FIG. 3. Temperature dependence of the ratio $(V_s - V_n)/V_n$ [Eq. (3)] for an indium specimen.

In a separate series of experiments we varied the strain rates over a factor of 200 and observed no significant dependence of difference in flow stress $\sigma_n - \sigma_s$ on strain rate, thus confirming the observation made by Alers, Buck, and Tittmann.[3]

The results of these experiments thus imply that, in looking for an explanation of the observed changes in flow stress between the normal and superconducting states in a metal, attention should be directed to a model in which the activation volumes change. Since the pinning mechanism for dislocations by obstacles must be at least partially electrical in nature it is perhaps reasonable to expect that the activation volume should change with electronic configuration at temperatures below T_c in the superconducting state but remain constant in the normal state.

Preliminary experiments on lead indicate that a similar behavior is found in this case, and we hope to report on this shortly.

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Amorphous Semiconductors as Undulatorily Graded Band-Gap Systems*

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We propose as a model of some amorphous semiconductors a system with undulations in composition or structure on a scale within the range of validity of the graded band-gap concept. Electronic states well within allowed bands are determined by perturbative analysis; states near band edges, by a modification of an effective-mass analysis. Localized states are obtained and the band edge identified as the locus of classical turning points of the effective mass functions.

The theoretical analyses of electronic structure of amorphous solids have been previously based on models involving only short-range order.[1] These analyses have predicted insensitivity of electronic properties to doping[2] and absence of an energy gap, replaced by a mobility gap.[3] The observed optical properties do not for some materials support the latter[4] and exceptions to the former have been reported.[5] There is experimental evidence that some amorphous solids are characterized by structural and/or compositional inhomogeneities on a scale of approximately 100 Å.[6,7] This scale is just within the range of validity of the concept of a graded band gap,[8] and we therefore propose a model amorphous semiconductor involving intermediate-range order on the scale in which substance A smoothly grades to substance B, not monotonically as with the usual graded band-gap system, but undulating in composition with a mean period of the order of 100 Å. A and B may be different substances or different structures of the same substance.

The theory of graded materials employs the virtual crystal approximation on a local basis where the potential from the statistical distribution of constituents A and B at position $\vec{r}$ is re-

placed by the potential for the average unit cell at $\vec{r}$ weighted for atomic composition. With unit cell potentials $V_A(\vec{r})$ and $V_B(\vec{r})$ respectively, the Hamiltonian is written

$$H = -\frac{\hbar^2}{2m}\Delta^2 + V_B(\vec{r}) + [V_A(\vec{r}) - V_B(\vec{r})]f(\vec{r}), \qquad (1)$$

where $f(\vec{r})$ is the atomic fraction of constitutent A. To facilitate the analysis we assume that $V_A(\vec{r})$ and $V_B(\vec{r})$ have the same lattice periods although for real materials this will not in general be so. The approximations of the theory of monotonically graded semiconductors were shown to remain valid for the distance over which f changes from 0 to 1 being 10^2 lattice distances.[8] Since the data on amorphous semiconductors indicate order on a scale of approximately 100 Å, i.e., globular morphology on a 100 Å scale, we conclude that a similar analysis is applicable. We have considered several forms of $f(\vec{r})$; the following will be used for extended electronic

states here:

$$f(r) = f(x) = \sum_i \tfrac{1}{2}[1 + a_i \cos(2\pi x/d_i)] \qquad (2)$$

with the d_i of the order of 100 Å and the a_i restricted by the condition $0 < f(x) < 1$. For localized states we shall treat a three-dimensional grading with a single d.

For the extended state problem, we solve the Schrödinger equation perturbatively since the term $|V_A(\vec{r}) - V_B(\vec{r})|$ is small compared with $|V_B(\vec{r})|$. This would be expected to work well for states away from the band edge of the unperturbed system, where $|V_A(r) - V_B(r)|$ is also small compared with the eigenvalue E. In the perfect B crystal, which is the unperturbed system, the idea of a band edge is clear but the idea of an E vs $\vec{k}$ curve having extrema in an amorphous material is not clear and a new definition of a band edge will be presented. From perturbation theory starting with Bloch states of the B crystal, expanding periodic factors in Fourier series of reciprocal lattice vectors, and relating k' to k and σ through the resulting δ functions, we obtain

$$\Psi(\vec{r}) = ae^{i\vec{k}\cdot\vec{r}} + \sum_{i=1}^{j}\beta_i \exp[i(\vec{k}+\vec{\sigma}_i)\cdot\vec{r}] + \sum_{i=1}^{j}\gamma_i \exp[i(\vec{k}-\vec{\sigma}_i)\cdot\vec{r}], \qquad (3)$$

where

$$\alpha = u_{n,\vec{k}}(\vec{r}) + \frac{1}{2}\sum_{n'\neq n}\frac{u_{n',\vec{k}}(\vec{r})}{E_n^0(\vec{k}) - E_{n'}^0(\vec{k})} \int u_{n'\vec{k}}^*(\vec{r})u_{n,\vec{k}}(\vec{r})[V_A(\vec{r}) - V_B(\vec{r})]d^3r, \qquad (4)$$

