

Conduction and Electrical Switching in Amorphous Chalcogenide Semiconductor Films*

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Studies performed on the conduction and switching phenomena in films of certain amorphous chalcogenide semiconductors indicate that the electrical switching may be associated with a field-influenced dielectric phase transition. The normalized conduction found at voltages below switching displays an Ohmic and an exponential region, both associated with the same conduction process. This conduction is independent of frequency from dc to 100 kHz.

THE physics of amorphous semiconductors is incompletely understood. For this reason, it is an area of active theoretical and experimental study.¹ A very important phenomenon in many disordered semiconductors is the rapid electrical switching such as described by Ovshinsky.² This paper presents experimental evidence on the low-current conduction and on the switching phenomena in thin films of certain amorphous chalcogenide semiconducting materials. The main results found are: (1) The low-current conduction data can be normalized over a wide range of temperature and voltage. The resulting currents have an "Ohmic" region linear with voltage and exponentially varying nonlinear region both of which arise from the same conduction process. (2) A field-influenced phase transition, perhaps dielectric, is implicated in the switching process. The phase-transition temperature is equal to the glass-transition temperature within experimental error.

A variety of experiments were performed mainly on commercial thin-film devices and to a lesser extent on thin films prepared in our laboratory. The commercial films³ are prepared by a flash evaporation from pre-melted solid ingots of approximate composition by weight: 49% Te, 33% As, 6% Ge, 3% Si, and 9% Ga.

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¹ Reviews relating to the subject are contained in N. F. Mott, *Advan. Phys.* **16**, 49 (1967); J. Tauc, *Science* **158**, 1543 (1967); A. R. Hilton *et al.*, *Phys. Chem. Glasses* **7**, 105 (1966); **7**, 112 (1966); **7**, 116 (1966); J. P. Mackenzie, in *Modern Aspects of the Vitreous State*, edited by J. P. Mackenzie (Butterworths Scientific Publications Ltd., London, 1964), Chap. 5; A. D. Pearson, in *Modern Aspects of the Vitreous State*, edited by J. P. Mackenzie (Butterworths Scientific Publications Ltd., London, 1964), Chap. 2; B. T. Kolomiets, *Phys. Status Solidi* **7**, 359 (1964); **7**, 713 (1964).

² S. R. Ovshinsky, U. S. Patent No. 3,721,591, 6 Sept. 1966; S. R. Ovshinsky, in *Fourth Symposium on Vitreous Chalcogenide Semiconductors*, Leningrad, 1967 (unpublished).

³ Supplied by ECD, Inc., registered trademark Ovonic Threshold Switches. The normal film thickness of 0-30, 0-20, and 0-10 devices are 1.2, 0.9, and 0.6 μ , respectively.

The phenomena reported are apparently not critically dependent on composition. The films are deposited on two graphite hemispheres of approximate radius of curvature 7 mm, spring loaded against each other under about 70-g force to form a conducting region of total thickness 0.6 to 1.2 μ , and circular conducting area of very approximately 3×10^{-5} cm². Our laboratory films were obtained by evaporating an amorphous ingot of 25% GaAs, 8% Ge, and 67% Te onto molybdenum substrates from 15 to 20 μ thick with a point contact as the opposite electrode. The phenomena in both films are apparently similar. The current-voltage characteristics of both types of films are completely symmetric, even for samples with asymmetric electrodes of various materials, thus indicating a bulk phenomenon controlled by the film material. Discrete changes in operation do occur at times, and are often apparent near the threshold of switching and hysteresis. The detailed information presented here was obtained from the commercial films.

The electrical switching⁴ occurs from a high-voltage, low-current state of several megohm resistance to a low-voltage, high-current conducting state of several ohms resistance. Once exceeding the threshold voltage V_{th} , the voltage drops rapidly, presumably through a current-controlled negative-resistance region. The transition for this switching effect is subnanosecond.

