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Magnetic susceptibility of the liquid semiconductor alloy system Tl_xTe_{1-x} †

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The magnetic susceptibility χ of liquid Tl_xTe_{1-x} alloys has been measured as a function of temperature for 19 different compositions ranging from pure Te to pure Tl. For alloys with compositions $x < 2/3$, $d\chi/dT$ is large and positive, indicating a rapid increase of $N(E_F)$ with temperature. In alloys with $x \gtrsim 2/3$, χ is almost constant near the liquidus but rises rapidly at high temperature. For $x > 0.7$, χ becomes roughly independent of temperature. These results parallel the behavior of electrical conductivity σ in these alloys, and it is found that χ and σ can be related quantitatively using Mott's diffusive transport model. Using these data we determine the proportionality constant A relating σ to $[N(E_F)]^2$. A is found to be an order of magnitude larger for conduction-band transport than valence-band transport. We also can deduce the diamagnetic core susceptibility of Tl and Te, and find them both to be -4.2×10^{-5} cm^3/mole. A paramagnetic deviation of χ from the diffusive model prediction is found in two instances at low temperature when $N(E_F)$ is small. This discrepancy is attributed to enhancement of χ by electronic correlations.

I. INTRODUCTION

Liquid Tl_xTe_{1-x} alloys are one of the most thoroughly studied liquid semiconductor alloy systems. The electrical conductivity σ has a minimum at the composition Tl_2Te, and the thermopower S changes sign at that composition. For $x<\frac{2}{3}$, where the positive thermopower indicates that the Fermi energy E_F is in the valence band, σ increases strongly with temperature as well as with composition.[1] For $x>\frac{2}{3}$ the thermopower is negative, indicating that E_F is in the conduction band. For these alloys σ is nearly independent of temperature except for concentrations close to Tl_2Te, where it is constant near the liquidus temperature but increases rapidly at high T. In the composition range $0.667<x<0.7$, where σ rises rapidly with x, the conductivity and thermopower have been explained successfully in terms of a rigid-band model in which Tl in excess of Tl_2Te is singly ionized, adding its valence electron to the conduction band.[2]

At all compositions $x\lesssim 0.8$ and temperatures below our experimental maximum of 1100 °C, σ is smaller than 2500 $(\Omega\,\text{cm})^{-1}$, and except for compositions very near $x=\frac{2}{3}$, it is greater than 200 $(\Omega\,\text{cm})^{-1}$. For this conductivity range, Mott[3] has shown that transport is governed by a diffusive motion of electrons in extended states, according to the equation

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

where $\sigma(E)$ is the differential conductivity at energy E, $N(E)$ is the density of states, and A is a constant related to the coordination number and overlap matrix elements. The theory has been derived in greater detail by Hindley[4] and Friedman.[5] This mechanism has been fairly well established through the relationship found by Warren between σ and the magnetic relaxation rate in NMR,[6] and by the relationship between σ and the Knight shift K in several liquid semiconductor alloys.[7-9] Also, successful analysis of the dependence of σ and S on temperature and composition in Tl_xTe_{1-x} in terms of the diffusive mechanism[2,10] provides support for its validity.

The dependence of σ on T for $x<\frac{2}{3}$ implies that $N(E_F)$ is increasing with T, and the possible mechanism for this is a subject of considerable interest. The magnetic susceptibility χ provides rather direct information about $N(E_F)$, so its measurement in Tl_xTe_{1-x} is of some importance. Measurements have been reported by Brown, Moore, and Seymour,[9] but these have not been extensive enough to permit useful analysis of its behavior in relation to σ. The more detailed and extensive measurements of χ undertaken in the present work provide a basis for a more thorough examination of the behavior of the density of states in Tl_xTe_{1-x}. Comparison of these data with existing conductivity data provides further support for the validity of the diffusive conduction model. Values for the core diamagnetic susceptibility and for the proportionality constant A are found. A is found to be about a factor of 10 larger for conduction-band transport than for hole transport. For some of the Te-rich alloys having particularly small conductivities, we find a paramagnetic deviation of χ from the value which would be expected from the conductivity. The cause of this discrepancy has not been established, but we believe it is not due to a breakdown of the diffusion model. The deviation may be caused by electronic correlations similar to those which are believed to be responsible for susceptibility enhancements in heavily doped semiconductor impurity bands.[11,12]

