qvist, Solid State Commun. 11, 149 (1972); O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[12] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966); O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B 10, 1319 (1974).

[13] O. Gunnarsson, P. Johansson, S. Lundqvist, and B. I. Lundqvist, to be published.

[14] J. Janak, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B 12, 1257 (1975).

[15] T. B. Grimley, in *Dynamics of Surface Physics*, edited by F. O. Goodman (Editrici Compositori, Bologna, 1974).

[16] J. R. Smith, S. C. Ying, and W. Kohn, Phys. Rev. Lett. 30, 610 (1973).

[17] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970), and 3, 1215 (1971).

[18] See, e.g., V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 1.

[19] This approach has earlier been used in Ref. 17 and by Z. D. Popovic and M. J. Stott, Phys. Rev. Lett. 33, 1164 (1974).

[20] This means that, e.g., the density dimple at the centered position is not described.

Low-Temperature Optical Investigation of the Urbach Tail in Amorphous Ge_xTe_{1-x} Alloys in the Light of the Anderson Model

A. Deneuville, A. Mini, and B. K. Chakraverty
Groupe des Transitions de Phases, Centre National de la Recherche Scientifique, 38042 Grenoble-Cédex, France

(Received 22 March 1976)

The recent Anderson model of the electronic structure of the amorphous chalcogenides predicts formation of paired localized singlet states through large electron-phonon interaction. We show that the interpretation of the absorption in the Urbach-tail region is completely consistent with modulation of band edges due to random internal electrical field associated with these bipolarons. They arise from electron transfer between Te dangling bonds, $x \leq 0.33$, or Ge dangling bonds, $x > 0.33$.

Recently, Anderson[1] has proposed a model for the electronic structure of amorphous chalcogenide semiconductors to explain the lack of EPR, of Curie paramagnetism, and of important optical absorption due to the high density ($\simeq 10^{19}$ cm^{-3}) of localized states needed for pinning of the Fermi level. He has convincingly argued that the localized states must be doubly occupied electron states through strong electron-phonon interaction that overcomes the on-site Mott-Hubbard Coulomb repulsion. According to Anderson these paired states must have the following properties: (a) They do not give rise to the usual kind of conductivity as pair states need an energy higher than the single-particle mobility gap to be broken. (b) They do not give optical absorption lower than the band gap. (c) They do not respond to an external magnetic field either, since they are magnetic singlets.

Thus to all intents and purposes, these bipolaron states are "invisible." We propose in the present Letter that the study of the Urbach tail in amorphous materials can provide a direct test of the Anderson model, besides being a valuable contribution to the understanding of localized states in these chalcogenides. For the Anderson mechanism to be operative, an electron gets transferred from one dangling bond to another —in the process, the dangling bond that is vacant becomes positively charged and the bond that receives the two electrons of opposite spin becomes negatively charged. We are thus left with a system of random positive and negative electrostatic charges, and the amorphous semiconductor resembles a highly doped compensated crystalline semiconductor (HDCCS). In this sense the Anderson model is reminiscent of the earlier models[2] of compensated semiconductor analogy used for amorphous semiconductors, but with the difference that now, over and above the random electrostatic fields, one will have superimposed intense local polar deformations responsible for the bipolaronic states. The number of positive and negative polar states resulting from the single-electron dangling bonds will depend strongly on the departure from the ideal tetrahedral coordination. For amorphous Ge_xTe_{1-x}, it seems now certain[3] that this ideal tetrahedral coordination is achieved for the nominal composition $GeTe_2$ while Ge and Te atoms remain respectively fourfold and twofold coordinated for $x < 0.5$.[4] On either side of $x = 0.33$, we shall expect to find an increasing number of polar "pair" states. Schematically Fig. 1 shows what one would ex-

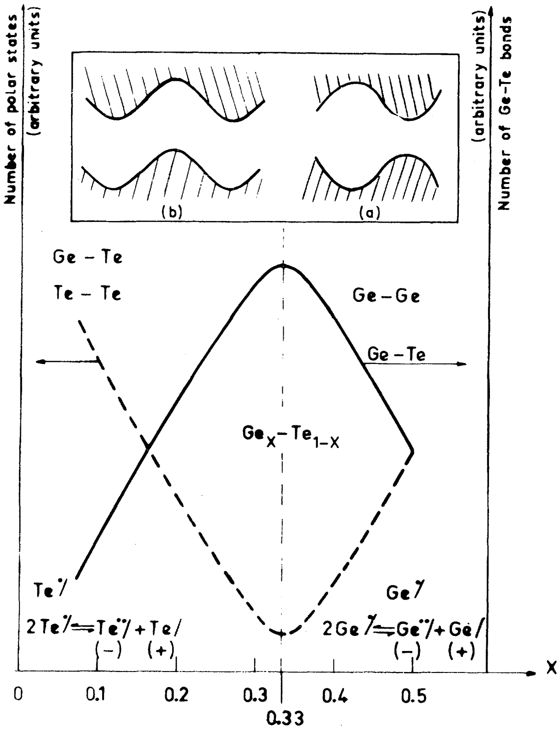

FIG. 1. Schematic variation of the number of Ge-Te bonds and polar states with x. Inset: band edge with (a) deformation potential and (b) electrostatic potential.

