

critical value which depends on Δ , m , and $q \equiv (2J+1)/(2J'+1)$, no first-order transition takes place, but the temperature dependence of the conductivity shows the gradual transition illustrated in curve (b) of Fig. 1 [$m=1, q=2$]; this behavior strikingly resembles the conductivity curves^{1,2} for SmB_6 and Ti_2O_3 . For $G \geq G_c$, a first-order phase transition takes place at $T = T_c$ to a value of n which remains essentially constant at all temperatures higher than T_c [see curve (c)]. For $G_c < G \leq \Delta$ there is a first-order transition from a state of small n to a state of $n \sim 1$ at a temperature T_c , while n decreases for $T > T_c$ [curve (d)]; such behavior is found in V_2O_3 . For $G > \Delta$, the state $n=1$ becomes stable at $T=0$ and the system is metallic at all temperatures.

For $k_B T_c \ll \Delta$, our simple model yields for the transition temperature

$$k_B T_c = (\Delta - G) [2m \ln(2m) - (2m-1) \ln(2m-1) + \ln q]^{-1}. \quad (14)$$

In this case n varies exponentially with T^{-1} for $T < T_c$ and extrapolates to $[2mq]^{1/2}$ for $T^{-1} = 0$. At T_c , n jumps to a value very close to 1 and decreases smoothly to another limiting value which is an algebraic function only of m and q as $T^{-1} \rightarrow 0$. This behavior is quite similar to those of V_2O_3 and VO . If we take $m=1$ and $q=2$ we obtain

$$\Delta = 0.365 \text{ eV}, \quad G = 0.336 \text{ eV for } \text{V}_2\text{O}_3;$$

$$\Delta = 0.248 \text{ eV}, \quad G = 0.226 \text{ eV for } \text{VO}.$$

Other substances, such as Fe_3O_4 and VO_2 which also exhibit first-order transitions, yield poorer agreement with this simple two-level model; improved agreement is found when a finite width of

the conduction band is considered.

For gradual transition cases, similar agreement is found. In our simple model, with $m=1$, $J=7/2$, and $J'=0$, we obtain for SmB_6

$$\Delta = 0.0044 \text{ eV}; \quad G \cong 0.0018 \text{ eV},$$

while a critical value $G_c = 0.0022 \text{ eV}$ would be required for a first-order transition. Conductivity data on Ti_2O_3 show too large an anomalous increase, which our simple model cannot produce without a first-order transition.

In conclusion we would like to point out that our model for a semiconductor-metal transition is basically different from a Mott transition³ or an excitonic-insulator transition.⁶ It is based on a change in the occupation numbers of electronic states which remain themselves basically unchanged in their character.

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¹A. Menth, E. Buehler, and T. H. Geballe, *Phys. Rev. Letters* **22**, 295 (1969).

²For a review of the properties of transition-metal oxides and the literature on the subject see D. Adler, *Rev. Mod. Phys.* **40**, 714 (1968).

³See the Proceedings of the International Conference on the Metal-Nonmetal Transition, *Rev. Mod. Phys.* **40**, 673ff (1968).

⁴The narrow-band assumption is not necessary and, in fact, is inconsistent with a band of good conduction electrons; calculations with wide bands have been performed and the changes are only quantitative.

⁵This implies a temperature independent mobility, which corresponds to impurity- and imperfection-dominated scattering.

⁶D. Jérôme, T. M. Rice, and W. Kohn, *Phys. Rev.* **158**, 462 (1967); B. I. Halperin and T. M. Rice, *Rev. Mod. Phys.* **40**, 755 (1968).

DENSITY OF "AMORPHOUS" Ge

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The density of vapor-deposited "amorphous" Ge was determined from x-ray-diffraction absorption measurements and found to be the same as the density of crystalline Ge within $\pm 5\%$.

