PHYSICAL REVIEW B VOLUME 58, NUMBER 8 15 AUGUST 1998-II

Carrier-type reversal in Pb-modified chalcogenide glasses

S. Murugavel and S. Asokan*
Department of Instrumentation, Indian Institute of Science, Bangalore 560012, India

(Received 30 October 1997)

Carrier-type reversal (p to n) has been observed, in $\mathrm{Pb}_x\mathrm{Ge}_{42-x}\mathrm{Se}_{48}\mathrm{Te}_{10}$ glasses ($0 \leqslant x \leqslant 20$) at 8 at. % of lead. dc electrical resistivity (ρ) and activation energy for electrical conduction (ΔE) are found to exhibit notable change at the p-n transition threshold, which are associated with the change in the electron concentration during p-n transition. The observed p-n transition has been explained in light of the recent Kolobov model on the basis of modification of charged defect states by the introduction of lead. Also, the influence of other factors, such as band structure, polarizability of the dopant, etc., on the carrier-type reversal, has been discussed. [S0163-1829(98)01928-6]

I. INTRODUCTION

It has been known for a long time that chalcogenide glasses are p-type semiconductors.[1–3] In these materials, the valence band is constituted by the chalcogen lone-pair orbitals.[4] The effect of structural disorder is less on the lone-pair band compared to that on the antibonding orbitals[2] (conduction band). Therefore, the range of localized tail states at the valence-band edge is smaller in comparison to the localized states at the conduction-band edge. As a consequence, the number of electrons excited above the conduction-band mobility edge is less than the number of holes excited below the valence-band mobility edge and the chalcogenide glasses behave as p-type semiconductors.[2] Chalcogenide glasses also contain positively and negatively charged defect states, known as valence-alternation pairs[5] (VAP's). During thermal excitation, the lifetime of free holes excited from the positively charged defect states are higher than the lifetime of free electrons excited from the negatively charged defects, which also account for the p-type conductivity.[3]

Amorphous chalcogenides are generally insensitive to doping, because of the pinning of the Fermi level at midgap by the valence-alternation pairs.[6] However, it has been realized by Mott[7] that charged additives could change the ratio of valence-alternation pairs to such an extent that the Fermi energy could become unpinned. Metallic additives such as Bi and Pb in chalcogenide glasses enter the network as charged species, altering the concentration of valence-alternation pairs.[5] When the concentration of charged additives exceeds that of valence-alternation pairs, the chalcogenide glasses can exhibit carrier-type reversal. p-n transition has been observed in Ge-Se and In-Se glasses, with the addition of Bi and Pb.[8,9]

The present paper reports the p-n transition in Ge-Se-Te glasses, induced by the addition of Pb. Efforts are also made to understand the origin of carrier-type reversal and the role of charged additives in glassy chalcogenides, on the basis of the defect structure of these materials revealed by recent experiments.[10] The critical role played by other factors such as the band structure, polarizability of the dopant, etc., on the carrier type reversal has been described.

II. EXPERIMENT

$\mathrm{Pb}_x\mathrm{Ge}_{42-x}\mathrm{Se}_{48}\mathrm{Te}_{10}$ glasses ($0 \leqslant x \leqslant 20$) were prepared by the two-stage melt-quenching method: Appropriate amounts of high-purity Pb, Ge, Se, and Te ($5N$) were taken in evacuated, sealed quartz ampoules. The ampoules were slowly heated and maintained at 600 °C for about 24 h with continuous rotation. They were subsequently taken to 1000 °C and kept under constant rotation for 36 h to facilitate homogeneity. The ampoules were quenched subsequently in ice-water+NaOH mixture. The amorphous nature and composition of the glasses were confirmed by x-ray diffraction and energy dispersive x-ray analysis, respectively.