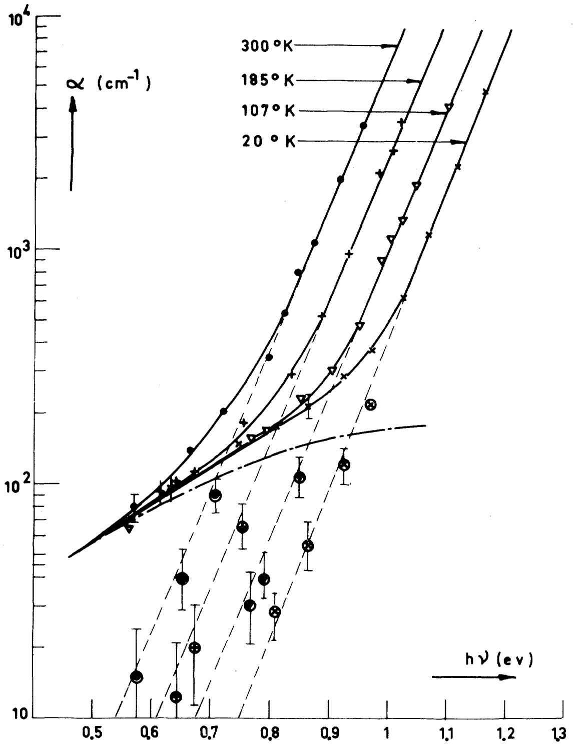

FIG. 2. α versus $h\nu$ at some temperatures for $x = 0.1$.

pect from such a simple consideration. In the inset we show what one expects would be the effect on the valence and conduction bands of these pair states resulting from both internal electrostatic field and local polar deformation. Thus the "invisible" bipolarons ought to affect profoundly the bulk band edges and, if so, a systematic study of the Urbach tail as a function of composition ought to be extremely revealing.

Films were prepared by sputtering[5] from $\mathrm{Ge}_x\mathrm{Te}_{1-x}$ targets ($x = 0.1$, 0.2, 0.3, 0.4, 0.5) on silica substrate. They were mounted in a Thor Cryogenic double-beam optical cryostat. Measurements were made between 300 and 4 K with $\Delta T \simeq 1$ K and between 0.5 and 3.5 μm with a Beckman DK2A spectrometer. The values of absorption versus photon energy were deduced from a single transmission measurement on each sample[6]; at each x we used several films ($0.7\ \mu\mathrm{m} < d < 3\ \mu\mathrm{m}$). They are in good agreement at room temperature with those deduced from transmission and reflection measurements on the same films and with our own previous results[5] on thinner films. Starting with an experimental uncertainty of ± 0.25% in the transmission measurements, we obtain an error on α of $\pm 25/d$ cm^{-1}, where d is the film thickness.

We obtain two types of variation according to the composition. For $x > 0.3$, absorption varies nearly exponentially with photon energy for $\alpha < 10^4$ cm^{-1}. The room temperature α versus $h\nu$ curve is in excellent agreement with that of Howard and Tsu,[7] but somewhat different from that of Bahl and Chopra.[7]

For $x \leq 0.3$, Fig. 2 shows the variation of α with photon energy at five temperatures between 300 and 20 K on $\mathrm{Ge}_{0.1}\mathrm{T}_{0.9}$. Absorption varies exponentially with photon energy for 5×10^2 cm^{-1} $< \alpha < 10^4$ cm^{-1}. For $\alpha < 5\times10^2$ cm^{-1}, α values are higher than values corresponding to the extrapolation of the exponential part. It can be decomposed into a part which is the extrapolation of the exponential range (dashed line) and a part which does not depend on temperature (dash-dotted line). This latter component keeps almost the same α versus $h\nu$ profile for all compositions $x \leq 0.3$, but its intensity decreases towards disappearance from $x = 0.1$ to $x = 0.3$.

