may be the loss of translational symmetry of the lattice with microscopic strains occurring over dimensions of the order of some unit cells. While we cannot identify the dominant defects, it would appear that the thin-film growth process minimizes those defects that may be partly responsible for bulk NbGe having a T_c of some 6 K.

The authors wish to thank W. A. Royer for technical assistance and W. F. Brinkman, H. J. Levinstein, M. T. Robinson, A. R. Sweedler, and J. H. Wernick for helpful conversations.

[1] J. R. Gavaler, Appl. Phys. Lett. 23, 480 (1973).

[2] L. R. Testardi, J. H. Wernick, and W. A. Royer, Solid State Commun. 15, 1 (1974).

[3] J. R. Gavaler, M. A. Janocko, and C. K. Jones, J. Appl. Phys. 45, 7 (1974).

[4] L. R. Testardi, R. L. Meek, J. M. Poate, W. A. Royer, A. R. Storm, and J. H. Wernick, Phys. Rev. B 11, 4304 (1975).

[5] O. Meyer, H. Mann, and E. Phrilingos, in Applications of Ion Beams to Metals, edited by S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum, New York, 1974), p. 15.

[6] R. Bett, Cryogenics 14, 361 (1974).

[7] A. R. Sweedler, D. G. Schweitzer, and G. W. Webb, Phys. Rev. Lett. 33, 168 (1974); A. R. Sweedler, D. Cox, and D. G. Schweitzer, IEEE Trans. Magn. 11, 163 (1975).

[8] N. Bohr, K. Dan. Vidensk. Selsk., Mat.-Fys. Medd. 18, No. 8 (1948).

[9] M. T. Robinson, in Proceedings of the British Nuclear Energy Society Conference on Nuclear Fusion Reactors, Culham Laboratory, 1969 (United Kingdom Atomic Energy, Culham, England, 1970), p. 364.

[10] M. Soell, H. Bauer, K. Boening, and R. Bett, Phys. Lett. 10, 83 (1975).

[11] J. H. Carpenter and A. W. Searcey, J. Am. Chem. Soc. 78, 2079 (1956).

[12] S. Geller, Acta Crystallogr. 9, 885 (1956).

[13] B. T. Matthias, T. H. Geballe, R. H. Willens, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. 139, A1501 (1965).

[14] G. W. Arnold, G. B. Krefft, and C. B. Norris, Appl. Phys. Lett. 25, 540 (1974).

[15] The increase in the transition width near (1 to 2) $\times 10^{16}$ cm^{-2} dose for this sample is due to unusual structure near the onset of the resistive transition. Further details will be published later.

[16] L. R. Testardi, to be published.

[17] J. F. Bachner and H. C. Gatos, Trans. Metall. Soc. AIME 236, 1261 (1966).

[18] C. M. Varma, J. C. Phillips, and S. T. Chui, Phys. Rev. Lett. 33, 1233 (1974).

[19] J. C. Phillips, to be published.

States in the Gap in Glassy Semiconductors

R. A. Street

Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany

and

N. F. Mott

Cavendish Laboratory, Cambridge, England

(Received 24 June 1975)

A model is discussed which for the first time provides a unified description of many electrical and optical properties of chalcogenide glasses. It is proposed that localized gap states are at dangling bonds, and that lattice-distortion effects are sufficiently strong that these states exhibit an effective negative electron-electron correlation energy.

In noncrystalline semiconductors, it is known that localized states in the gap determine many of the electrical properties. For example, the work of Spear on amorphous silicon shows them to be responsible for the pinned Fermi energy, recombination in photoconductivity, variable-range hopping, and observation of ESR.[1] Spear proposes that divancancies are present which have properties similar to those in the crystal.[2] This defect acts either as a deep donor, or as an acceptor lying at higher energy in the gap. The

separation between the two states is the Hubbard correlation energy.

The situation in chalcogenides is different. Neither an ESR signal,[3] Curie paramagnetism at low temperatures,[4] nor variable-range hopping[5] has yet been observed. Despite this, ample evidence that these materials contain high concentrations of defect states comes from photoluminescence,[6-8] field effect,[9] photoconductivity,[10] drift mobility,[11] and a pinned Fermi energy.[5] Several different energy levels have been suggest-

ed to explain these experiments, but there has been no satisfactory explanation of the origin of these states. In this paper, we discuss a new model which can account for all these observations in terms of a single defect.