The electrical conductance was measured in sandwich geometry, using a Keithley 614 electrometer. A preamplifier with a high input impedance was used in conjunction with an electrometer, for the measurement of the thermovoltages. The preamplifier consisted of two stages. The first stage was comprised of an AD-542 operational amplifier with an input impedance of $10^{12}\ \Omega$. In the second stage, an operational amplifier (ADOP-07) with a gain of ten was used. The output of the second stage was fed to the electrometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the dependence of the Seebeck coefficient on composition of $\mathrm{Pb}_x\mathrm{Ge}_{42-x}\mathrm{Se}_{48}\mathrm{Te}_{10}$ glasses ($0 \leqslant x \leqslant 20$). It can be seen from this figure that the sign of the thermopower changes from positive to negative around 8 at. % of Pb, which indicates a transition from p-type to n-type conduction.

A. p-type conduction in amorphous chalcogenides

The defect states play a very important role in deciding many of the properties of chalcogenide glasses.[11] The two types of neutral, bonding defects that can occur in chalcogenides are the dangling bond and the threefold coordinated chalcogen. These defects are denoted by C_1^0 and C_3^0, respectively, where C represents the chalcogen and the subscripts and the superscripts represent the coordination and the charge state. Mott and Davis assumed that C_1^0 is the only native defect in these materials; if two dangling bonds are present sufficiently close, charge transfer occurs between

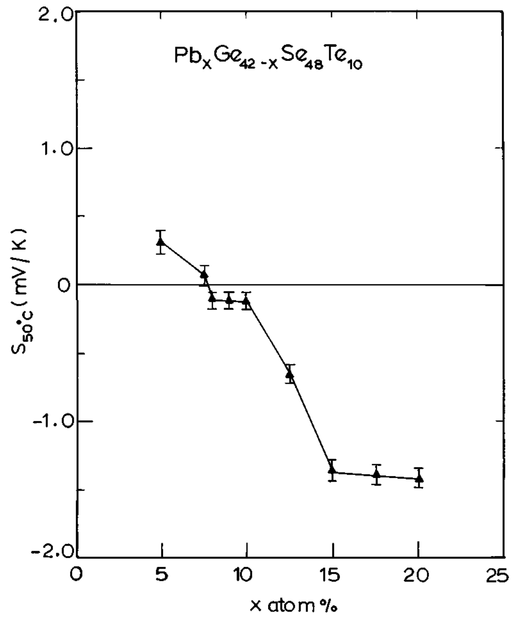

FIG. 1. Compositional dependence of thermopower of $Pb_xGe_{42-x}Se_{48}Te_{10}$ ($0 \leq x \leq 20$) glasses at 50 °C.

them, which results in the creation of two charged-defect states (C_1^- and C_3^+).[1] Kastner, Adler, and Fritzsche,[5] on the other hand, suggested that the dangling bond (C_1^0) is energetically unfavorable and the lowest-energy neutral defect is only C_3^0; the C_3^0 centers spontaneously transform into C_3^+ and C_1^- centers (VAP's). However, self-consistent pseudopotential calculations of Vanderbilt and Joannopoulos[12] showed that at least in glassy Se, C_1^0 is the lowest-energy defect and C_3^0 centers do not exist. The recent *in situ* optically induced electron spin resonance (ESR) and extended x-ray-absorption fine structure measurements also confirm that in amorphous Se, singly coordinated neutral defects are more stable than the triply coordinated defects;[9] C_3^0 defects are found to decay easily into C_1^0 centers.[13]

Based on Vanderbilt and Joannopoulous,[12] Kolobov[3] proposed a model to explain the origin of p-type conduction in amorphous chalcogenides. This model considers the thermal excitation of the charged-defect states C_3^+ and C_1^-. In the case of the C_3^+ defect, the direct excitation is not possible, as the nonbonding states are removed when the extra bond is formed during threefold coordination. When one of its nearest neighbors (C_2^0) is excited, an electron-hole pair is created. This electron is attracted by the C_3^+ center, while the hole created in the valence band is mobile and contributes to the conductivity.[3] The electron trapped by the C_3^+ defect converts it into a C_3^0 center, which subsequently decays forming a C_1^0 center.[13] The net result of the whole process is therefore the conversion of a C_3^+ defect into a C_1^0 center and a simultaneous creation of a hole in the valence band. It is not possible for the hole, excited as above, to return to the place of its origin, as the structure of the defect itself is modified during the excitation and the hole is left in the valence band as a free carrier.[3]

