* structure, in contradiction with the present experimental results.

On the basis of the present EXAFS results, therefore, we feel able to rule out several of the contending models for the doping activity of Bi. We see no evidence for fourfold-coordinated Bi sites,[6,7] nor do we see any direct evidence for sixfold-coordinated sites.[6,10] The sixfold coordination around Bi in crystalline Bi sulfosalts invariably comprises three nearest S neighbors at distances in the range 2.5–2.7 Å, together with a further three S neighbors at distances beyond 3 Å. In the present case, it could be that if similar sixfold-coordinated Bi sites do exist in the Bi-doped glasses, the three distant S neighbors are not detected by EXAFS because of a large degree of site disorder and a concomitantly large Debye-Waller factor; however, we do not think this to be the case.

We are left, therefore, with the conclusion that Bi is predominantly threefold coordinated in $Bi_xGe_{20}C_{80-x}$ glasses, and in this regard, therefore, Bi behaves similarly to the other Group V elements, which utilize predominantly *p*, and not *d*, orbitals in their bonding. Photoemission experiments[5] on amorphous Bi_2Se_3 films have indicated that the Bi atoms are *positively* and not negatively charged and, although similar experiments have not yet been performed on the Bi-doped glasses studied here, it is not unreasonable to assume that charge transfer in the same sense would occur in the latter glasses too. We postulate, therefore, that at low concentrations, the Bi atoms are incorporated in an "alloying" sense, being covalently bonded to three S atoms by three equivalent bonds having approximately equal bond lengths. At higher concentrations, it is presumed that the Bi-S bonding acquires more ionic character (as found in the crystalline sulfosalts); the Bi atom becomes positively charged and the conjugate negative charge is localized on a neighboring S atom. As a result of this charge transfer, the $Bi^{\delta+}$—$S^{\delta-}$ bond length becomes longer[18] than the other two more covalent Bi—S bonds (although the magnitude of the difference is difficult to evaluate since it depends on the extent of charge transfer[18] and the coordination[19]); the static contribution to the Debye-Waller factor is therefore expected to increase, as observed. In addition, an overall increase is predicted in the average Bi—S bond length, and this seems to be observed (see Table I).

The doping effect is presumed to arise because the S^- centers introduced by the Bi impurities unbalance the equilibrium between the native S_1^- and S_3^+ centers by the law of mass action,[20] and consequently allow the Fermi level to become unpinned, and E_F moves towards the conduction band; the observation of *n*-type doping[3,4] and the decrease of the dc conductivity activation energy to approximately $\frac{2}{3}$ of its value on doping[12] can be explained in this manner.[13]

We have also directly observed the doping effect of Bi in these glasses by ESR.[13] Undoped Ge-S glasses exhibit an ESR signal in the dark arising from unpaired electrons residing on S dangling bonds[21]; the addition of more than 3 at.% Bi causes the ESR signal to become undetectably small,[13] presumably as the Fermi level rises through the defect band near midgap, converting singly occupied paramagnetic centers to doubly occupied diamagnetic centers, as observed in the case of doping in *a*-Si:H.[22]

Finally we believe that Bi is special in its doping ability because of two factors which distinguish it from other (Group V) elements[13]: Its larger polarizability makes the formation of partially ionic Bi-chalcogen bonds more likely; in addition, the small band gap of Bi-doped glasses[6] makes a shift in E_F possible. Fritzsche and Kastner have shown[20] that the addition of electropositive impurities, when incorporated as positively charged species A^+, increases the concentration of C_1^- defect centers at the expense of C_3^+ centers. They have shown that the concentrations of free electrons (n), dopants ($[A^+]$), and native charged defects (N_0) are interrelated via

$$n^2(2N_0^2/[A^+]+n)=2[A^+]n_0^2, \tag{1}$$

where n_0 is defined by the equation

$$n^2[C_3{}^+]/[C_1{}^-]=N_c^2\exp(-2\epsilon_n/kT)=n_0^2, \tag{2}$$

describing the equilibrium $C_1{}^- \rightleftharpoons C_3{}^+ + 2e$ with reaction energy $2\epsilon_n$, and N_c being the density of states of band states at the conduction-band (mobility) edge; N_0 is defined by the equation

$$[C_3{}^+][C_1{}^-]=N_A^2\exp(-E_{\text{vap}}/kT_g)=N_0^2, \tag{3}$$

describing the creation of charged defects from normally bonded atoms at the glass-transition temperature, T_g, viz., $2C_2 \rightleftharpoons C_3{}^+ + C_1{}^-$. In the case $n >> 2N_0^2/[A^+]$, Eq. (1) simplifies to

$$n=(2[A^+])^{1/3}n_0^{2/3}, \tag{4}$$

i.e., the thermal activation energy for conduction E_σ is reduced to $\frac{2}{3}$ of its original value. We ascribe[13] the observation[12] of a discontinuous reduction in E_σ from 0.9 to 0.6 eV at $x=10$ in glassy $\text{Bi}_x\text{Ge}_{20}\text{Se}_{80-x}$ to this effect. Since $N_0 \simeq 10^{17}$ cm^{-3} and $[A^+] \simeq 3\times10^{21}$ cm^{-3}, n needs to be greater than $\simeq 5\times10^{12}$ cm^{-3} in order for Eq. (4) to be valid; with $\epsilon_n=0.9$ eV and $N_c \simeq 10^{20}$ cm^{-3}, Eq. (2) gives $n \simeq 1\times10^{13}$ cm^{-3} at a temperature of $T \simeq 400$ K at which the p-n transition has been observed.[8,11]

It has been noted[8] that incorporation of Sb into Ge chalcogenide glasses does *not* lead to n-type doping and large conductivity changes; alloying, instead of doping, behavior is observed. EXAFS measurements beyond the Sb K edge on $\text{Sb}_x\text{Ge}_{20}\text{S}_{80-x}$ glasses have revealed[13] that there is *no* observable change in the local structure of Sb as its concentration is increased; it therefore appears to be incorporated into threefold-coordinated, covalently bonded, alloying sites for all compositions.

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