The current in the high-resistance state varies over at least 9 orders of magnitude depending on voltage and temperature and is illustrated in the inset of Fig. 1. All of the current-voltage data in a given film can be normalized to a single curve such that $I/I_0 = F[V/V_0]$ as shown in Fig. 1. The normalizing current I_0 and voltage V_0 are defined in the inset of Fig. 1. If I/I_0 is plotted against V/V_0 , a single curve results for similar

⁴ Somewhat similar behavior has been found by other investigators. See, for example, J. F. Dewald, A. D. Pearson, W. R. Northover, and W. F. Peck, *J. Electrochem. Soc.* **109**, 243C (1962); Y. Mizushima *et al.*, *Proc. IEEE* **53**, 322 (1965); C. Feldman and W. Guitierrez, *J. Appl. Phys.* **39**, 2474 (1968).

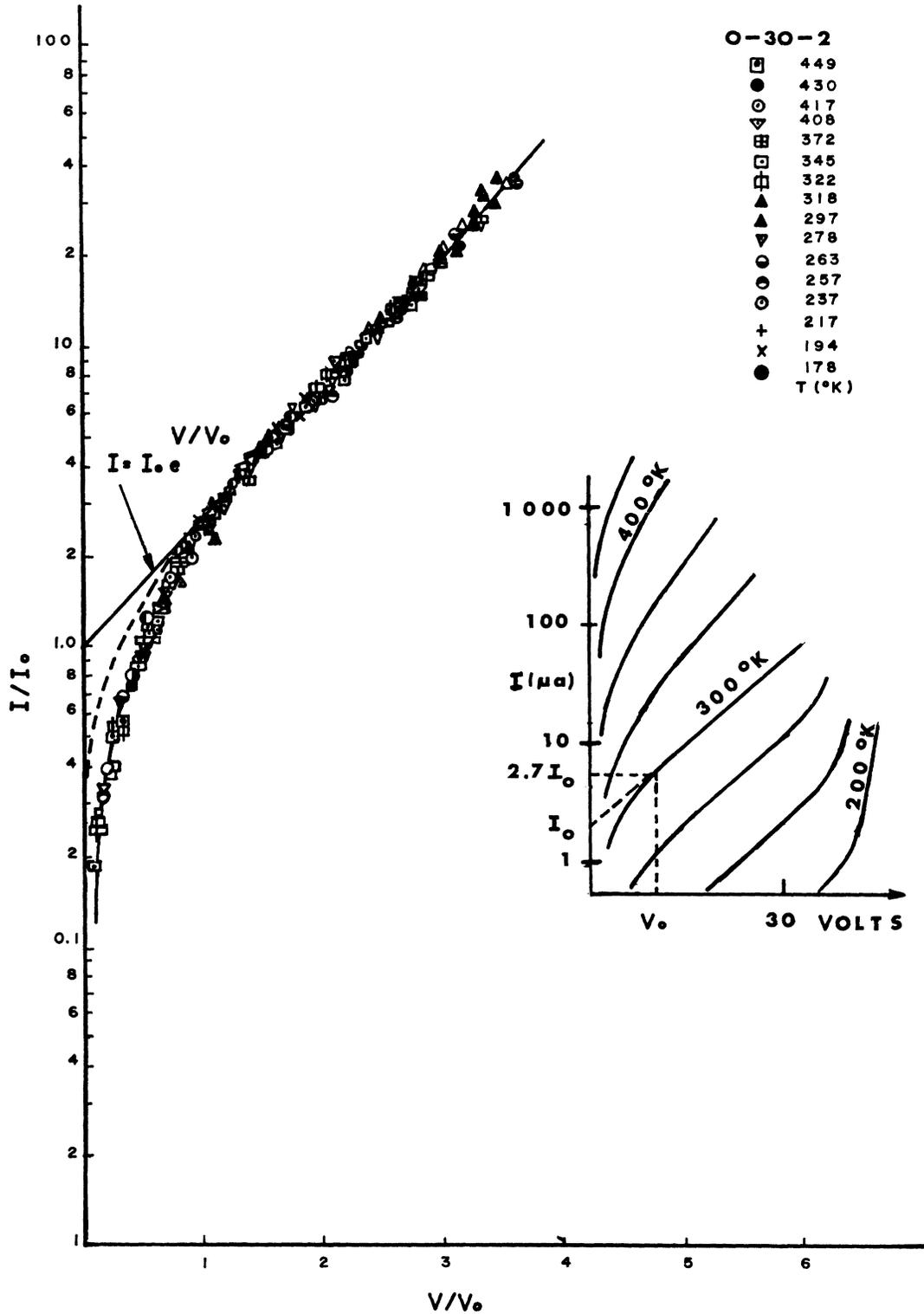


FIG. 1. Normalized data for a 1.2- μ film. An approximate fit to the curve is $I/I_0 = \exp(V/V_0) - \exp(-0.7V/V_0)$. Our data are obtained at 60 cycles from a curve tracer. The dashed curve is a normalized curve (Ref. 5) at essentially dc in a 0.9- μ film. It continues into our normalized curve at higher V/V_0 .