Similarly, when a negatively charged defect center C_1^- is excited, it results in the formation of a C_1^0 center and a free electron. However, no structural reconstruction takes place in the C_1^- center during excitation. The initial state is restored during recombination and the excited electron is removed from the conduction band.[3]

Thus, the thermal excitation of positively charged defect states creates a long-living hole, whereas the electrons excited from the negatively charged defects recombine. This results in a larger concentration of holes and consequently, amorphous chalcogenides behave as p-type semiconductors. As the p-type conduction is intrinsically connected to the defect states, any change in the concentration of the charged-defect centers, effected, say, by the addition of a third element, can change the conduction type in these materials.

B. p-n transition in Pb-doped chalcogenide glasses

In Ge-C glasses, there are two different types of structural units present, depending on the Ge content. At higher Ge contents, homopolar Ge-Ge bonds are predominant, in addition to the heteropolar Ge-C bonds. The charged-defect states in these glasses are primarily the Ge_3^- and C_3^+ centers.[14]

The nature of chemical binding in lead chalcogenides is usually mixed (ionocovalent).[15,16] The ionic component of the binding can be associated with the strong polarizability of lead and the large difference in electronegativity between Pb and the chalcogen. There is an uneven sharing of the bonding electrons between Pb and the chalcogen, which imparts a partial negative charge to the initially more electronegative chalcogen atom and leaves a partial positive charge on the initially less electronegative Pb atom.[17] In Pb-Ge-C glasses, it is postulated[14] that the lead atoms transfer an electron to a C_3^+ center and modifies it into a C_2^0 center. Simultaneously, it also creates a C_1^- center by donating another electron to an adjacent C_2^0 site. There is a resultant ionic bonding between the Pb^{2+} ion and the C_1^- and C_2^0 centers created. Earlier investigations also indicate that the lead atoms reside in the Pb^{2+} state in lead chalcogenide glasses.[16]

It can be seen that the addition of Pb in Ge-C glasses converts some of the C_3^+ centers into C_1^- centers, while the Ge_3^- centers remain unchanged. Consequently, the number of C_3^+ centers that can undergo thermal excitation as per the Kolobov model[3] decreases. Hence, there is a decrease in the number of free holes formed by the conversion of C_3^+ centers into C_1^- centers. Also, with the decrease in the number of C_3^+ centers, the number of *shallow traps*[18] that capture the electrons excited into the conduction band decrease, which can account for an increase in electron concentration. In addition, there is a simultaneous increase in the negatively charged defects (C_1^-). With this, the number of *shallow acceptors*[18] that capture a hole from the valence band increases. As an overall consequence, there is a shifting of the Fermi level towards the conduction band that accounts for the p-n transition.

It has been recently suggested that the suppression of C_3^+ centers and enhancement of C_1^-, alone may not be adequate to explain the p-n transition in chalcogenide glasses, and band structural effects also have to be considered.[19] In Pb-doped chalcogenide glasses, for example, the sp^3d^2 orbital of Pb^{2+} ion occupies a slightly higher level than the Se lone pair level. The triplet t_{2g} levels of Pb are still higher and