II. EXPERIMENTAL RESULTS AND PROCEDURE

The susceptibilities were measured with a very precise Faraday apparatus. The samples were made from 99.999% purity Tl and Te (supplied by United Mineral). The materials were sealed in glass and were melted and shaken for $\frac{1}{2}$ h before being air quenched. After the room-temperature magnetic susceptibility of the sample was measured, it was sealed in a quartz capsule and suspended from the balance by a fine quartz rod. From the known sample susceptibility the susceptibility of the quartz holder could be found at room temperature. Since the quartz susceptibility has negligible temperature dependence, the Tl-Te susceptibility could then be determined accurately at all temperatures. Other than an overall calibration uncertainty of about 2%, the only significant source of experimental error was due to small changes in the Tl-Te ingot susceptibility as it was being sealed in the quartz capsule. Some heating of the ingot was unavoidable, and since this material is metastable and heterogeneous at room temperature, heat treatment can affect the susceptibility. We estimate that this introduced an overall uncertainty of no more than 0.2×10^{-5} cm^3/mole in the Tl-Te susceptibilities.

During measurements, the sample capsule and balance were kept in a 20-Torr pressure of argon. Temperatures were maintained by a tantalum-wound furnace within the magnet gap, and the temperature was measured to an accuracy of 10 °C with a Pt vs Pt–10%Rh thermocouple next to the sample. The experimental procedure was to heat the sample above its liquidus for 1 or 2 h to allow it to homogenize, and then raise the temperature in steps to the maximum (900 °C except for alloys near the Tl_2Te composition which were heated up to 1100 °C). Data taken on the heating cycle and on cooling were identical in every case except for occasional small differences near the liquidus when the alloy was not completely homogenized before data taking was begun. On cooling, the alloys would typically supercool by as much as 50 °C before beginning to freeze. The solidification point was easily identified by a discontinuity in the susceptibility versus temperature curve.

In Fig. 1, the molar susceptibility of most of the Tl_xTe_{1-x} alloys is shown versus temperature. Only data in the liquid state are shown. The closed symbols show data taken on heating, the open symbols indicate data taken on cooling. The numbers in Fig. 1 give x. A number of alloy compositions with x between 0.6667 and 0.69 are not shown in Fig. 1. For clarity these are shown in Fig. 2 on the expanded scale.

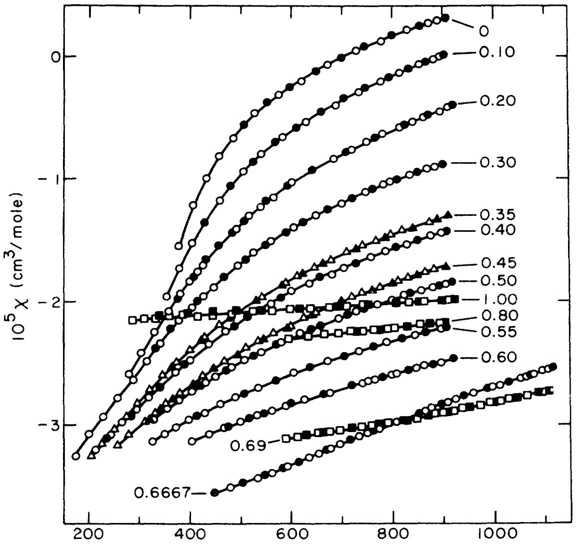

FIG. 1. Molar magnetic susceptibility of liquid $Tl_x Te_{1-x}$ alloys. Filled (open) symbols represent data taken on heating (cooling) cycle. Labels give x.