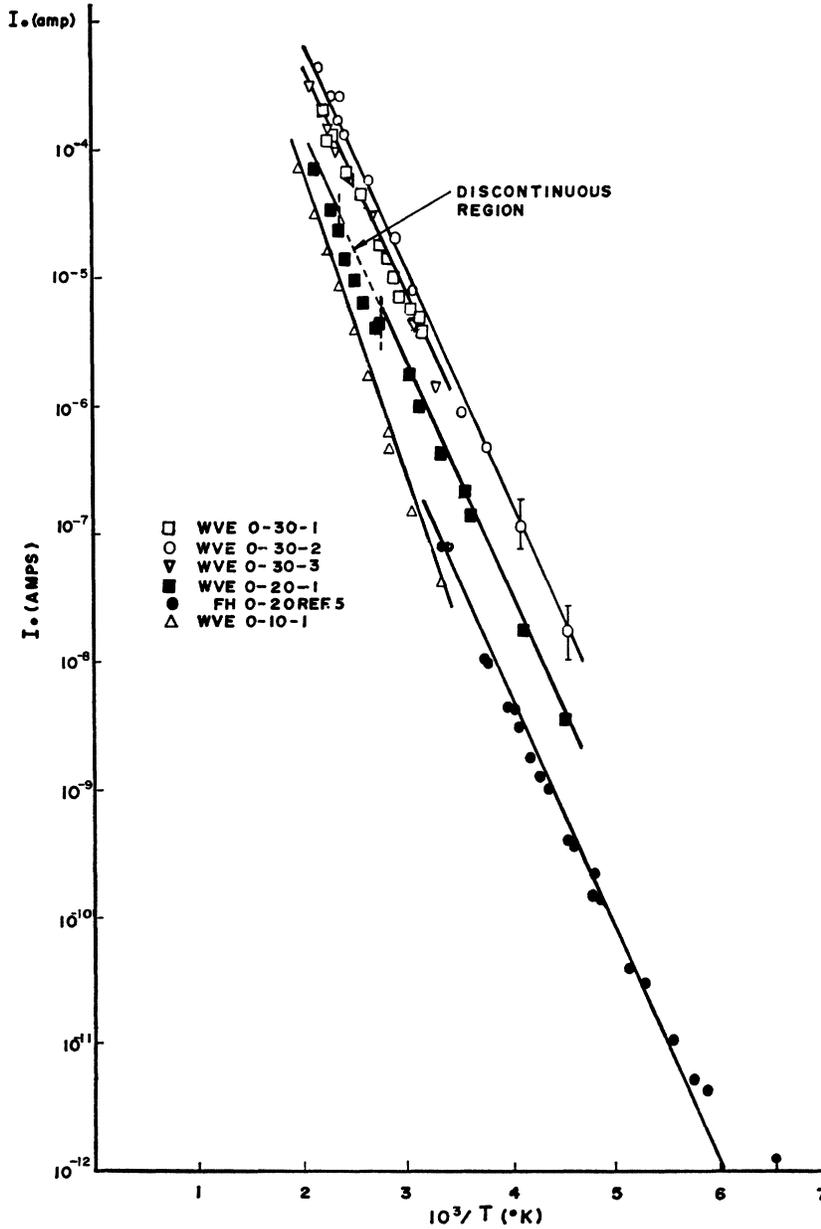


FIG. 2. Temperature dependence of I_0 . The straight lines correspond to $I_0 = I_0' \exp(-\Delta T/T)$. The $0.6\text{-}\mu$ (0-10-1) film has a ΔT near 6000°K . All the other films have a ΔT near 4500°K . The discontinuous region in the 0-20-1 film is real and was accompanied by a drop of $\frac{1}{2}$ in the threshold voltage. 0-30-1 and 0-30-2 have essentially the same value of I_0 , and only a single line is drawn through their data.

films for temperatures⁵ from 77°K up to about 500°K and for voltages up to 35 V in the $1.2\text{-}\mu$ films or up to 21 V in the $0.9\text{-}\mu$ films.⁶ An "Ohmic" and an exponential region occur. The universality of the curve for different temperatures indicates that the Ohmic region and the exponential region are low- and high-field regions of the same process, and do not constitute two separate processes. This has been further checked by plotting

⁵ E. Fagen of ECD has kindly supplied us with current-voltage data on a $0.9\text{-}\mu$ film similar to ours in the temperature region 77 to 295°K , supplementing our higher-temperature data from 180 to 500°K . He has also supplied information on the bulk properties of these materials.

⁶ Above these voltages, which can only be reached at temperatures below about 300°K , another exponential region exists with higher slope.

the reciprocal Ohmic resistance at different temperatures versus I_0/V_0 on log-log paper (not shown). A curve of slope 1 fits the data over two decades yielding, $R_0^{-1} = KI_0/V_0$, where $K \approx 1.7$ in the $1.2\text{-}\mu$ films. The linear fit and the closeness of K to unity indicate one single process in both regions. K is apparently geometry-dependent. These results are summarized in the empirical relation⁷

