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Experimental magnetic-susceptibility study of the electronic properties of liquid Se-Te alloys

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The electronic properties of liquid Se-Te alloys have been investigated by measurement of the magnetic susceptibility χ in a temperature range up to 1100 °C. χ is assumed to be composed of a temperature-independent diamagnetic term χ_D and a paramagnetic contribution χ_p. χ_D is found to be a linear function of composition. In the Te-rich alloys, χ_p is proportional to the square root of electrical conductivity indicating diffusive electronic transport. In the Se-rich alloys, the temperature dependence of χ_p is found to be exponential with a composition-independent activation energy of 0.68 eV. This is interpreted as the energy required to produce a paramagnetic dangling bond. The entropy of bond breaking is found to increase strongly with Te content.

I. INTRODUCTION

Liquid Se and Te and many alloys containing one or both of these elements are called liquid semiconductors because the magnitude and temperature dependence of their electronic conductivity σ are similar to those of intrinsic semiconductors.[1] For liquid Se near its melting point, σ is of order 10^{-6} $(\text{ohm cm})^{-1}$ and follows an Arrhenius temperature dependence with a large activation energy.[2] The Fermi energy appears to be near the center of a band gap. For liquid Te near its melting point σ is of order 10^3 $(\text{ohm cm})^{-1}$ and increases with T but does not have Arrhenius behavior.[3] It is believed that E_F lies within the Te valence band and moves deeper into the band as T rises.[1] These materials have been studied extensively not only because of their intrinsic interest but because of the insight provided into electronic properties of solid amorphous chalcogenides.

The magnetic susceptibility provides very useful information about the density of states $N(E_F)$ in high-conductivity liquid semiconductors and has been utilized by the present authors in an experimental study of electronic properties of liquid $\text{Tl}_x\text{Te}_{1-x}$ alloys.[4] In low-conductivity liquid semiconductors, the high-temperature magnetic susceptibility provides fruitful information about the density of paramagnetic defects, and hence the stability of the bonds. Both types of liquid semiconductors are found in the $\text{Se}_x\text{Te}_{1-x}$ alloy system, and in this paper we present our magnetic susceptibility measurements on these alloys. The experimental results cover the entire composition range and temperatures up to 1100 °C. Analysis of the data for Te-rich alloys provides information about the quantitative relationship between σ and $N(E_F)$. The diamagnetic "core" susceptibility is found to be rather different for pure Te than for Te bonded to Se, possibly due to a bonding change from threefold to twofold when Se is added to Te. For pure Se, the activation energy of paramagnetic centers is found to be 0.685 ± 0.015 eV. Within an experimental accuracy of approximately 15%, all the Se-rich alloys have this same activation energy, although the contribution of the paramagnetic centers to the magnetic susceptibility increases with increasing Te content. This latter observation is interpreted as an indication that the entropy of formation of dangling bond atoms is increased by addition of Te to Se.

Magnetic susceptibilities of several of these liquids have been reported by others,[5–8] and in general our results are in satisfactory agreement with these previous measurements. A report of some of our preliminary results has been published previously.[9]

II. EXPERIMENTAL PROCEDURE

The magnetic susceptibility was measured by a standard Faraday method. Samples sealed in quartz capsules were suspended from a vacuum electronic balance by a thin quartz rod and heated by a tantalum-wound furnace mounted within a 2-in. magnet gap. The magnet was a 12-in. Varian electromagnet with shaped and tapered pole caps which provide a constant value of $H(dH/dx)$ over the sample volume, typically about 2 cm^3. Data were recorded automatically by a microcomputer which computed the magnetic susceptibility from the apparent sample weight change when the magnetic field was turned on. The magnetic force was calibrated relative to aluminum whose susceptibility was taken as 1.62×10^{-6} cm^3/mole at 20 °C.[10] Typically the temperature was slowly increased to a maximum of at least 700 °C and then reduced back to room temperature during a run.

Alloys were made *in situ* by sealing carefully weighed quantities of 99.999% purity ASARCO Se and 99.995% purity UMC Te into the quartz sample capsule and allowing the sample to homogenize during the run. The heating time of 6–8 hours needed to reach maximum temperature was usually sufficient for the alloy to become homogeneous. Only data taken on cooling were retained, but reproducibility of results was checked occasionally by cycling two or more times to maximum temperature.