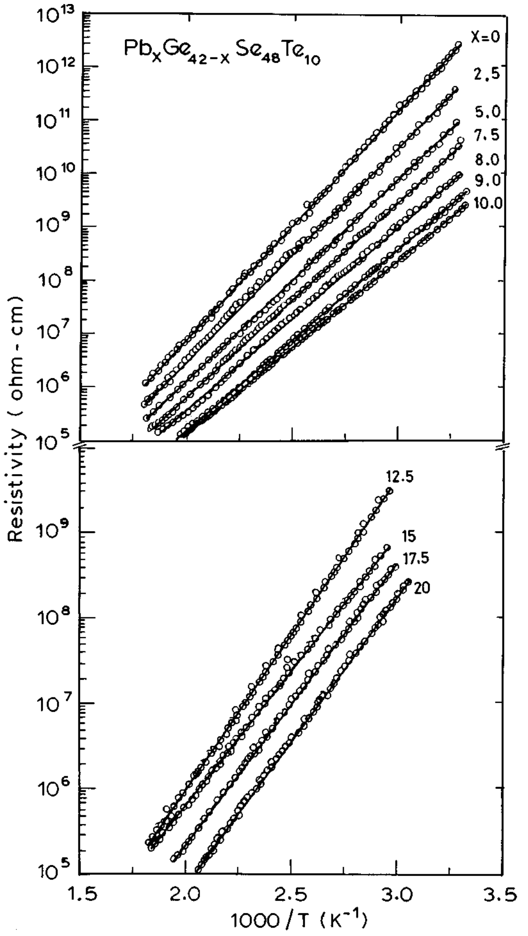

FIG. 2. The variation of log (resistivity) with (1000/T) for $Pb_xGe_{42-x}Se_{48}Te_{10}$ ($0 \leq x \leq 20$) glasses, in the range 300–500 K.

overlap with the empty antibonding σ^* levels. As the top of the lone-pair band is constituted of Se^- or C_1^- type of states, electron transport can occur from these levels through the empty sp^3d^2 state. With the increase in concentration of Pb width of both sp^3d^2 and C_1^- bands increase, accounting for an increase in the electron contribution to the conductivity that can exceed the contribution from holes. Thus, there is also the contribution from the changes in the band structure with Pb content, in the p-n transition.[19]

Recent photoemission and inverse photoemission studies[20] suggest that in Bi-Ge-Se glasses also, the Bi-Se antibonding states are mixed up with the Ge-Se antibonding states, to lower the conduction-band minimum (CBM). With the addition of Bi, the CBM moves towards the Fermi level, while the valence-band maximum shows no notable change. The p-n transition has been attributed mainly to the new unoccupied states that appear just above the Fermi level.[20] This result also underlines the importance of band structural effects in the carrier-type reversal in glassy chalcogenides.

In any given system, the carrier-type reversal threshold will be decided by the combination of the aspects described above (defects and band structural effects). Further, the p-n transition is not drastically altered by the replacement of one chalcogen by another, as seen earlier in Bi-Ge-Se (Ref. 8) and Bi-Ge-Se-Te samples.[21] The present results also confirm that the p-n transition threshold of Pb-Ge-Se glasses[19] is unaltered by the replacement of Se by Te.

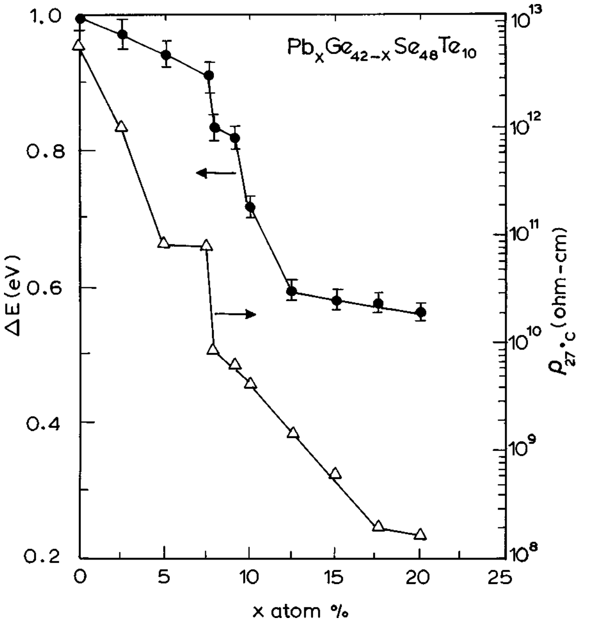

FIG. 3. Compositional dependence of the electrical activation energy (ΔE) and dc electrical resistivity (ρ) for $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses ($0 \leq x \leq 20$) at 300 K.

C. Composition dependence of resistivity and conductivity activation energy of Pb-Ge-Se-Te glasses

Figure 2 shows the variation of electrical resistivity of Pb-Ge-Se-Te samples, with temperature, in the range 300–500 K. It can be seen that the conduction is a thermally activated form with a single activation energy. Figure 3 shows the composition dependence of the conductivity activation energy (ΔE) of $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses of different compositions, estimated from the variation of electrical resistivity (ρ) with temperature. The composition dependence of electrical resistivity at ambient temperature (27 °C) is also shown in Fig. 3. It is interesting to see from Fig. 3 that the addition of Pb in Ge-Se-Te glasses (replacing Ge) leads to an appreciable decrease in resistivity and the activation energy. Also, there is a notable drop in both electrical resistivity and activation energy at the p-n transition threshold.

