where t_c^{-1} is the diffusion rate of μ,

$$t_c^{-1} = \langle[\mu(t+\tau) - \mu(t)]^2\rangle/\mu^2\tau.$$

Using the experimental result $(t''-t')_{cr} \sim 60$ μsec, we obtain $t_c \sim 3$ msec. This result is consistent with diffusion under Coulomb collisions for a temperature of 300 eV and a density of $\sim 10^{11}$ cm^{-3}. This confirms previous analysis showing that the turbulence at $n\omega_{ci}$ $(n = 1, 2, 3)$ usually observed in DECA II B plays a negligible role in the diffusion of particles in velocity space.[3]

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Phase Separation in the Semiconducting Binary Liquid Selenium-Thallium*

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We report the first detailed study of phase separation in a semiconducting binary liquid (Se-Tl). We have studied both the electrical conductivity σ and the location of the miscibility gap in the concentration-temperature (x-T) plane. Even though the conductivity varies by 3 to 4 orders of magnitude in the transition region, it is found that (i) the law of rectilinear diameters holds with high precision, (ii) the critical exponent β_x for the x-T phase boundary agrees to within experimental accuracy with β_σ for the σ-T phase boundary, and (iii) $\beta = 0.348 \pm 0.015$.

Binary liquid mixtures very often exhibit miscibility gaps in the temperature-concentration (T-x) plane. The behavior near the critical point of the miscibility phase transition has been studied carefully in a number of systems. These systems include many insulating binaries[1] and a few metallic binaries,[2-4] but not—to our knowledge—semiconducting binaries or binaries involving a metal and a semiconductor. In particular, the shape of the coexistence curve—which may be characterized near the critical point by the equation $x_A - x_B \sim \epsilon^\beta$, where $\epsilon = (T_c - T)/T_c$—has been determined precisely for a number of insulating binaries, and β is found to lie in the range $0.30 \leq \beta \leq 0.38$.[1] In addition, a few metallic binaries have been studied, notably gallium-mercury.[2,3] Using a phenomenological relation connecting resistivity and concentration, Schürmann and Parks[2] employed resistive techniques and found β(Ga-Hg) to be 0.335 ± 0.005. This is to be contrasted with the results of d'Abramo, Ricci, and Menzinger,[3] who found β(Ga-Hg) to be 0.373 ± 0.005 by using a neutron radiography technique to measure concentration indirectly. It should be noted that in neither of these experiments was the concentration locus of the phase boundary measured directly. This work presents a direct measurement of β_x, the critical exponent for phase separation in the x-T plane, namely $\beta_x = 0.348 \pm 0.015$. To our knowledge this is the first direct measurement of β_x for a semiconducting or metallic binary. Following Schürman and Parks,[2] we have also measured β_σ, the critical exponent for the conductivity-temperature phase boundary. The value obtained, $\beta_\sigma = 0.358 \pm 0.020$, agrees within experimental uncertainties with the directly measured exponent.

In studying the semiconductor-metal binary liquid Se-Tl, we have employed accurate resistivity-measurement techniques to study the resistivity as a function of both concentration and temperature throughout the region of interest and to precisely characterize the shape of the phase boundary. This system has previously been studied by Kanda, Faxon, and Keller,[4] who outlined the phase diagram using density-temperature measurements.