The two most significant sources of experimental error were the uncertainty in the correction for the quartz capsule susceptibility, and possible temperature differences between sample and thermocouple. This temperature difference could be as large as ±15 °C. Since the thermocouple and furnace heating elements had to be changed relatively often, this error is not necessarily systematic from run to run. The susceptibility of quartz is independent of temperature, but part of the capsule extended outside the constant force region, so the magnitude of the capsule correction had to be determined by breaking the sample open after the run and measuring the room-temperature susceptibility of the alloy ingot. Because of the difficulty of repositioning the sample precisely, an uncertainty of approximately $\pm 1\times 10^{-6}$ cm^3/mole in the susceptibility is introduced by this procedure. Other errors are negligible.

III. EXPERIMENTAL RESULTS

The total magnetic susceptibility χ of Te-rich $\mathrm{Se}_x\mathrm{Te}_{1-x}$ alloys is shown in Fig. 1. These data include a range of about one hundred degrees in which the liquid is supercooled. In the Se-rich liquids, the susceptibility becomes nearly temperature independent at lower temperatures, although typically there is a very small abrupt increase on cooling at about 300 °C or below. This is interpreted as evidence of solidification. For clarity the susceptibility of the Se-rich alloys shown in Fig. 2 is the differential susceptibility,

$$\chi_p(T)=\chi(T)-\chi(325\ ^\circ\mathrm{C})\ .$$

The low-temperature limit of the liquid-state suscep-

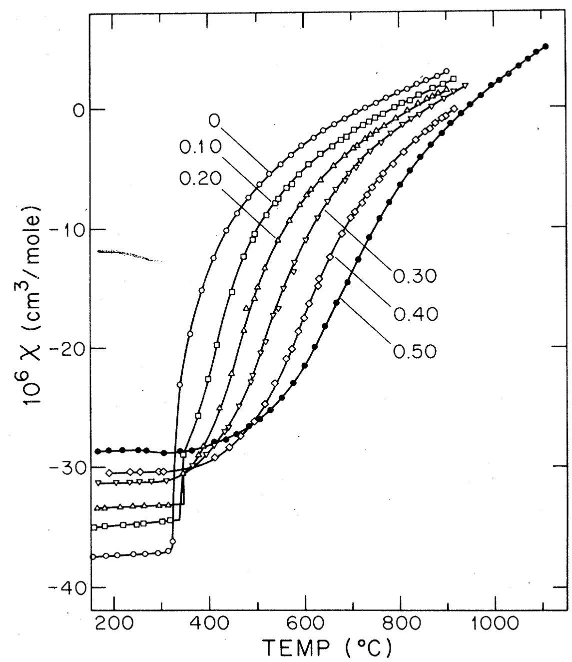

FIG. 1. Magnetic susceptibility of Te-rich $\mathrm{Se}_x\mathrm{Te}_{1-x}$ alloys. x is shown. Data is taken on cooling, and liquid supercooling is evident between 300 and 440 °C.

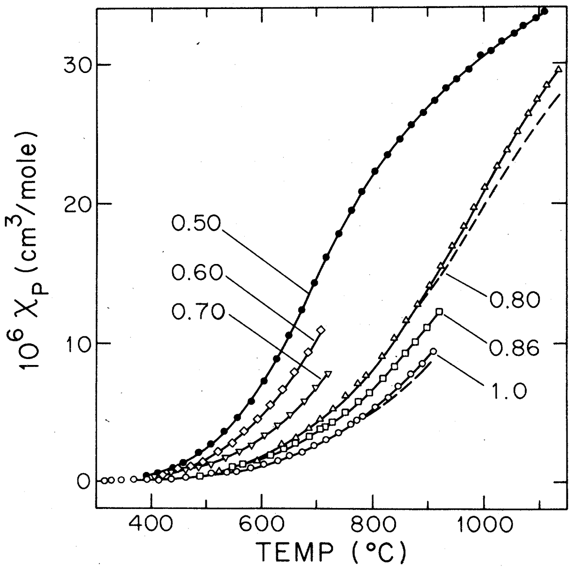

FIG. 2. Magnetic susceptibility of Se-rich liquid $\mathrm{Se}_x\mathrm{Te}_{1-x}$. x is shown, and for clarity, each set of data is shifted to zero at the lowest temperature shown by subtracting $\chi(325\ ^\circ\mathrm{C})$, which is indistinguishable from the low-temperature asymptote for these alloys. The dashed lines for $x=0.8$ and $x=1.0$ show the true liquid susceptibility when corrections for vapor paramagnetism are included.

tibility is shown by circles in Fig. 3. For $x \geqslant 0.5$, this is indistinguishable from $\chi(325\,^{\circ}\mathrm{C})$ but for the more Te-rich alloys, the alloy freezes before reaching the asymptote, and the limiting value is determined approximately by free-hand extrapolation.