$$I/I_0(T) = F[V/V_0(T)]; \quad F(x) = e^x, \quad x \gg 1; \\ F(x) = Kx, \quad x \ll 1.$$

⁷ The simplified model of Austen gives a reasonable fit to the data. See S. Whitehead, *Dielectric Breakdown of Solids* (Oxford University Press, New York, 1951), p. 20ff.

The temperature dependence of I_0 is shown in Fig. 2 and implies a carrier-activation energy. In the temperature range $180 < T < 500^\circ\text{K}$, we see that $I_0 = I_0' e^{-\Delta T/T}$, where I_0' is geometry-dependent and perhaps slightly temperature-dependent, and ΔT is the carrier-activation temperature. Under high fields the current increases exponentially with voltage. Empirically the current can then be written $I = I_0' e^{-\Delta T/T} e^{V/V_0}$. This exponential dependence suggests that the conduction-activation energy is lowered by an amount δT by the field present in the high-resistance state. The high-field current can then be written $I = I_0' \exp[-(\Delta T - \delta T)/T] = I_0 \exp(\delta T/T)$, and hence $\delta T = (T/V_0)V$. V_0/T thus represents the external voltage required to produce a one-degree change in activation energy. The temperature dependence of V_0/T is illustrated in Fig. 3(a). Note the linear decrease in V_0/T extrapolating to zero at a transition temperature at which only a small voltage is required to produce a significant change in activation energy.

All films but one had a zero-field activation temperature near 4500°K .⁸ If the activation energy is assumed to correspond to half an energy gap, the gap has a value of approximately 0.8 eV. The Ohmic resistance at low fields shows no substantial dependence on frequency from dc up to 100 kHz. Similarly, the ac resistance tested from 60 Hz to 100 kHz, at different voltages up to threshold, is essentially independent of frequency at room temperature.