In the discussion that follows we are primarily interested in the (Pauli and Landau) contributions

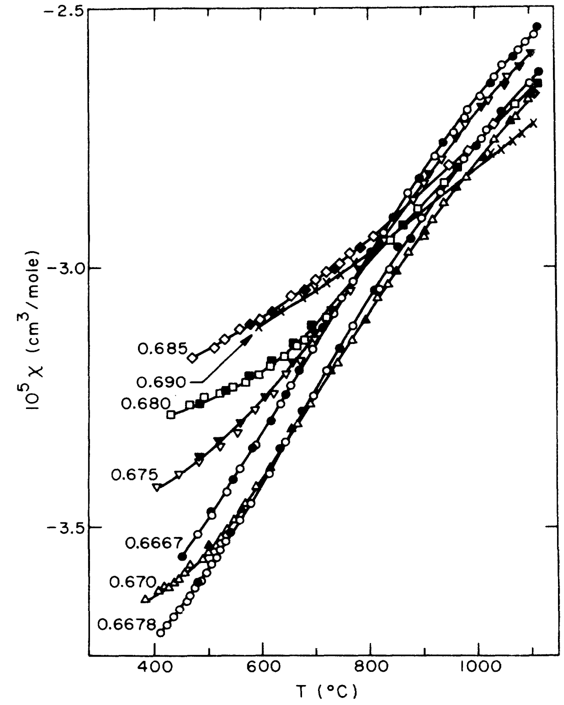

FIG. 2. Molar magnetic susceptibility of liquid Tl_xT_{1-x} alloys for $\frac{2}{3} < x < 0.69$. Filled (open) symbols are data taken on heating (cooling) cycle. Labels give x.

to the magnetic susceptibility which arise from electronic states near the Fermi energy. Apart from small corrections, this part is proportional to $N(E_F)$. In amorphous materials the remainder of the susceptibility is believed to be due almost completely to core diamagnetism, which is typically of order -5×10^{-5} cm^3/mole for heavier elements. Although the core susceptibility is large in the liquid, it should be independent of temperature and should vary roughly linearly with composition.

The data shown in Figs. 1 and 2 appear to be qualitatively consistent with the general picture for the electronic structure of liquid Tl-Te which is suggested by the behavior of the conductivity. The striking increase of χ with temperature for $x<\frac{2}{3}$ is in agreement with the supposition that $N(E_F)$ rises rapidly with temperature. The much smaller temperature dependence of χ for $x>0.69$ is also expected, since the conductivity of these alloys is nearly independent of T. The susceptibility is most diamagnetic at low temperature near $x=\frac{2}{3}$, where the electrical conductivity is smallest.

III. DISCUSSION OF RESULTS WITH COMPOSITION $x<\frac{2}{3}$

The conductivity is related to $\sigma(E)$ by[7]

$$\sigma=-\int\sigma(E)\,\frac{\partial f}{\partial E}\,dE, \tag{2}$$

where $f(E)$ is the Fermi-Dirac distribution function. Equation (1) for $\sigma(E)$ is believed to hold when $\sigma(E)$ lies between ~200 and ~2500 $(\Omega\,\text{cm})^{-1}$. The lower limit is Mott's estimate of the conductivity at the mobility edge E_c, and at the upper limit, electronic scattering becomes so weak that the diffusion model must give way to a weak-scattering approximation.[7] For materials with conductivity between approximately 500 and 2500 $(\Omega\,\text{cm})^{-1}$, $-\partial f/\partial E$ is well approximated by a δ function, and the conductivity is given by the "metallic approximation"

$$\sigma=A[N(E_F)]^2. \tag{3}$$

If the conductivity is smaller, one needs to know $N(E)$ in detail to evaluate Eq. (2). Since $\sigma(E)$ is believed to drop abruptly by several orders of magnitude at E_c, it is adequate for these alloys to take $\sigma(E)=0$ below E_c.

The magnetic susceptibility is given by

$$\chi=\chi_{\text{dia}}+\mu_B^2\int(\alpha-\beta)\,\frac{-\partial f}{\partial E}\,N(E)\,dE, \tag{4}$$

where χ_{dia} is the ion core contribution, μ_B is the Bohr magneton, and α and β are factors describing, respectively, the electron-electron enhancement and the diamagnetic response of the band electrons. In a free electron model, $\alpha=1$ and $\beta=\frac{1}{3}$. In normal metals $\alpha-\beta$ is usually not $\frac{2}{3}$, but it is normally of order unity. In the metallic approximation, Eq. (4) becomes