During the course of this experimental work, a number of samples of each composition were run in order to assess the reproducibility of the experimental procedure. Most samples were heated to a maximum temperature of only 700 °C, because the Se vapor pressure becomes large above this temperature, and sample capsules often exploded. The Se vapor is known to be paramagnetic[8] and can contribute significantly to the total susceptibility if the filling factor of liquid in the capsule is small. In the latter stages of this work, a containment baffle was devised to protect the system when capsules exploded, and a series of higher temperature runs on pure Se and $\mathrm{Se_{0.8}Te_{0.2}}$ were made for samples with different filling factors. Extrapolation to unity filling factor gave the true liquid susceptibility shown by dashed lines in Fig. 2. Except possibly for $x = 0.5$ at temperatures above 1000 °C, the vapor corrections for other samples shown in Fig. 2 should be negligible. The data points in both Figs. 1 and 2 were taken with samples having filling factors of approximately 50%. Only the highest temperature run is shown for each composition.

IV. DISCUSSION OF RESULTS

For the Te-rich alloys there is a significant temperature range in which the electrical conductivity σ is within the "diffusive transport" region between roughly 100 and 2000 $(\mathrm{ohm\,cm})^{-1}$. Mott's[1,11] theory indicates that in this range the Fermi energy E_F must be within an electronic energy band, and σ is related to the density of states $N(E_F)$ by

$$\sigma = A\,[N(E_F)]^2\,, \tag{1}$$

where A is a constant which depends on the interatomic spacing and coordination number. For this situation the magnetic susceptibility should be given by[4]

$$\chi = \chi_D + (\alpha - \beta)\mu_B^2 N(E_F)\,, \tag{2}$$

where χ_D is the temperature-independent diamagnetism, and the second term is the sum of the Pauli and Landau susceptibilities of the carriers. For free electrons $\alpha = 1$, $\beta = \frac{1}{3}$, but though neither is known for these materials, $\alpha - \beta$ should be of order unity. Within this model, the temperature dependence of σ and χ is ascribed to a temperature-dependent $N(E_F)$. Combining Eqs. (1) and (2) to eliminate the density of states, one obtains

$$\chi = \chi_D + [(\alpha - \beta)\mu_B^2 A^{-1/2}]\,\sigma^{1/2}\,. \tag{3}$$

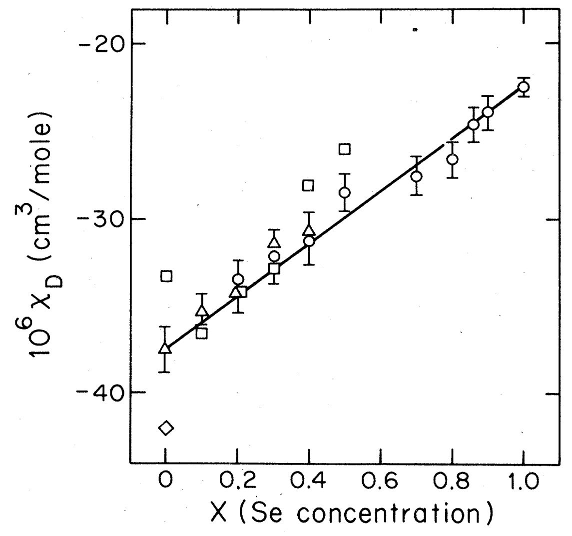

FIG. 3. Diamagnetic susceptibility of liquid $\mathrm{Se}_x\mathrm{Te}_{1-x}$ obtained in different ways. Circles are the low-temperature asymptotic limit of the liquid state susceptibility. Squares and the diamond are the χ_D found by fitting high-temperature data to Eq. (3) as shown in Fig. 4. The triangles are the susceptibilities of the room-temperature solid.