Our experiments were performed using quartz cells with either six or nine tungsten electrodes (for the critical-region measurements, nine-electrode cells were employed exclusively). A current was passed between the top and bottom electrodes, and $n-3$ voltage drops were obtained between the $n-2$ intermediate electrodes. The cells were calibrated at room temperature using triply distilled mercury. Temperatures were measured using thermocouples to an *absolute* accuracy of 3 K (or 0.7% at 450°C). Temperature gradients along the cell were monitored with differential thermocouples and controlled to better than 0.05 K using an auxiliary heater coil. The *absolute* accuracy of the resistance measurements was at least 1.0% over the entire resistance range. Accurately weighed amounts of Se (99.99993% metallic purity) and Tl (99.9999% metallic purity) were added to each cell such that the composition was known to within 0.02 at.%, barring evaporative losses and/or adherence of material to the stirrer. The system was maintained in an ultrahigh-purity argon atmosphere (even during stirring, when this was accomplished by maintaining a rapid flow of argon). Each cell was initially heated to well above the transition temperature, and then stirred with a very efficient paddle until the resistivities measured between the $n-2$ intermediate electrodes agreed with one another to within less than 0.5%, and did not change upon further stirring.[5] The sample was then gradually cooled down to and well below the phase-separation temperature. In practice, phase separation occurred very rapidly. The cooling rate on most runs was 20 K/h. However, no change in the phase-separation temperature occurred when the cooling rate was lowered to 7 K/h. This is taken as evidence that the experiments were performed at equilibrium with no supercooling of the homogeneous phase. For the run at critical composition, x_c, the cooling rate was lowered to 5 K/h. In practice, the phase-separation temperature was located by a kink in the resistivity of a sample. The uncertainty in the location of the kink was less than 0.5 K.

Finally, although the absolute temperature accuracy was 3 K, the relative temperatures were accurate to better than 1 K. This improved accuracy was achieved by requiring the conductivity measured along the phase boundary in the various runs to agree with that measured in one run (at very nearly the critical composition) which covered the entire phase boundary. This agreement was obtained by adjusting only the zero of temperature. [In most cases a shift in temperature zero of less than 1.5 K sufficed.] With this adjustment, the limiting accuracy is now defined by the conductivity uncertainty of 1.0% which corresponds to a temperature uncertainty of 0.9 K.

In Fig. 1 we present the locus of the x-T phase boundary—including its diameter—as determined from resistance kink measurements. The previous results of Kanda, Faxon, and Keller[4] are also presented. Letting x_A and x_B respectively denote the selenium- and thallium-rich branches of the phase boundary, the diameter x_D is defined as $x_D = \frac{1}{2}(x_A + x_B)$. At the critical point T_c we have $x_A = x_B = x_D = x_c$. Note that a serious curvature in the diameter is present in the results of Ref. 4. In contrast, this curvature is completely absent from our results. Indeed, we find that the law

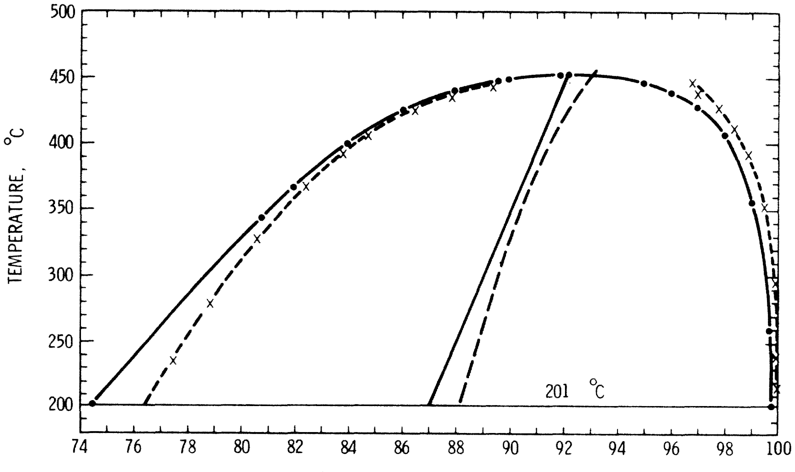

FIG. 1. Closed circles, Se-Tl phase boundary as determined from resistance kink measurements, together with the previous results of Ref. 4 (crosses). For concentrations below 80 at.% Se, the phase boundary has been continued by using the measurements at high selenium concentrations together with the extended diameter.

of rectilinear diameters apparently holds over the entire transition region.[6]