Recently Herman and Van Dyke¹ estimated the electronic density of states of amorphous Ge by assuming a dilated Ge crystal having the same density as "amorphous" Ge. The density value used was that (3.9 g/cm^3) determined by Clark²

using film scraps shattered from the substrates. These scraps were weighed in air and in Dow-Corning No. 704 silicone oil. It is possible that the shattered scraps had many microcracks that would not have been penetrated by the oil thus

causing the density to be underestimated. A less readily available density value is that of Lytle³ who used an x-ray-absorption fine-structure technique to determine the densities of "amorphous" and crystalline Ge and obtained values that were within 2% of each other and of the accepted value for the density of crystalline Ge. The purpose of this Letter is to present experimental information which indicates that the density of "amorphous" Ge is the same as that of crystalline Ge within $\pm 5\%$, confirming Lytle's result.

The density values were calculated from measured values of the x-ray linear absorption coefficient obtained during a study of the structure of vapor-quenched Ag-Ge alloy films.^{4,5} The details of the film preparation and measurements are given in Refs. 4 and 5; so only a summary is presented here. The scattered intensity of the substrate material was measured, using Bragg-Brentano diffraction geometry, as a function of scattering angle ($2\theta = 5^\circ - 120^\circ$, Mo K_α radiation). The film was deposited, and the scattered intensity of the film plus substrate was measured as a function of scattering angle. The scattered intensity of the film alone was derived by an iterative procedure in which the substrate scattered intensity was corrected for film absorption by the factor $\exp(-2\mu t/\sin\theta)$, where t is the film thickness and μ is the linear-absorption coefficient, for a series of values of μt . The corrected substrate scattered intensities were subtracted from the film-plus-substrate scattered intensities. The "correct" value of μt was determined by the criteria that no negative values, and only slightly positive values, of film scattered intensities were allowed at high values of 2θ (where the effective film thickness is minimum), and low values of 2θ (where the amorphous-substrate scattering persists below the angular range where the film scattering is rapidly falling off to small values). The thickness of the film was measured using multiple-beam interferometry techniques. A value for μ_{meas} was thus obtained. This value was divided by the appropriate mass absorption coefficient μ/ρ , where ρ is the density, to obtain an experimental value for the density (ρ_{meas}). Subsequent analysis of the film scattered-intensity data confirmed the accuracy of the method.⁵

This procedure was carried out for Ge and five alloy compositions of Ag-Ge vapor quenched at rates from 160 to 430 Å/min onto 5-mil-thick vitreous silica plates held at liquid-nitrogen tem-

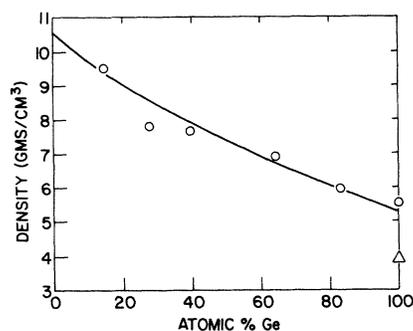


FIG. 1. Density as a function of composition for Ag-Ge alloys. Smooth curve through data points is drawn between accepted values for density of crystalline Ge and Ag. Triangle denotes value for density of "amorphous" Ge determined by Clark, Ref. 2.

perature. The resulting values for the density are plotted in Fig. 1 as a function of composition. The smooth curve through the data points terminates at the crystalline density values for Ag and Ge (10.49 and 5.35 g/cm³, respectively). The density value determined by Clark² falls considerably below the present data. A density value for "amorphous" Ge within $\pm 5\%$ of the crystalline density value is indicated by the data.

The diffracted-intensity data for the Ge film were used to calculate the radial distribution function, assuming the atomic density of crystalline Ge, and the resulting nearest neighbor distance and coordination number agree completely with the respective values for crystalline Ge (2.45 Å, four nearest neighbors).

Taken together, these results indicate that the structure of "amorphous" Ge deviates very little from the structure of crystalline Ge, which supports the micropoly-crystalline hypothesis.⁴ The dilated-lattice model of Herman and Van Dyke¹ and the "amorphon" model of Grigorovici⁶ are not consistent with the values determined for the density, nearest-neighbor distance, and coordination number.

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