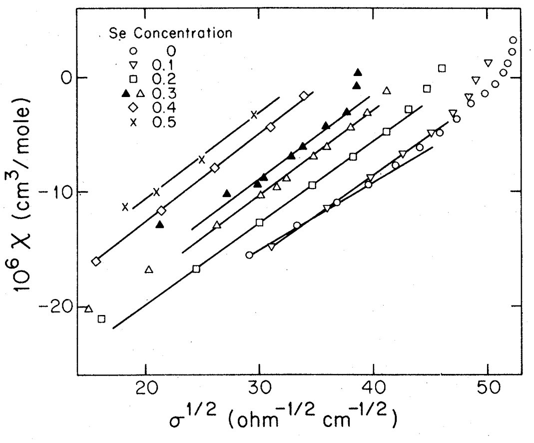

FIG. 4. Magnetic susceptibility of liquid $\mathrm{Se}_x\mathrm{Te}_{1-x}$ vs square root of electrical conductivity. Conductivity taken from J. C. Perron (Ref. 2) except closed triangles, which are taken from A. A. Andreev. The squares in Fig. 3 are the extrapolation to $\sigma^{1/2} = 0$ of the lines (excluding the one through the solid triangles) in this figure.

This relationship has been observed experimentally in a number of previous instances. It also seems reasonably well satisfied for these Se-Te alloys as is clear from Fig. 4 which shows χ vs $\sigma^{1/2}$. The slopes are the same within experimental error, indicating that A is independent of composition in alloys containing between 10 and 50 at.% selenium. Assuming $\alpha-\beta$ to be unity, one finds from the slope a value of

$$A = 2.0 \times 10^3 \text{ eV}^2 \text{atom}^2 (\text{ohm cm})^{-1}$$

for $0.1 \leq x \leq 0.5$ and

$$2.7 \times 10^3 \text{ eV}^2 \text{atom}^2 (\text{ohm cm})^{-1}$$

for pure liquid Te. This compares to

$$A = 1.2 \times 10^3 \text{ ev}^2 \text{atom}^2 (\text{ohm cm})^{-1}$$

for liquid $\text{Tl}_x\text{Te}_{1-x}$ between $0.1 \leq x \leq 0.6$.[4]

χ_D for each alloy is found by extrapolating the lines in Fig. 4 to $\sigma^{1/2}=0$, and these are shown by squares in Fig. 3. Within experimental uncertainty χ_D is not distinguishable from the low-temperature liquid-state asymptotic susceptibility also shown in this figure, and both are apparently linear in concentration. This observation suggests that diamagnetism in the alloys is simply the sum of a core plus bond diamagnetic susceptibility which is constant for each constituent. This constant can be found from Fig. 3 to be $(-22.5 \pm 0.5) \times 10^{-6}$ cm^3/mole for Se and $(-38 \pm 2) \times 10^{-6}$ cm^3/mole for Te. A similar conclusion was reached for the diamagnetism in $\text{Tl}_x\text{Te}_{1-x}$ alloys,[4] where the Te diamagnetic susceptibility of $(-42 \pm 2) \times 10^{-6}$ cm^3/mole is shown by the diamond in Fig. 3. For pure Te, both the different value of the constant A and the smaller χ_D of $(-33 \pm 2) \times 10^{-6}$ cm^3/mole indicate that the bonding structure is rather different than that of Te when alloyed with Se or Tl. It is known that pure liquid Te is threefold coordinated, but there are several reasons to believe that it is twofold bonded when alloyed with either Se or Tl.[1] It is not unreasonable that the Te diamagnetism is nearly the same when alloyed with either Se or Tl and larger in magnitude than in pure Te, since the denser threefold coordinated structure is expected to be less diamagnetic. It is interesting to note from Fig. 3 that the magnetic susceptibilities of solid $\text{Se}_x\text{Te}_{1-x}$ alloys are virtually identical to χ_D of the liquid and that the solid Te (which is crystalline because of the slow cooling rates employed here) susceptibility is in line with the alloy results. Crystalline Te is twofold coordinated.

Due to the rather uncertain extrapolations of Fig. 4, the accuracy of χ_D is difficult to assess. In the preliminary report of this work,[9] there was some indication that χ_D was smaller in magnitude than the low-temperature liquid-state extrapolation. This observation led to a speculation that a decrease in the diamagnetic susceptibility accompanies the structural anomaly[12] that has been observed at roughly the temperature where σ becomes "metallic" ($\sigma \sim 100$ ohm^{-1} cm^{-1}), and that a change from twofold to threefold coordination may be occurring there. The more complete results shown in Fig. 3 however, indicate that the diamagnetic susceptibility does not change greatly between the low- and high-conductivity regions.