A first attempt to give a model that pins the Fermi energy without producing free spins was made by Anderson.[12] He supposed that there are more bonding states than pairs of electrons, but that all such states are either doubly occupied or empty. The reason given for this is that the polaron energy gained by the contraction of a bond more than compensates for the electron repulsion, and so an effective negative correlation energy results. Here, we apply this concept specifically to point defects and obtain a model which can explain a wider variety of phenomena than Anderson's.

We consider As_2Se_3 and suppose that it contains 10^{18}–10^{19} cm^{-3} dangling bonds. These are point defects at which the normal coordination (2 for Se, 3 for As) cannot be satisfied because of the constraints of local topography; the neutral dangling bond therefore contains an unpaired electron. We assume that a dangling bond may be occupied by zero, one, or two electrons, and label these states D^+, D^0, and D^-, respectively, the superscripts denoting the total charge of the center. Following Anderson,[12] we also assume that local lattice distortion occurs when the electron occupation of the dangling bond changes and that it is sufficiently strong for the reaction

$$2D^0 \rightarrow D^+ + D^- \tag{1}$$

to be exothermic. All defect centers are therefore either positively or negatively charged and D^0 only occurs by excitation.

The strongest evidence for our model comes from photoluminescence studies of As_2Se_3 and As_2S_3. A charge on the radiative recombination center was deduced from excitation spectra and thermal quenching experiments.[6,7] Furthermore, the broad emission band which also occurs in the crystal and the energy difference between absorption and emission (Stokes Shift) are a consequence of strong lattice distortion.[8] Experiments also suggested that the recombination centers are at dangling bonds.[13]

The strong lattice distortion has a profound effect on the energy levels of electrons at the dangling bonds, yielding properties similar to F centers or small polarons. Possible transitions of an electron between the valence band and D^+ are illustrated in a configurational-coordinate dia-
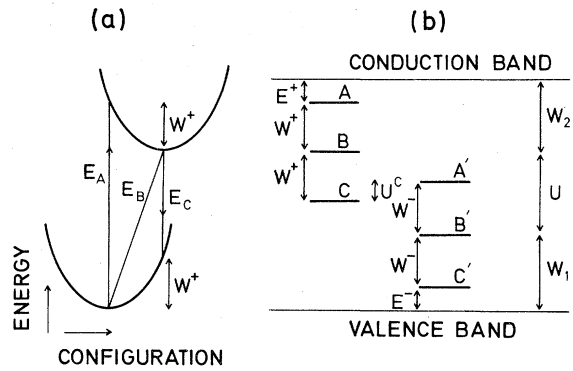
FIG. 1. (a) Configurational-coordinate diagram for the singly occupied dangling bond; the lower level represents D^+ plus the filled valence band. The upper level represents D^0 with a hole at the top of the valence band. (b) Combined level diagram for both the singly and doubly occupied dangling bonds, as described in the text. Energy definitions of W_1, W_2, and U are also included.

gram shown in Fig. 1(a). E_A and E_C are optical excitation and recombination energies and are "vertical" because of the Franck-Condon principle. E_B is the difference between the total energy of the ground and excited states and is the energy of thermal excitation. For simplicity, we assume that the local vibrational frequency is unchanged by the electronic transition and therefore

$$E_A - E_B = E_B - E_C = W^+, \tag{2}$$

where W^+ is the "polaron energy." An equivalent diagram applies to the electron energy levels of the doubly occupied center.

The six important energy levels of the singly and doubly occupied centers are shown in Fig. 1(b).[14] Levels A, B, and C are, respectively, E_A, E_B, and E_C above the valence band, and represent the transitions in Fig. 1(a). A', B', and C' are the corresponding energies of the doubly occupied center. W^+ and W^- are the respective polaron energies. U^c is the true correlation energy, the difference between the electron energy of the one-electron and two-electron states at *identical* distortional configurations, and $-U$ is the effective correlation energy when distortion is included. E^+ and E^- define the positions of the energy levels relative to the band edges; their magnitudes are inferred below.