The shape of the coexistence curve near T_c is expected to be described by the critical exponent β, which is introduced through the equation[7]

$$x_B(T) - x_A(T) \approx X_0 \epsilon^\beta \quad (\epsilon \to 0), \tag{1}$$

where, as above, $\epsilon = (T_c - T)/T_c$. The exponent β may be obtained from the data of Fig. 1 as the slope of $\ln(x_B - x_A)$ as a function of $\ln(\epsilon)$. Of course, T_c is also an unknown. Thus, we performed a least-squares fit of the data to obtain T_c and β. From this analysis, we find that $\beta_x = 0.348 \pm 0.015$ and $T_c = 448.64 \pm 0.4°\mathrm{C}$ over the range $2\times 10^{-3} \leqslant \epsilon \leqslant 0.6\times 10^{-1}$. The resulting plot of $\ln(x_B - x_A)$ versus $\ln(\epsilon)$ is shown in Fig. 2. Using the above value for T_c, the law of rectilinear diameters[6] predicts a critical composition $x_c = 92.06 \pm 0.32$ at.% Se, in agreement with our measured value, $x_c = 92.05 \pm 0.10$ at.% Se.

As an additional check on these results, we have also determined a five-parameter least-squares fit to the data. This fit assumes Eq. (1) together with a rectilinear diameter

$$x_D = x_c + x_1 \epsilon. \tag{2}$$

Thus, β, T_c, x_c, X_0, and x_1 are parameters of the fit. As is seen from Fig. 1, the assumptions of this fit are well justified for our data. From this fit, we obtain $\beta_x = 0.335 \pm 0.006$, $T_c = 448.56 \pm 0.32$, and $x_c = 92.05 \pm 0.04$ at.% Se. Here, as above, the stated uncertainties are the confidence limits of the least-squares fit, and in the case of β are considerably smaller than actual experimental uncertainties. In fact, the values for T_c, x_c, and β obtained from the two methods are, to within experimental accuracy, in complete agreement. Because it involves fewer assumptions, we are somewhat more confident of the results of the first fit, and therefore take $\beta_x = 0.348 \pm 0.015$ as our estimate for β and its experimental uncertainty.

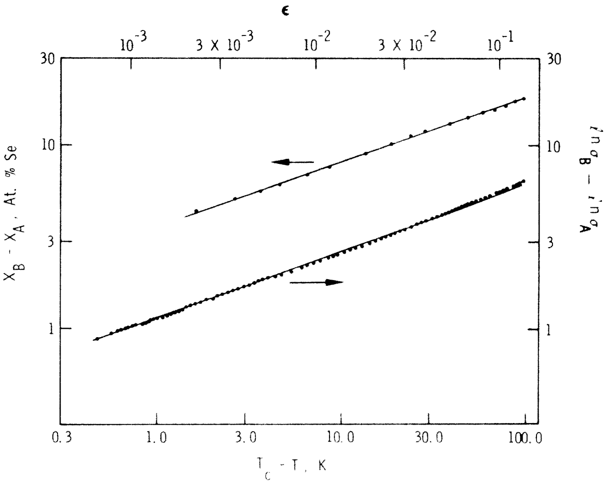

FIG. 2. Log-log plot of the composition difference and the ln(σ) difference along the phase boundary.

Following the analysis of Schürmann and Parks[2] we have also determined the critical exponent β indirectly from electrical-conductivity measurements along the phase boundary. Over the range of compositions spanned by the miscibility gap, the mixture is semiconducting with electrical conductivity well represented by the formula

$$\sigma = \sigma_0 e^{-\Delta/T}, \tag{3}$$

where the activation energy Δ/k and prefactor σ_0 are functions of composition only. [Actually Δ and σ_0 must depend on T as well as x. However, no such dependence was found over the range of temperature studied. This can be understood on the basis of effective-medium theory. One of us[8] has shown that effective-medium theory predicts—for the parameters of our system—no detectable temperature dependence over the range of temperature studied.] Because of the strong temperature dependence of the exponential in Eq. (3), we will be concerned with $\ln(\sigma)$ rather than σ in the following discussion.