The threshold voltage for switching is illustrated in Fig. 3(b) as a function of temperature. Note that the threshold voltage extrapolates to zero at temperatures in the vicinity of 500°K in the films tested. These temperatures agree well with the data in Fig. 3(a), where very similar temperature values are obtained although extracted from a very independent type of information. This suggests that, in a given film, there is one transition temperature and that this temperature plays a central role in both the conduction and switching phenomena. Below this transition temperature the material is a high-resistance state and above this temperature the material is in a conducting state. The curves of threshold voltage versus temperature can then be interpreted as arising from a reduction of transition temperature with electric field. The threshold voltages are approximately linear with film thickness⁵ indicating that electric field and not voltage drop initiates the switching. The inferred change of transition temperature with field is approximately $1.4^\circ\text{K}/(\text{V}/\text{cm})$ at 70-g loading.⁹ The phase transition may involve a transition

from one material phase to another or from one distributed free charge distribution to another.¹⁰ The transition temperature found in these materials does coincide within experimental error with the glass-transition temperature¹¹ (500°K) found in the bulk material from which the films were made.⁵

We have noted that the fractional decrease in activation energy at threshold $\delta T_{\text{th}}/\Delta T = TV_{\text{th}}/V_0\Delta T$ is substantially independent of temperature. This ratio ranges near 0.26 in the several 1.2- μ films tested, averages near 0.23 in 0.9- μ films, and is near 0.21 in the single 0.6- μ films.¹²

Our results described above may have several interpretations. One appealing simple interpretation is that the transition involved is a dielectric phase transition. If the change in activation energy due to a field is linearly related to the dielectric constant of the material,¹³ then the V_0/T curves would vary as the inverse dielectric constant. A linear decrease in inverse dielectric constant is characteristic of a dielectric material approaching a dielectric phase transition according to a Curie-Weiss law. Hence, the linear decrease in V_0/T that we observe as T increases could be explained by the approach to a dielectric phase transition at a field-dependent transition temperature.¹⁴ The dependence of V_0/T on inverse dielectric constant is further indicated by the approximate constancy¹³ of C_0V_0/T of film 0-30-4 in Fig. 3. Although phase transitions of the type imagined here are not usually associated with the glass transition, the glass transition may act to initiate a dielectric transition in the materials we have studied.

The authors would like to acknowledge the assistance

¹⁰ N. F. Mott, Proc. Phys. Soc. (London) A62, 416 (1949); B. K. Ridley, *ibid.* 82, 954 (1963).

¹¹ The glass-transition temperature here means the temperature at which the thermal expansion of the material shows a marked increase in slope when plotted against temperature.

¹² If the transition temperatures in the linear variation of V_0/T and V_{th} are the same, then $\delta T_{\text{th}}/\Delta T$ is a constant independent of temperature. This seems true in our data, although a variation of 30% in $\delta T_{\text{th}}/\Delta T$ cannot be ruled out. In these glassy materials the transition temperature may actually cover a range of temperatures.

¹³ As an example, for states of suitable symmetry, the stork shift in the energy levels is given approximately by El , where l is an average extent of the wave function in the direction of the field. If the orbit covers several atomic distances, a Bohr model gives $l = (\epsilon/\epsilon_0)l_0$, where l_0 is the size at unit value of the (high-frequency) dielectric ratio ϵ/ϵ_0 . Then $\delta V = El = \epsilon V l/\epsilon_0 L$, where L is the thickness of the film over which the voltage drop occurs. If δT is taken as $\frac{1}{2}(\delta V/k)$, then $V_0/T = V/\delta T = (2kL\epsilon_0/K\epsilon l) = (2k\epsilon_0 A/KlC_0)$. A is an effective area and C_0 the low-voltage capacitance. Thus V_0/T is inversely related to the relative dielectric constant and to the capacitance. C_0V_0/T is a constant for the one film tested. Note, however, that we find that V_0/T is only approximately linear with actual film thickness.

¹⁴ If the conducting state were similar in properties to a ferroelectric state, a decrease in transition temperature with field would be expected with rate of decrease with electric field and with pressure comparable to that found in the materials tested with switching times of similar magnitude.