$$\beta_i(\vec{k},\vec{\sigma}_i) = \frac{u_{n,\vec{k}+\vec{\sigma}_i}(\vec{r})a_i}{E_n^0(\vec{k}) - E_n^0(\vec{k}+\vec{\sigma}_i)}\frac{1}{4}\int u_{n,\vec{k}+\vec{\sigma}_i}^*(\vec{r})u_{n,\vec{k}}(\vec{r})[V_A(\vec{r}) - V_B(\vec{r})]d^3r$$

$$+ \sum_{n'\neq n}\frac{u_{n',\vec{k}+\vec{\sigma}_i}(\vec{r})a_i}{E_n^0(\vec{k}) - E_{n'}^0(\vec{k}+\vec{\sigma}_i)}\frac{1}{4}\int u_{n',\vec{k}+\vec{\sigma}_i}^*(\vec{r})u_{n,\vec{k}}(\vec{r})[V_A(\vec{r}) - V_B(\vec{r})]d^3r, \qquad (5)$$

$$\gamma_i(\vec{k},\vec{\sigma}_i) = \beta_i(\vec{k},\vec{\sigma}_i), \qquad (6)$$

and

$$\vec{\sigma}_i \cdot \vec{r} = 2\pi x/d_i. \qquad (7)$$

Here the $u_{n,\vec{k}}(\vec{r})$ is the periodic part of the Bloch function. To get some idea of what these wave functions look like, we assume that the interband contributions are small because of the size of the energy denominators and examine the contribution from the intraband terms. The contribution from these terms will be smallest for a typical band structure in the middle of the band since there the difference $E_n^0(\vec{k}) - E_n^0(\vec{k}+\vec{\sigma}_i)$ is largest. At lower $\vec{k}$ values the difference $E_n^0(\vec{k}) - E_n^0(\vec{k}+\vec{\sigma}_i)$ is smaller so the contribution from the perturbation terms is larger assuming the integrals do not vary appreciably with $\vec{k}$ value. In the limiting case of a single d, as the amplitudes β and γ in-

crease the plane wave part of the wave function acquires a modulation with a wavelength d. The $\vec{k}$ values spoken of here are values acceptable in both the perfect A and perfect B crystals and correspond to energies large enough to avoid conflict with comparison with $[V_A - V_B]$, see Fig. 1.

In this model the possibility exists for having electronic particles localized by the composition fluctuations when the material of smaller band gap acts as nuclei for the globules and the material of larger band gap forms the matrix. We choose as an example a modification of Eq. (2) with a three-dimensional radial grading and a single d. To obtain an analytical solution we make the following mathematical simplification and inquire about its physical justification. We expand $\cos 2\pi r/d$ to get $[1 - 2\pi^2 r^2/d^2]$ which is a good approximation for $r < 20$ Å since $d \sim 100$ Å.
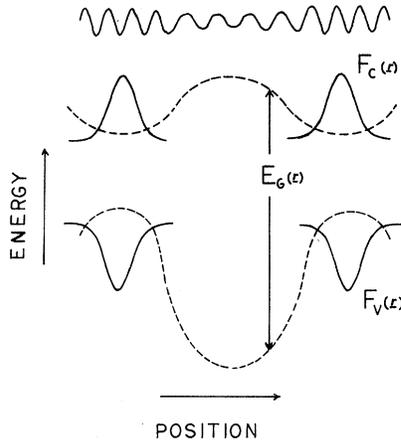
FIG. 1. Schematic representation of modulated plane-wave part of wave functions for extended states (top curve, well within conduction band), effective-mass functions for localized states near conduction band edge $F_c(\vec{r})$, effective-mass functions for localized states near valence band edge $F_v(\vec{r})$, and position-dependent band edges (shown dotted) with position-dependent energy gap designated $E_G(\vec{r})$.

Similar to the analysis of Ref. 8 we go to a Wannier representation and we then take the case for which the effective mass is not position dependent. This leads to an effective-mass equation

$$\left[-\frac{\hbar^2}{2m_n^*}\nabla^2 + \lambda_n\frac{\pi^2 r^2}{d^2}\right]F_n(\vec{r}) = E_n F_n(\vec{r}),\qquad(8)$$

where

$$\lambda_n = \int u_{n,\vec{k}}^*(\vec{r})[V_B(\vec{r})-V_A(\vec{r})]u_{n,k}(\vec{r})d^3r.\qquad(9)$$