In the Se-rich alloys with $x \geq 0.6$, the electrical conductivity is small, and E_F must be well within the band gap at all temperatures reached in these measurements. At the lower temperatures χ_P must be due to thermally excited paramagnetic defects, so we expect

$$\chi_P = N\mu^2/3k_B T \,, \tag{4}$$

where

$$\mu = g\mu_B[J(J+1)]^{1/2} \tag{5}$$

is the magnetic moment, and the number of defects N is thermally activated. These defects are known to have $g=2$ and $J=S=\frac{1}{2}$, and they are believed to be electrically neutral broken bonds.[8,9,13] The number of such defects per mole can be written

$$N = N_A e^{-F/k_B T} \,, \tag{6}$$

where N_A is Avogadro's number, and $F = E_0 - TS_0$ is the free energy of formation of a dangling bond atom from a twofold bonded atom. Now

$$\chi_P = \frac{1}{k_B T}(N_A \mu_B^2 e^{S_0/k_B}) e^{-E_0/k_B T} \,. \tag{7}$$

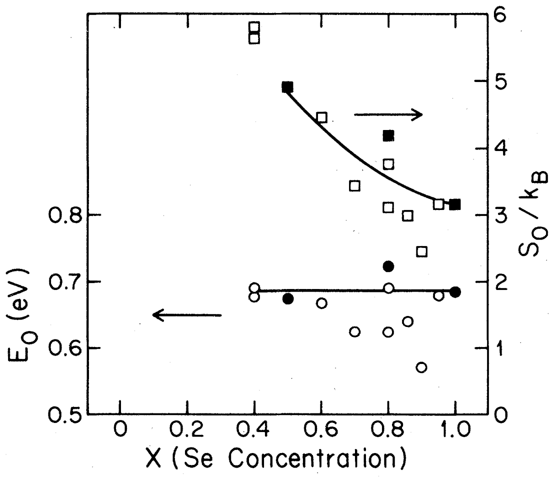

FIG. 5. Activation energy E_0 and amplitude parameter S_0/k [defined by Eq. (7)] of the magnetic susceptibility of liquid $\text{Se}_x\text{Te}_{1-x}$. The solid symbols are believed to be the most accurate.

E_0 and S_0 can be found by fitting Eq. (7) to the experimental susceptibilities. For $x \geqslant 0.4$, the fit is excellent up to 800 °C, and the resulting parameters are shown in Fig. 5. Fitting uncertainty is smaller than the size of the data points.

Although each experimental run could be fit well by Eq. (7), the fits often were substantially different for samples of the same composition which were run at different times. This nonreproducibility is traced to small differences in the low-temperature susceptibilities. Since the reproducibility for pure Se was markedly better than for the alloys, it is likely that the problem is due to alloy inhomogeneity or reaction of Te with impurities in the quartz. In the later runs, samples were heated longer and at higher temperatures to improve homogeneity, and sample capsules were baked to eliminate volatile dissolved impurities prior to a run. The filled symbols in Fig. 5 are believed to be more reliable than others because of these precautions and because more than one sample was run with essentially identical fits. For pure Se, E_0 is 0.685 ± 0.015 eV and S_0/k_B is 3.2 ± 0.2. Although some minor dependence of E_0 on concentration cannot be excluded, it is quite clear that E_0 is constant within 15% for $0.4 \leqslant x \leqslant 1.0$ and that S_0 rises with Te content.

When interpreted in terms of bond equilibrium theory, these results shed considerable light on the molecular structure of Se-Te alloys. A detailed discussion of the application of this theory is presented in other papers,[14,15] but some broad implications can be described here. The fact that E_0 is constant over the entire composition range in which it can be determined implies that Se-Se and Se-Te bonds have the same energy, $E_b = 2E_0 \simeq 1.33$ eV. The large values of S_0/k_B imply that the formation of branched polymer molecules enhances the entropy of formation of dangling bonds. In Ref. 14, it is shown that such enhancement does not occur unless the molecular structure contains branched chain molecules. Earlier studies have assumed the presence only of linear chains and rings. The increase in S_0 with decreasing x supports the hypothesis that Se_8 ring molecules attached to chains by threefold bonded molecules play a key role in limiting the average size of the polymer molecules. The concentration of Se_8 rings is roughly proportional to x^8 and decreases rapidly with decreasing x. It has been suggested that Se_6Te_2 rings are also relatively stable in Se-Te alloys.[16] Our experimental results imply that if such hybrid rings exist, they must have a relatively small concentration, for otherwise S_0 would not increase with small addition of Te. The theoretical curve for S_0 shown in Fig. 5 is derived from this bond equilibrium model, and the excellent agreement with experiment lends support to its validity.

Note added in proof. The above theoretical interpretation in terms of a ring mechanism may be incorrect, since the evidence for Se_8 rings in liquid Se has recently been brought into question.[17]

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