⁸ We have noted large discrete increases in ΔT , apparently related to large discrete drops in threshold voltage in some devices during operation.

⁹ We have found that high uniaxial loading will produce the conducting state at room temperature with a voltage threshold of essentially zero volts. We obtained separate hydrostatic pressure data which can be extrapolated to give a rate of change of transition temperature with hydrostatic pressure of $1^\circ\text{K}/(1000 \text{ psi})$.

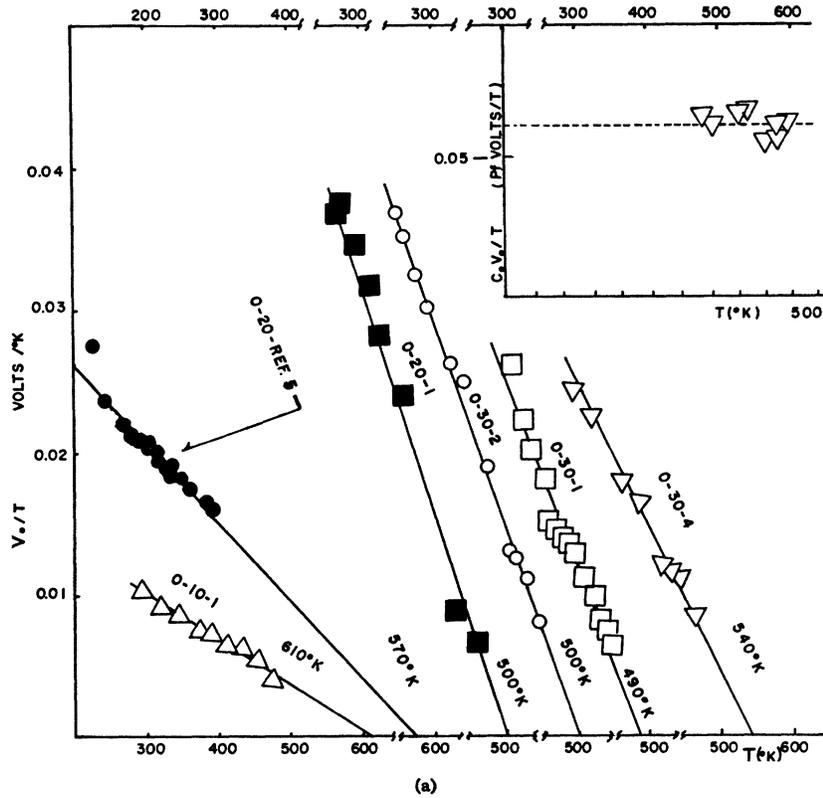
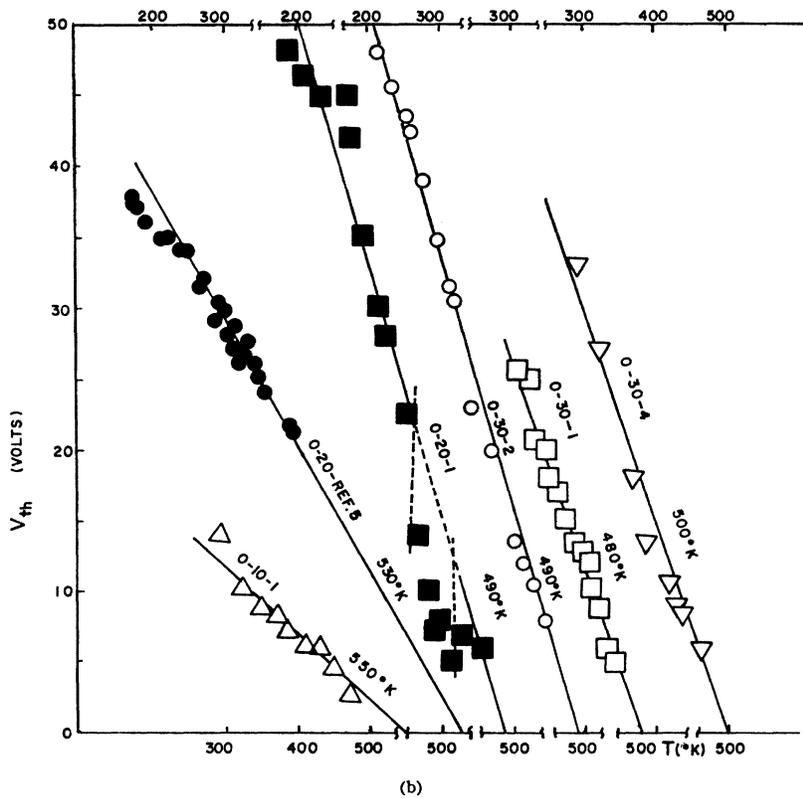