We report elsewhere[9] that upon addition of Tl to Se, the activation energy Δ changes abruptly from 1.06 eV at $x_{\mathrm{Tl}} = 0$ to 0.53 eV at $x_{\mathrm{Tl}} = 0.002$, and shows only a very slight decrease from the latter value with increasing Tl concentration to $x_{\mathrm{Tl}} \simeq 0.38$, the largest Tl composition we studied. However, the prefactor σ_0 is a strong, but smooth, function of composition. If we assume that both Δ and σ_0 have Taylor-series expansions about the critical point (x_c, T_c),[10] we find, below T_c, that

$$\ln(\sigma_B) - \ln(\sigma_A) \sim (1 - b/aT)\epsilon^\beta, \tag{4}$$

with $a \simeq 0.29$ at.% Se and $b \simeq -30$ K/at.% Se. Over the temperature range of the phase boundary (623 K $< T <$ 723 K) the temperature-dependent prefactor in Eq. (4) represents less than a 1% correction to the dominant behavior, and has been ignored. In Fig. 2, we display on a log-log scale $\ln(\sigma_B)$-$\ln(\sigma_A)$ as a function of ϵ, over the range $7\times 10^{-4} \leqslant \epsilon \leqslant 1.4\times 10^{-1}$. Using a three-parameter fit we have obtained $\beta_\sigma = 0.358 \pm 0.020$ and $T_c = 448.66 \pm 0.15°\mathrm{C}$, which agree very well with the directly measured values. Figure 3 is a presentation of $\ln(\sigma)$ as a function of temperature for a run at critical composition. Note that the entire

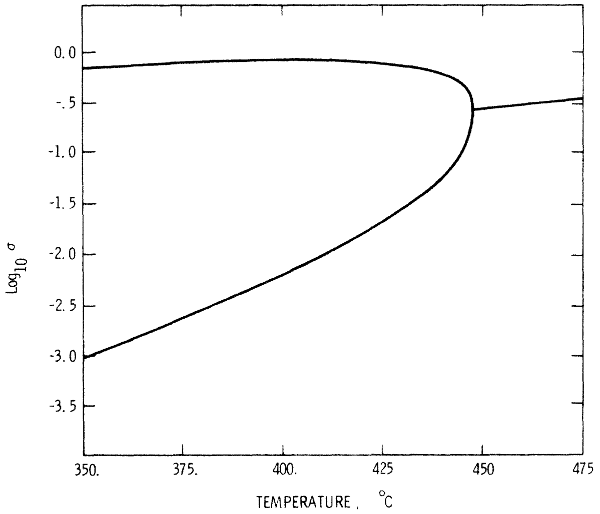

FIG. 3. The electrical conductivity as a function of temperature in the region of the phase boundary. The high- (low-) conductivity branch represents the thallium- (selenium-) rich phase.

$\ln(\sigma)$-T phase boundary is thus obtained in a single run.

Thus, even though the electrical conductivity changes by 4 orders of magnitude in the vicinity of the phase boundary, we have found that the critical exponent β_x determined *directly* from concentration-temperature measurements agrees within experimental accuracy with the exponent β_σ determined *indirectly* from electrical conductivity measurements. The "best" value of β is taken to be $\beta = 0.348 \pm 0.015$. Furthermore, the law of rectilinear diameters holds over the entire transition region for which we have data $(0.80 < x < 0.998)$.

In conclusion, we compare this system to the density-driven liquid-vapor phase transition in simple metals. The critical regions of cesium and mercury have been extensively studied.[11] Although extreme experimental difficulties prevent accurate measurement of the density-temperature phase boundary in the critical region of these materials, electrical properties near the critical region have been quite accurately determined.[11] Elsewhere[9] we discuss the electrical properties of Se-Tl mixtures throughout the region of the miscibility gap, and show them to be strikingly similar to those of metals near their liquid-vapor critical points.[11] According to the universality hypothesis,[12] which has been strongly confirmed by renormalization-group theory,[13] one would therefore expect the critical behavior—especially the critical exponents[7]—of the Se-Tl binary to be the same as that of metallic liquid-vapor systems.

We would like to thank Dr. J. P. Van Dyke for the use of his least-squares routine, and for several illuminating discussions.

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[5] This typically entailed 30–45 min stirring time.

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