We assume the following state of affairs to prevail. An interaction with valence electrons on neighboring atoms is responsible for the local

lattice distortion. In chalcogenides, lone-pair orbitals form the upper part of the valence band; bonding states are much deeper and antibonding states form the conduction band.[15] A dangling bond interacts primarily with neighboring lone pairs because bonding electrons are located between bonding atoms. D^+ is strongly attracted to such a lone pair, bonding with it by distorting its environment. A large electronic energy is released in this way because the lone-pair electrons are transformed into deep bonding states; this in itself argues strongly for local distortion. An extra electron introduced into this D^+ complex occupies the next highest level, which is the conduction-band-like antibonding orbital. Because of the charge on D^+, a shallow donor level results. This is represented by level A in Fig. 1(b) as we have assumed no change from the configuration of the unoccupied D^+. Thus, E^+ is a typical donor binding energy and hence not greater than about 0.1 eV.

In contrast to D^+, the two electrons on D^- cannot form a covalent bond with a neighboring atom but instead occupy a valence-band-like lone pair. An acceptor level is formed because of the charge on D^- and we find that $E^- \simeq E^+$ using a similar argument as for D^+. The configuration of D^0 lies intermediate between that of D^+ and D^- and therefore approximate equality of W^+ and W^- is expected.

A discussion follows of the interpretation of various experiments according of the above model. Because of lattice distortion, it is no longer possible to assign a single energy to a localized state. In particular, the energies of thermal and optical transitions differ by the polaron energy.

(a) *DC conductivity.*— In As_2Se_3 the observed activation energy is 0.9 eV and the band gap 1.9 eV[5] (values extrapolated to 0 K). In our model, the Fermi energy is pinned midway between levels B and B', at energy $W_1 + U/2$ above the valence band. [The energies W_1 and U are defined in Fig. 1(b).] The expected similarity of W^+ and W^- automatically positions E_F near midgap.

(b) *Drift mobility.*— Experimentally, the mechanism is a trap-limited drift of holes and the observed activation energy is 0.45–0.06 eV.[11] The trap is D^- which rapidly captures a hole through the Coulomb interaction and the energy required to thermally re-excite the hole is W_1.

(c) *Optical absorption.*— In the absence of D^0 centers, the only optical transitions involving the dangling bond are from the valence band to D^+

(level A) and from D^- (level C') to the conduction band. The energies are $E_g - E^+$ and $E_g - E^-$, respectively, both of which are close to E_g. These transitions successfully account for the shallow absorption tail near the band edge,[16] and for the absence of absorption at lower energy.

(d) *Photoluminescence.*— This occurs when an electron-hole pair is excited very close to a charged center.[6,7] If the center is D^- then the hole will be captured nonradiatively, leaving the conduction-band electron to make an optical transition to the resulting D^0. The relevant energy level in Fig. 1(b) is A' and the Stokes shift (experimentally about 1.0 eV[8]) is $2W^- + E^- \simeq 2W_1$. Thus we predict a Stokes shift which is approximately twice the drift mobility activation energy, in agreement with experiment [see section (b) above]. The alternative possibility of recombination through D^+ leads to a similar Stokes shift.

(e) *Photoconductivity.*— Free photoexcited electrons and holes are rapidly captured by D^+ and D^-, in each case contributing to an excess concentration ΔN of D^0 centers. Photoconductivity σ_{ph} results from thermal excitation of these trapped "holes" to the valence band. Hence,

$$\sigma_{ph} = \text{const } \Delta N \exp(-W_1/kT). \qquad (3)$$

The rate determining recombination is Reaction (1) which occurs when an electron tunnels between two D^0 centers. The recombination rate is therefore $b(\Delta N + N_T)$. Here N_T is the thermal equilibrium concentration of D^0, proportional to $\exp(-U/2kT)$ since the Fermi energy is midway between B and B'. Although exothermic, Reaction (1) involves a small polaron hopping energy, and possibly a small disorder energy. The polaron term originates because the electronic energy U^c must be overcome before tunneling can occur. Thus, b is expected to be weakly activated and we denote its energy by V. The magnitude of b can be estimated by assuming that Reaction (1) proceeds by phonon-assisted tunneling[5] over a distance equal to the average separation of the centers. Elsewhere[17] we show that reasonable agreement with observation[10] is obtained.