We emphasize that λ_n is dependent on band identity so that the effective potential of the oscillator is band dependent. Also, of course, m_n^* is band dependent. The effective-mass function $F_n(\vec{r})$ enters the wave function through the equation

$$\Psi(\vec{r}) = \sum_{n,\vec{l}} F_n(\vec{l})a_n(\vec{r}-\vec{l}),\qquad(10)$$

where the $a_n(\vec{r}-\vec{l})$ are Wannier functions of band n at site l. In the approximation that only one band contributes to Ψ and that the $\vec{k}$ dependence of $u_{n,\vec{k}}(\vec{r})$ can be neglected the above wave function can be written

$$\Psi(\vec{r}) = u_{n,0}(\vec{r})F_n(\vec{r}).\qquad(11)$$

In Eq. (8) a separation of variables can be accomplished which leads to three simple harmonic oscillator equations in the variables x, y, and z with the same force constant. This yields for $F_n(\vec{r})$

$$F_n(\vec{r}) = Ce^{-\delta^2 r^2}H_i(\gamma y)H_j(\gamma y)H_m(\gamma z),\qquad(12)$$

where

$$\delta^2 = (\pi/\hbar d)[\lambda_n m_n^*/2]^{1/2},\qquad(13)$$

$$\gamma = [\pi/\hbar d]^{1/2}[2\lambda_n m_n^*]^{1/4},\qquad(14)$$

C is a normalization constant, and H_i are the Hermite polynominals. Incidentally we have verified, for a reasonable choice of matrix elements [Eq. (9)], stability of localized electrons or positive holes against both thermal activation to extended states and tunneling between globules. A discussion of this verification will be given elsewhere.

From Eq. (12), a definition of a band edge can now be made as follows: It is the locus of points where damped solutions have decreased to a prescribed value; specifically, the edge can be identified as the locus of the classical turning points of the effective-mass functions. This definition is similar to the one adopted in discussing the monotonically graded semiconductor,[9] see Fig. 1.

We emphasize that the theory of amorphous semiconductors just described is in a preliminary form and that its limitations and consequences have not yet been fully revealed. No ad hoc assumptions are made to introduce states in the band gap. Modulated Bloch states well within allowed bands and localized states near band edges arise quite naturally. The undulatory band edges are identified as the loci of the classical turning points of the effective-mass functions of the localized states. The effective potential for the effective-mass equation is clearly different for the different bands. It is not yet certain as to the absolute lowest scale of inhomogeneity for which the model and analyses remain valid: The virtual crystal approximation, effective-mass theory, and the graded band edge are all expected to become quantitatively in question for a scale somewhere below 10^2 lattice distances or about 10^2 Å, however, the qualitative results of the model and the analyses may remain valid to a somewhat lower scale. The model and the analyses herein appear to account for many of the gross electrical and optical properties of some amorphous semiconductors. We defer until a later publication a full discussion of what properties are accounted for but indicate here that these include the following: (1) The possibility of sensitivity of electrical properties of amorphous semiconductors to doping is built into the undula-

tory graded model, in contrast to the traditional model[2]; local symmetry (within the virtual crystal approximation) is high so that doping is not locally compensated for by changes in coordination number. (2) A close relationship between the band gaps of crystalline and amorphous semiconductors of the same composition and coordination number is evident from our model. (3) Nonlinear current-voltage characteristics are predicted; for example, for those systems with the troughs for the band edge of majority carriers in the nuclei of the globular structure the current will be limited by tunneling or by thermal activation at low fields; at high fields, i.e., 10^5 V/cm, the crests of the band edge (the locus of the turning points of the effective-mass functions of the total effective Hamiltonian including the applied fields) will be wiped out. In fact, the nonlinear current observed before switching of amorphous chalcogenides[10] can be interpreted as field-assisted thermally activated carrier transport with a characteristic jump distance of approximately 100 Å.

We also emphasize that it is not yet clear to which real amorphous materials the model is applicable. As noted earlier, we assumed in the analyses that $V_A(\vec{r})$ and $V_B(\vec{r})$ have the same lattice constants. For real materials the lattice constants will be different, however, the effects on electronic structure of compositional or structural inhomogeneities on a scale within the range of validity of the graded band gap concept is believed to be the same for these as for the case analyzed. The same simplification was earlier used with monotonically graded materials.[8] With undulatorily position-dependent lattice constants diffraction patterns qualitatively similar to those observed for amorphous materials are expected. Our model does not rule out other types of disorder contributing to the electronic structure of amorphous materials; the model analyzed clearly isolates the effects of globular structure from the effects of more local disorder, for example, broken bonds. Also effects of inhomogeneous space charge distributions arising either from abrupt heterojunctions between phases or from inhomogeneous doping with charged dopants are obviously not included. In general, we believe

that any interpretation of electronic properties of materials with compositional or structural inhomogeneities on a scale within the range of validity of the graded band-gap concept must include the effects herein described and that some of the phenomena previously attributed to other types of disorder in such materials arise in whole or in part from these inhomogeneities. In addition to the materials cited in the preceding references we note that there is experimental evidence for ordinary glass having compositional inhomogeneities on a scale of 100 to 200 Å.[11] Inhomogeneities on a somewhat smaller scale have been proposed for specific amorphous materials, for example, "amorphons" in germanium and "vitrons" in vitreous silica.[12] The application of the theory to specific properties of particular materials will be described elsewhere.

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