Figure 3 shows the variation of F $[\alpha = \alpha_0 \exp(h \times \nu/F)]$ with T for the various compositions. The variations of F with x are most important. But we also observe a weak increase of F with tem-

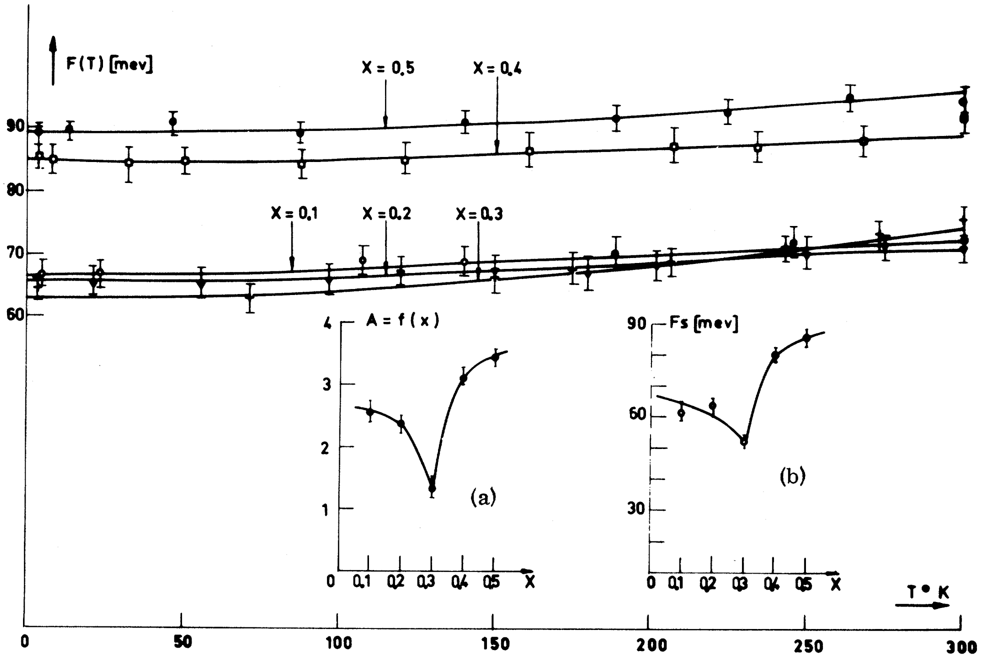

FIG. 3. $F(T)$ for $x=0.1$, 0.2, 0.3, 0.4, 0.5. Inset (a), $A(x)$; inset (b), $F_s(x)$.

perature whose amplitude varies with composition.

In its most general interpretation,[8] the Urbach tail has been attributed to an internal electrical microfield arising either from localized charges (HDCCS), or from optical phonons ω_0 (ionic crystal). Like other authors,[9] we can decompose F into two parts:

$$F=F_s+\frac{\hbar\omega_0}{2A}\coth\frac{\hbar\omega_0}{2kT}, \tag{1}$$

where F_s is a structural part independent of temperature and the second term represents the contribution with a coupling constant A^{-1} ($A \geqslant 1$) due to the electric field from optical phonons. For Ge_xTe_{1-x} the phonon spectrum has been studied by infrared absorption and Raman effect. Several characteristic frequencies independent of composition are found, with a dominant infrared absorption at 220 cm^{-1} originating from the Ge-Te bond.[4] At each composition A and F_s values can be found so that the experimental points agree with the theoretical expression (1) shown as the full line in Fig. 3. The variations of A and of the structural term F_s with x are given in the insets.

In the light of these results, we can now come back to some further justification of the scheme in Fig. 1.

(1) *Chemical bonding and Ge-Te bonds.*—If one measures the bond strength by the band gap of corresponding material the Ge-Te bond (1.2 eV in $GeTe_2$)[3] is stronger than the Ge-Ge bond ($\simeq 1$ eV) or the Te-Te bond (0.87 eV).[10] So, at each x value, a maximum number of Ge-Te bonds will appear. For $x \leqslant 0.3$ there will be Te-Te bonds and Ge-Te bonds while for $x > 0.3$ there will be Ge-Te bonds and Ge-Ge bonds. This picture agrees with infrared and Raman measurements[4] and with the annealing behavior of Te crystallites in an amorphous Ge_xTe_{1-x} matrix.[11] Corresponding variation of the number of Ge-Te bonds is shown in the full line in Fig. 1. It is reflected in the variation of A^{-1} (coupling with the Ge-Te-bond phonons) and the minimum value of A for $x=0.3$ [inset (a), Fig. 3] of 1.3 which is nearly ideal ($A \neq 1$) when there are nearly all Ge-Te bonds.