$$\chi=\chi_{\text{dia}}+(\alpha-\beta)\mu_B^2N(E_F), \tag{5}$$

and combination with Eq. (3) gives

$$\chi=\chi_{\text{dia}}+[(\alpha-\beta)\mu_B^2/A^{1/2}]\sigma^{1/2}. \tag{6}$$

If χ_{dia} is independent of temperature, then according to Eq. (6), χ should be a linear function of $\sigma^{1/2}$. In Fig. 3, the susceptibility is plotted as a function of $\sigma^{1/2}$, which is taken from published transport data. The lower points, represented by circled crosses, are for alloys with $x\gtrsim\frac{2}{3}$ and are discussed later. The remainder are all taken from data for alloys with $0.1\lesssim x\lesssim0.55$. These latter points all fall nicely around the straight line shown in Fig. 3. It is somewhat surprising that the data points fall so closely together for different compositions. This indicates that χ_{dia} is independent of composition. From the intercept in Fig. 3, χ_{dia} is found to be -4.2×10^{-5} cm^3/mole. This is reasonably close to theoretical estimates[13] of the atomic diamagnetism of Te and Tl, but to our knowledge there is no independent experimental information on the magnitude of χ_{dia} for either element.

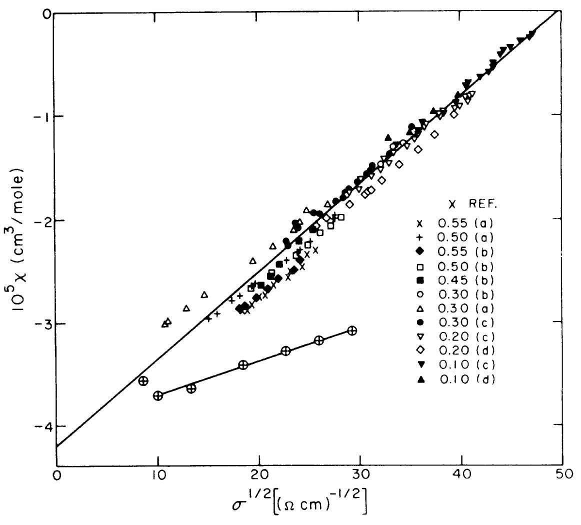

FIG. 3. Magnetic susceptibility vs $\sigma^{1/2}$. Conductivity references: (a) C. E. Mallon and M. Cutler, Philos. Mag. 11, 667 (1963); M. Cutler and C. E. Mallon, Phys. Rev. 144, 642 (1966); (b) B. I. Kazandzhan, A. A. Lobanov, and A. A. Tsurikov, Sov. Phys.-Semicond. 5, 2063 (1972); (c) D. N. Lee, Ph.D. thesis (Vanderbilt University, 1971) (unpublished); (d) J. E. Enderby and C. J. Simmons, Philos. Mag. 120, 125 (1969).

Most of the experimental conductivity data used for Fig. 3 are in the higher conductivity range, $\sigma > 500$ $(\Omega\,\mathrm{cm})^{-1}$, and here the points for all compositions with $0.1 < x < 0.55$ fall very accurately parallel to the pictured straight line. This is illustrated in Fig. 4 which shows the higher conductivity region on an expanded scale, with data points for different compositions displaced successively for visual clarity.

Figure 4 also shows χ vs $\sigma^{1/2}$ for pure liquid Te. These points clearly do not fall parallel to the same straight line as the alloys, and we attribute the difference to a change in the parameter A due to different atomic bonding in pure Te. Neutron-diffraction results[14] have shown evidence for threefold coordination in liquid Te, whereas chemical considerations suggest twofold coordination for Te in alloys containing sufficient metal (such as Tl) with which Te forms strong chemical bonds.[15] The curvature of the Te data points at very high conductivity may be due to failure of the diffusion approximation, but since these data encompass a large temperature range (700–900 °C), the curvature may instead reflect a further change in atomic structure with increasing T.