FIG. 3. (a) Temperature dependence of V_0/T . Estimated transition temperatures are indicated along each curve. The values of V_0/T in the discontinuous region of 0-20-1 are difficult to analyze and are not shown. The inset illustrates the approximate constancy of $C_0 V_0/T$ the 0-30-3 film. (See Ref. 13.) (b) Threshold voltage versus temperature. The estimated transition temperatures here are to be compared with Fig. 3(a). The discontinuous region of 0-20-1 is given.



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Electronic Structure and Optical Properties of SnS_2 and SnSe_2 †

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The electronic band structures of SnS_2 and SnSe_2 are calculated by using the empirical pseudopotential method. The potentials were obtained by scaling those used in other energy-band calculations. The symmetry properties of the crystals are treated in detail, and the optical constants are calculated. Comparison with experiment is also made.

I. INTRODUCTION

THE concept of associating a pseudopotential with each ion core independent of its chemical state has been successfully exploited recently to yield electronic states of semiconductors both in elemental¹ and in compound forms.^{2,3} In the first case, the elemental pseudopotential is extracted from semiconductors containing that element, e.g., Se from ZnSe .¹ In the second case, the pseudopotential form factors in a compound are derived from the known pseudopotentials of the constituent elements, e.g., Mg and Si, to give Mg_2Si .² In these calculations, the empirical pseudopotential method⁴ (EPM) is used. The combination of assigning a fixed pseudopotential to each ion and the use of the EPM, then, essentially involves the variation of pseudopotential form factors to fit optical data and the existing information on the pseudopotentials.

The success we have had in the Mg_2X calculations³ and the availability of good optical data have stimulated us to attempt calculations of the electronic structure of SnS_2 and SnSe_2 . The similarity of these two classes of compounds, Mg_2X and SnX_2 , lies in the shape of the unit molecule: A dumbbell formed from the two identical atoms weighted at the center by the third, different

atom. This structure preserves the inversion symmetry of the lattice. This yields a Hamiltonian with real matrix elements which is easier to diagonalize than one with complex matrix elements. In addition to calculating the electronic structure of SnS_2 and SnSe_2 , we have also determined the optical constants for these materials.

The properties of SnS_2 and SnSe_2 have only been sporadically investigated experimentally and, to our knowledge, no band-structure calculations exist. The direct and indirect energy gaps of SnS_2 have been measured optically,^{5,6} and those of SnSe_2 have been measured both optically⁵ and electrically.^{7,8} The combined data seem to have fixed the energy gaps to within a small range of values. Reflectivity data in the range of 1 to 12 eV have also been obtained for SnS_2 , for light with polarization perpendicular to the *c* axis of the crystal.⁶

The pseudopotentials of the constituent ions in the calculation, i.e., those of Sn, Se, and S, are not available to a high degree of accuracy as are those of the group-IV elements, Si and Ge. The pseudopotential for Sn, for example, differs greatly between grey tin⁴ and white tin,⁹ especially for large $|G|$ values. We have based our calculations on the Sn, Se pseudopotentials of Animalu and Heine,⁹ and the S pseudopotential as extracted from ZnS .⁴

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