The decrease in resistivity with the addition of more metallic lead is not unexpected. With the increase in Pb, there is a decrease in the number of Ge-Se and Ge-Ge covalent bonds and an increase in Pb-Se ionic bonds, which can account for the decrease in resistivity. The sharp change in resistivity at the p-n transition threshold is linked with the discontinuity in the activation energy. The sudden decrease in activation energy at the p-n transition can be understood by considering the effect of charged impurities ($[A^+]$) on the defect density ($[C_1^-]$ and $[C_3^+]$) and carrier concentrations (n).

The total density of valence alternation centers (N) is given by

$$N=[C_1^-]+[C_3^+]. \tag{1}$$

In the absence of a metal additive, the positively and negatively charged native defects are equal in number ($[C_1^-]=[C_3^+]$) and $N=2N_0$, where N_0 denotes the concentrations of individual native-charged defects.

The concentration of native VAP's equilibrating at the quenching or glass transition temperature (T_g), is also given by

$$N_0^2=[C_3^+][C_1^-]=N_A^2\exp(-E_{\mathrm{VAP}}/k\ T_g), \tag{2}$$

where N_A is the density of the chalcogen and E_{VAP} is the energy required to create a valence-alternation defect pair from a normally bonded chalcogen.

The electron concentration in the absence of additives (n_0) is given by[22]

$$n^2[C_3^+]/[C_1^-]=N_C^2\exp(-2\epsilon_n/kT)=n_o^2 \tag{3}$$

where N_C is the effective density of conduction-band states. The activation energy for the electron, $\epsilon_n\approx E_g/2$, where E_g is the mobility gap.

It is assumed that additives such as Pb equilibrate at T_g and yield positive centers of concentration $[A^+]$, where A denotes the additive. In order to calculate the thermal activation energy for various concentration of $[A^+]$, the total density of valence-alternation centers (N) that equilibrate with $[A^+]$ during glass transition, and remaining constant in the range of interest, $T<T_g$, has to be determined.

Assuming that n_0 is small compared to N_0, the defect concentrations after the addition of metal atoms into the chalcogenide glass, can be estimated from[22]

$$[C_1^-]^*=1/2[A^+]+(N_0^2+1/4[A^+]^2)^{1/2}, \tag{4}$$

$$[C_3^+]^*=-1/2[A^+]+(N_0^2+1/4[A^+]^2)^{1/2}. \tag{5}$$

Here, $[A^+]$ is treated as an independent variable for determining $[C_1^-]^*$ and $[C_3^+]^*$ at T_g. The total concentration of VAP's, after the addition of metal atom (N_{mod}) is given by

$$N_{\mathrm{mod}}=[C_1^-]^*+[C_3^+]^*=2(N_0^2+1/4[A^+]^2)^{1/2}. \tag{6}$$

From Eq. (6), it is clear that the concentration of charged additives has to approach or exceed N_0 in order to have any appreciable effect. The electron concentration after the incorporation of the additive can be estimated from

$$n^2(2N_0^2/[A^+]+n)=2[A^+]n_0^2. \tag{7}$$

When $n\gg 2N_0^2/[A^+]$, i.e., for high additive concentrations, Eq. (7) simplifies to the form

$$n=(2[A^+])^{1/3}n_0^{2/3}. \tag{8}$$

For lower impurity concentrations, $n\ll 2N_0^2/[A^+]$, Eq. (7) reduces to

$$n=[A^+]n_0/N_0. \tag{9}$$

It is clear from the above that a discontinuous change in the conductivity activation energy to $\frac{2}{3}$ of original value can be expected, when the electron concentration (n) is increased by the incorporation of charged impurities to a threshold value $n_c=2N_0^2/[A^+]$. Fritzsche and Kastner have estimated n_c, using the more common values of N_0 ($\approx 10^{17}$ cm^{-3}) and $[A^+]$ ($\approx 10^{21}$ cm^{-3}), to be of the order of 10^{13} cm^{-3}. For Bi-Ge-Se glasses,[23] n_c has been found to be $\approx 10^{12}$ cm^{-3} at 9 at. % of Bi (p-n transition threshold) and an abrupt change in the conductivity activation energy has indeed been observed at this composition.[23]