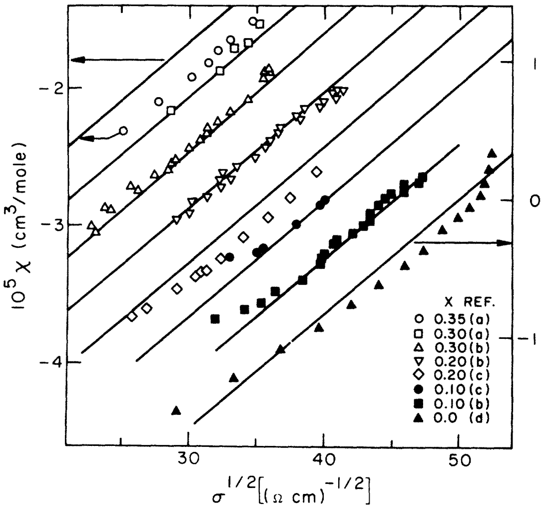

FIG. 4. Magnetic susceptibility vs $\sigma^{1/2}$ of liquid $\mathrm{Tl}_x\mathrm{Te}_{1-x}$ with $x = 0.35$ and $\sigma > 500$ $(\Omega\,\mathrm{cm})^{-1}$. The left ordinate refers to the $x = 0.35$ composition and the right ordinate to pure Te. Other data are displaced successively between these two extremes in increments of 0.4×10^{-5} cm^3/mole to separate data for different compositions. The same straight line of Fig. 3 is shown on the appropriate scale for each composition. Conductivity references: (a) B. I. Kazandzhan, A. A. Lobanov, and A. S. Tsurikov, Sov. Phys.-Semicond. 5, 2063 (1973); (b) D. N. Lee, Ph.D. thesis (Vanderbilt University, 1971) (unpublished); (c) J. E. Enderby and C. J. Simmons, Philos. Mag. 120, 125 (1969); (d) J. C. Perron, Adv. Phys. 16, 657 (1967).

From the slope of the best-fit straight line in Figs. 3 and 4, the coefficient $A^{1/2}/(\alpha - \beta)$ is found to be 35 eV atom$(\Omega\,\mathrm{cm})^{-1/2}$. ($A^{1/2}$ can be converted to volume units by multiplying by the atomic volume 3.7×10^{-23} cm^3/atom.) If $\alpha - \beta$ is unity, A is 1200 eV^{2}atom$^2(\Omega\,\mathrm{cm})^{-1}$. In the higher-temperature Te-rich alloys, the Pauli susceptibility is of order 4×10^{-5} cm^3/mole, which corresponds to $N(E_F)$ of order 1.0/eV atom. Since E_F is in the valence band, which is believed to contain two (nonbonding) electrons per tellurium atom, this large value of $N(E_F)$ suggests that the valence band is only 1 or 2 eV in width. This conclusion is in accord with the determination that $N(E)$ is parabolic for $-E < 0.25$ eV, but falls below this parabolic curve at larger values of $-E$.[10]

Careful examination of the data for compositions $x = 0.50$ (indicated by plus signs in the Fig. 3) and $x = 0.30$ (open triangles) shows that $d\chi/d\sigma^{1/2}$ decreases at low σ, indicating a paramagnetic deviation from the behavior described by Eq. (6). These are presently the only two compositions for which the conductivity has been measured over a wide enough range to show this behavior clearly. In this range of σ, the metallic approximation becomes poor. A more accurate evaluation of Eqs. (2) and (4) is desirable, and this requires information about the shape of $\sigma(E)$ and $N(E)$. In a recent study,[10] one of us has found that the behavior of the conductivity and the thermopower indicates that the valence band is rigid in this range of x and T and is described by $\sigma(E) = -BE$, where $B = 2960$ $(\Omega\,\mathrm{cm\,eV})^{-1}$ and the top of the valence band is taken as the zero of E. Substituting this into Eqs. (2) and (4) gives

$$\chi = \chi_{\mathrm{dia}} + \mu_B^2(\alpha - \beta)\sigma^{*1/2}/A^{1/2}, \tag{7}$$

where

$$\sigma^{*1/2} = \left(\frac{BkT}{4}\right)^{1/2} \int_0^\infty y^{-1/2}(e^{y-\xi} + 1)^{-1}\,dy \tag{8}$$

and

$$\xi = -E_F/kT = \ln[1 + \exp(\sigma/BkT)]. \tag{9}$$

When σ is large, it becomes equal to σ^*. When χ is plotted vs $\sigma^{*1/2}$ instead of $\sigma^{1/2}$, a straight line should result regardless of whether or not the metallic approximation is valid.