The rate equation for recombination is[5]

$$d\,\Delta N/dt = G - b[(\Delta N)^2 + 2N_T\Delta N], \qquad (4)$$

where G is the photogeneration rate. There are two limiting cases of interest. *Regime I:* $N_T \gg \Delta N$. From Eq. (4) in the steady state,

$$\Delta N = G/2bN_T. \qquad (5)$$

Combining Eqs. (5) and (3), we find that σ_{ph} has

activation energy $W_1 - U/2 - V$, and from Eq. (5), $\tau = \Delta N/G$ has energy $-(U/2 + V)$. σ_{ph} is proportional to G. *Regime II:* $N_T \ll \Delta N$. In this case, Eq. (4) gives

$$\Delta N = (G/b)^{1/2}. \tag{6}$$

From Eqs. (6) and (3), the activation energies for σ_{ph} and τ are now $W_1 - V/2$ and $-V/2$, respectively. Here σ_{ph} varies as $\sqrt{G}$.

These two regimes of G dependence are clearly observed in the photoconductivity of all chalcogenide glasses so far investigated. In regime II of As_2Se_3,[10] the observed activated energy of τ gives $V = 0.16$ eV, a small value as suggested. The activation energy of σ_{ph} is 0.37 eV and implies $W_1 = 0.45$ eV, in agreement with that obtained from the drift mobility. In regime I, the activation energy of σ_{ph} is -0.25 eV; U is therefore about 1.0 eV, a value which is fully consistent with the position of the Fermi level.

(f) Finally, we consider the recent experiments of Bishop, Strom, and Taylor.[18] In As_2Se_3, they observe a metastable ESR signal, induced by illumination with above-gap radiation. An associated induced absorption band extending down to ~0.8 eV is also seen, and both effects may be quenched by illumination with below-band-gap radiation. We propose that the ESR active centers are singly occupied D^0, induced by trapping of free electrons and holes. These are metastable at low T because of the activation energy V of Reaction (1). Optical transitions from D^0 to extended states in the bands involve levels A' or C in Fig. 1(b) and therefore occur at energies greater than about $E_g/2$. The presence of metastable D^0 at low T also accounts for the fatiguing of photoluminescence.[6]

A more detailed discussion of this model together with a comparison with the different ideas of Emin, Seager, and Quinn[19] and also with the quite different behavior of silicon, is given in another paper.[17]

---

[1]W. E. Spear, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen, West Germany, 1974*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 1, and references therein.

[2]G. D. Watkins and J. W. Corbett, Phys. Rev. 138, 543 (1965).

[3]S. C. Agarwal, Phys. Rev. B 7, 685 (1973).

[4]F. J. DiSalvo, A. Menth, J. V. Waszczak, and J. Tauc, Phys. Rev. B 6, 4574 (1972).

[5]N. F. Mott and E. A. Davis, *Electronic Process in Non-Crystalline Materials* (Clarendon Press, Oxford, England, 1971).

[6]R. A. Street, T. M. Searle, and I. G. Austin, J. Phys. C: Solid State Phys. 6, 1830 (1973).

[7]R. A. Street, T. M. Searle, and I. G. Austin, Philos. Mag. 30, 1185 (1974), and in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen, West Germany, 1974*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 953.

[8]R. A. Street, I. G. Austin, T. M. Searle, and B. A. Smith, J. Phys. C: Solid State Phys. 7, 4185 (1974).

[9]J. M. Marshall and A. E. Owen, to be published.

[10]C. Main, Ph.D. thesis, Edinburgh, 1974 (unpublished).

[11]J. M. Marshall and A. E. Owen, Philos. Mag. 24, 1281 (1971); F. D. Fisher, J. M. Marshall, and A. E. Owen, to be published.

[12]P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[13]R. A. Street, T. M. Searle, and I. G. Austin, Philos. Mag. 30, 1181 (1974).

[14]A combined configurational coordinate diagram for both singly and doubly occupied centers is too complicated to be useful.

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

[16]R. A. Street, T. M. Searle, and I. G. Austin, Philos. Mag. 32, 431 (1975).

[17]N. F. Mott, E. A. Davis, and R. A. Street, to be published.

[18]S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. 34, 1346 (1975).

[19]D. Emin, C. H. Seager, and R. H. Quinn, Phys. Rev. Lett. 28, 813 (1972).