In the present case (Pb-Ge-Se-Te), the actual value of N_0 is not available. Assuming $N_0\approx 10^{17}$ cm^{-3} and using the estimated value of $[A^+]$ (calculated from the density using the earlier procedure[23]), the electron concentration at the p-n transition threshold has been estimated for Pb-Ge-Se-Te samples, to be equal to $7.3\times 10^{12}/\mathrm{cm}^3$. It can be seen that the estimated value of n is of the order of the threshold electron concentration (n_c), which accounts for the discontinuity in the conductivity activation energy.

D. Comparison between Pb and other dopants in effecting p-n transition in glassy chalcogenides

Elliott and Steel proposed that for carrier type reversal, the polarizability of the doping element is an important criterion;[24] the larger polarizability of the dopant makes the formation of a partially ionic bond with the chalcogen likely. The polarizability of the two well-known dopants that bring about carrier-type reversal in chalcogenide glasses, namely, Bi and Pb, are 0.45 and 0.61×10^{-24} cm^3, respectively.[25] The higher polarizability of Pb, compared to Bi, is reflected in the more ionic character of its bond with the chalcogen; each Pb atom donates two electrons, passivating one C_3^+ center and creating one C_1^- center.[14] On the other hand, Bi enters as a Bi$^+$ ion, creating only one C_1^- center. Also, the electron concentration at the p-n transition threshold, in $\mathrm{Bi}_x\mathrm{Ge}_{20}\mathrm{Se}_{80-x}$ glasses ($\cong 10^{12}/\mathrm{cm}^3$),[24] is about one order of magnitude smaller than that for Pb chalcogenide glasses (Sec. III C).

Based on the polarization criterion and from the point of view of modification of the defect structure, one can expect that Pb will be more effective compared to Bi in the conduction-type reversal in chalcogenide glasses. However, the present investigation and earlier reports[7,19] indicate that the p-n transition thresholds of Pb-Ge-C glasses and Bi-Ge-C glasses are not widely different (8 and 9 at. %, respectively). It is likely that in Bi, the band structural effects play a major role in the p-n transition. The rapid decrease in CBM (1.5–0.4 eV) with Bi concentration (0–15 at. %), observed experimentally,[20] confirms this conjecture.

In this context, it is also interesting to note that Tl, in spite of its high polarizability (0.86×10^{-24} cm^3), is not known to produce p-n transition in Ge-C glasses even at concentrations up to 35 at. %.[26] Tl supposedly enters in eightfold coordinated Tl$^+$ sites in glassy chalcogenides.[27] Though one would expect that the positively charged Tl$^+$ should reduce the C_3^+ centers and thereby decrease the density of electron traps, no enhancement in electron displacement was noted experimentally.[28] Further, it has been proposed that, in addition to Tl being incorporated as a positive defect with a singly coordinated chalcogen as a compensating center, some fraction of thallium atoms introduce a shallow trapping level above the hole trapping states; the defect centers that are associated with photoluminescence and photoinduced ESR are different from the trapping centers that limit the hole mobility.[28] The absence of carrier-type reversal in Tl doped chalcogenides may be due to this difference in the defect structure.

IV. CONCLUSIONS

The reversal in conductivity type (p-n) has been observed in Ge-Se-Te glasses, with the addition of Pb. Marked changes have been observed in the composition dependence of electrical resistivity and conductivity activation energy at the p-n transition threshold, due to the change in the electron concentration. The observed p-n transition in Pb-modified chalcogenide glasses has been understood in light of the modification of defect states by the incorporation of Pb. Further, the crucial role played by other features such as band structure, polarizability of the dopant, etc., on carrier type reversal has been described.

---

*Author to whom correspondence should be addressed. Electronic address: sasokan@isu.iisc.ernet.in

[1] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).