In Fig. 5 we show χ plotted vs $\sigma^{*1/2}$ for $x = 0.50$ and 0.30. The paramagnetic deviation is even more pronounced than in Fig. 3. Although the exact size of the deviation depends on the model assumed for $\sigma(E)$, we believe that this result is rather accurate. In any case, it appears unlikely that any reasonable model for $\sigma(E)$ could result in a linear dependence of χ on $\sigma^{*1/2}$. We believe

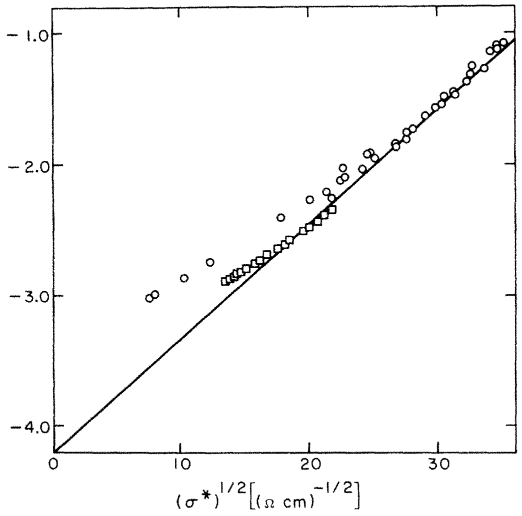

FIG. 5. Magnetic susceptibility vs $\sigma^{*1/2}$ for Tl_xTe_{1-x}. σ^* is defined by Eq. (8).

that the most plausible explanation for this paramagnetic deviation is that the susceptibility is enhanced by electronic correlations in the low-conductivity region; i.e., we suppose that α is increasing as E_F approaches the band edge. We note that the band width is narrow, and the effect occurs when the density of states becomes small, both situations tending to favor enhanced correlation.

A similar situation is believed to occur in heavily doped silicon, where the susceptibility associated with carriers in the impurity band displays a small Curie-like temperature dependence for impurity concentrations just above the critical value for metallic conduction.[16,17] This behavior apparently reflects the beginning of a transition from Pauli to Curie magnetic behavior as the carrier density becomes very small. The susceptibility enhancement in Tl_xTe_{1-x} also appears to have a strong inverse temperature dependence since it is larger for a given σ^* for $x=0.30$ than for $x=0.50$, and the same σ^* occurs at a higher T for the second composition. The less complete data for compositions $x=0.40$, 0.45, and 0.55 also suggests enhancements which fall into this pattern.

It is also of interest to compare the susceptibility with the Te Knight shift which has been measured in liquid Te by Cabane and Froideveaux[18] and by Warren,[8] and in liquid Tl_xTe_{1-x} by Brown, Moore, and Seymour.[9] The Knight shift is related to the carrier spin susceptibility by

$$K_{Te}=8\pi P_F\chi_{spin}/3N_0 \tag{10}$$

$$=8\pi P_F\alpha\mu_B^2N(E_F)/3N_0, \tag{11}$$

where N_0 is Avogadro's number, and P_F is the average probability amplitude at the Te nucleus for electronic states at E_F. If α, β, and P_F are constant, χ and K_{Te} should be linearly related. In Fig. 6, χ is plotted vs K_{Te} for liquid Te and a number of Tl_xTe_{1-x} liquid alloys. The slight curvature at low K_{Te} may be associated with enhancement of α as discussed above. There appears in addition to be a systematic change in $d\chi/dK$ over the entire range. This is probably due to a decrease of P_F as E_F moves deeper into the valence band. Since P_F is a measure of the s character of the electronic states near E_F, this observation implies that the valence band has strong s character near the top, but progressively less for energies deeper in the band. Since the valence band is derived from Te p orbitals, this is not unexpected behavior. We also note that the susceptibility at the $K_{Te}=0$ intercept should be equal to χ_{dia} found above but in fact is somewhat more positive. This apparently stems from a negative chemical shift of about 0.15% as first pointed out by Brown *et al.*[9] Consequently the true Knight shift of Tl_xTe_{1-x} is somewhat larger than that shown in Fig. 6. The discontinuity between alloy and pure Te data in this figure may be due to a change in this chemical shift.