(2) *Polar states.*—We expect the local polar deformation to occur more on the relatively weaker Ge-Ge or Te-Te bonds. So the F_s variation [inset (b), Fig. 3] for Ge_xTe_{1-x} with a minimum at $x=0.3$ is completely consistent with the scheme in Fig. 1. F increases on either side of $x=0.33$ with the number of polar states arising from Te ($x<0.33$) or from Ge ($x>0.33$) (dashed line) just as F increases with doping in (HDCCS).[12]

(3) *Compensation.*—Local polar deformation arises from electron transfer between dangling bonds as in the Anderson model. Our weak variation with T for the slope of the Urbach tail compared with results on HDCCS[12] [$F(T)$ is constant

for compensated material; $F(T)$ varies strongly with T for uncompensated materials] indicates for all compositions a high degree of compensation which is consistent with intrinsic conductivity.[3,5] However, in all cases, compensation does not seem to be exactly perfect. For $x \leq 0.3$ we find a low-energy absorption component independent of temperature usually attributed to a defect on a chalcogen bond.[9]

After illumination, this type of signal strongly increases with the appearance of a small EPR signal.[13] So it can be more precisely attributed to a low density of single-electron Te dangling bonds. We only observe it for $x<0.33$ and its intensity increases with Te content. For $x>0.33$ the material becomes more and more covalent and therefore the deformation needed for creation of polar states becomes larger and larger. This leaves a number of unpaired dangling bonds increasing with x giving rise to extrinsic conductivity increasing with x^5 ($x \leq 0.5$) and, in the extreme case of pure Ge, strong extrinsic conductivity and EPR signal result.

In conclusion, we have presented experimental results of the optical absorption in the Urbach-tail region at low temperatures in amorphous chalcogenide $\mathrm{Ge}_x\mathrm{Te}_{1-x}$ (for $0.1<x<0.5$). We have shown that the Anderson model, with its implied random internal electrical field applied to dangling bonds field, fits quite coherently with the experimental data.

We want to thank C. Bianchin at the Centre National de la Recherche Scientifique for the preparation of the films.

---

[1] P. W. Anderson, Phys. Rev. Lett. 34, 1346 (1975).

[2] H. Cohen, J. Non-Cryst. Solids 4, 391 (1970); J. D. Dow and J. J. Hopfield, J. Non-Cryst. Solids 8–10, 664 (1972).

[3] H. K. Rockstad and J. P. de Neufville, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972,* edited by The Polish Academy of Science (PWN—Polish Scientific Publisher, Warsaw, 1972), p. 423.

[4] G. B. Fisher, J. Tauc, and Y. Verhelle, 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. 1259.

[5] A. Deneuville, J. P. Keradec, P. Gérard, and A. Mini, Solid State Commun. 14, 341 (1974).

[6] J. P. Keradec and A. Deneuville, to be published.

[7] W. E. Howard and R. Tsu, Phys. Rev. B 1, 4705 (1970); S. K. Bahl and K. L. Chopra, J. Appl. Phys. 40, 4940 (1969).

[8] J. J. Dow and D. Redfield, Phys. Rev. 123, 1560 (1971).

[9] J. Cornet and D. Rossier, Philos. Mag. 27. 1335 (1973); R. A. Street, T. M. Searles, I. G. Austin, and R. S. Sussman, J. Phys. C 7, 1582 (1974).

[10] J. Stuke, J. Non-Cryst. Solids 4, 1 (1970).

[11] A. Deneuville, P. Gérard, and J. Devenyi, to be published.

[12] J. R. Dixon and J. N. Ellis, Phys. Rev. 123, 1560 (1961); A. B. Fowler, W. E. Howard, and G. E. Broch, Phys. Rev. 128, 1664 (1962); J. F. Pankove, Phys. Rev. 140, 2059 (1965); D. Redfield and H. Aframowitz, Appl. Phys. Lett. 11, 138 (1967).

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

Orientational Dependence of the Ta L_3 Edge Absorption in $1T$-TaS_2 As Measured by Polarized X Rays*

E. A. Stern and D. E. Sayers
Department of Physics, University of Washington, Seattle, Washington 98195

and

F. W. Lytle
The Boeing Company, Seattle, Washington 98124

(Received 17 May 1976)

We find a strong dependence of the strength of the peak in the absorption coeficient at the Ta L_3-absorption edge of $1T$-TaS_2 as a function of the orientation of the x-ray polarization with respect to the crystal layers. This variation can be related to the character of the unfilled d states just above the Fermi energy.

In this paper we report the results of measurements of the large peak in the absorption coefficient just above the Ta L_3 threshold in a single crystal of $1T$-TaS_2 using the polarized x rays from the Stanford Synchrotron Radiation Project (SSRP). We find, for the first time, a significant