[2] S. D. Baranovskii *et al.*, Fiz. Tekh. Poluprovodn. **18**, 1016 (1984) [Sov. Phys. Semicond. **18**, 633 (1984)].

[3] A. V. Kolobov, J. Non-Cryst. Solids **198-200**, 728 (1996).

[4] M. Kastner, Phys. Rev. Lett. **28**, 355 (1972).

[5] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976); M. Kastner, J. Non-Cryst. Solids **31**, 223 (1978).

[6] N. F. Mott, Adv. Phys. **16**, 49 (1967); D. Adler and E. J. Yoffa, Phys. Rev. Lett. **36**, 1197 (1976); D. Adler, in *Structure and Excitations of Amorphous Solids*, edited by G. Lucovsky and F. L. Galeenor, AIP Conf. Proc. No. **31** (AIP, New York, 1996), p. 11.

[7] N. F. Mott, Philos. Mag. **34**, 1101 (1976). **36**, 413 (1977).

[8] N. Tohge, T. Minami, Y. Yamamoto, and M. Tanaka, J. Appl. Phys. **51**, 1048 (1980); N. Tohge, H. Matsuo, and T. Minami, J. Non-Cryst. Solids **95&96**, 809 (1987); K. L. Bhatia, G. Parthasarthy, Ashwani Sharma, and E. S. R. Gopal, Phys. Rev. B **38**, 6342 (1988).

[9] R. M. Mehra *et al.*, J. Appl. Phys. **81**, 7842 (1997).

[10] A. V. Kolobov *et al.*, Phys. Rev. B **56**, 485 (1997).

[11] R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975); N. F. Mott, E. A. Davis, and R. A. Street, Philos. Mag. **32**, 961 (1975).

[12] D. Vanderbilt and J. D. Joannopoulos, Phys. Rev. Lett. **42**, 1012 (1979).

[13] D. Vanderbilt and J. D. Joannopoulos, Solid State Commun. **35**, 535 (1980); Phys. Rev. B **22**, 2927 (1980).

[14] A. Feltz, J. Non-Cryst. Solids **45**, 335 (1981).

[15] I. Weinberg, J. Chem. Phys. **36**, 1112 (1962).

[16] S. C. Rowland, F. Ritland, D. HaferBurns, and A. Bienenstock, in *Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors*, edited by W. E. Spear (Institute of Physics, Bristol, 1977), p. 135.; R. K. Shukla *et al.*, Philos. Mag. Lett. **64**, 165 (1991).

[17] R. T. Sanderson, *Chemical Bonds and Bond Energy* (Academic, New York, 1976).

[18] E. A. Davis, in *Amorphous Semiconductors*, edited by M. H. Brodsky, Topics in Applied Physics Vol. 36 (Springer-Verlag, New York, 1979), p. 41.

[19] B. Vaidhyanathan, S. Murugavel, S. Asokan, and K. J. Rao, J. Phys. Chem. **101**, 9717 (1997).

[20] O. Matsuda *et al.*, J. Non-Cryst. Solids **198-200**, 688 (1996).

[21] N. Tohge, T. Minami, and M. Tanaka, J. Non-Cryst. Solids **38&39**, 283 (1980).

[22] H. Fritzsche and M. Kastner, Philos. Mag. B **37**, 285 (1978).

[23] S. R. Elliott and A. T. Steel, J. Phys. C **20**, 4335 (1987).

[24] S. R. Elliott and A. T. Steel, Phys. Rev. Lett. **57**, 1316 (1986).

[25] L. Pauling, Proc. R. Soc. London **114**, 181 (1927).

[26] N. Tohge, K. Kanda, T. Minami, and Yogyo-Kyokai- Shi, J. Ceram. Soc. Jpn. **96**, 226 (1986).

[27] J. A. A. Ketelaar, W. H. t'Hart, M. Moorel, and D. Porter, Z. Kristallogr. **101**, 329 (1939); S. G. Bishop and P. C. Taylor, Phys. Rev. B **7**, 5177 (1973).

[28] G. Pfister *et al.*, Phys. Rev. Lett. **41**, 1318 (1978).