IV. DISCUSSION OF RESULTS FOR $x > \frac{2}{3}$

In this region the relationship between χ and σ is more complex than for $x < \frac{2}{3}$. The general behavior of χ vs T and x is in accord with the model for electronic transport proposed by Cutler.[2] In that model, the band gap is positive at low T and E_F is in the conduction band. The band gap decreases rapidly with T, however, and for $T > 770$ °K the valence band overlaps the conduction

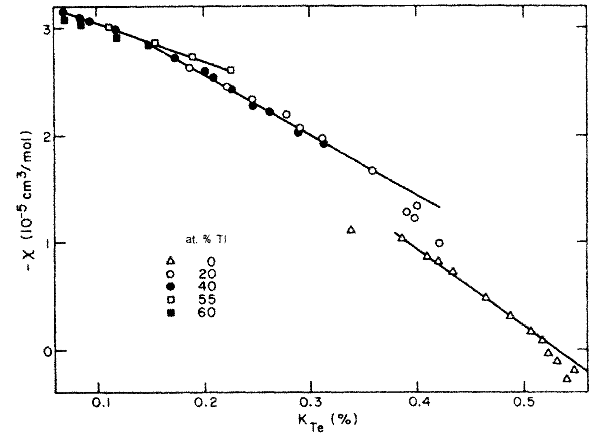

FIG. 6. Magnetic susceptibility vs Te Knight shift in liquid Tl_xTe_{1-x}.

band. According to the model, χ should be independent of T at low temperature, but for compositions with x near $\frac{2}{3}$, χ should increase rapidly when the valence-band edge rises above E_F ($T > 800\,^\circ\mathrm{K}$). This is what is observed.

It seems possible to derive more detailed information about the density of states near the pseudogap from a careful analysis of the behavior of $\chi(T)$ at compositions in the range $2/3 < x < 0.7$, where the bands overlap, and we plan to do this in later work. For the present, we have made only a crude analysis of data which reflect conduction-band properties only. This is done by taking points at the lowest temperature for each composition and plotting χ vs $\sigma^{1/2}$, as shown for compositions between $x = \frac{2}{3}$ and 0.7 by circled crosses in Fig. 3. A straight line is obtained which corresponds to $A = 1.0 \times 10^4$ $(\mathrm{eV\,atom})^2(\Omega\,\mathrm{cm})^{-1}$ (assuming $\alpha - \beta = 1$), and $\chi_{\mathrm{dia}} = -4.0 \times 10^{-5}\ \mathrm{cm}^3/\mathrm{mole}$. These values are fairly rough because of a sizeable experimental uncertainty in the slope, and because the metallic approximation is poor in the lower conductivity range. The value of A agrees well with the value 8670 $(\mathrm{eV\,atom})^2(\Omega\,\mathrm{cm})^{-1}$ obtained from analysis of the transport data alone.[2]

It is interesting to note that A is much larger in the conduction band than in the valence band. It is likely that this is a consequence of the differing character of the conduction- and valence-band molecular orbitals. As pointed out by Mott,[3] the transfer matrix of p-orbital wave functions is much smaller than for s orbitals in disordered materials.

V. CONCLUSIONS

We find that the magnetic susceptibility can be related in a useful way to conductivity data in terms of the diffusive model for transport. Our results provide further support for the validity of the diffusive model for transport, and for the conclusions about the electronic structure of Tl-Te alloys which have been derived from transport data in terms of the diffusive model. Our results provide relatively direct information about the density of states, and yield values of the parameter A in the diffusive equation for both bands. For the valence band, A is found to be equal to 1200 $\mathrm{eV^2 atom^2 \Omega^{-1} cm^{-1}}$, and the density of states is fairly large. χ is strongly dependent on T and x, paralleling the behavior of σ. For the conduction band, A is an order of magnitude larger. Since $\sigma(E)$ is comparable for the two bands, the density of states in the conduction band is correspondingly smaller. The difference between the two bands is consistent with a p character for the valence band, and s character for the conduction band.

In the analysis of our results, we have attempted to minimize the use of detailed conclusions which have been derived previously from transport studies, so as to arrive at independent results as much as possible. Thus, the relation between χ and σ in the metallic approximation does not depend on the form of $\sigma(E)$. It was necessary to incorporate the form of $\sigma(E)$ in order to evaluate the paramagnetic enhancement, which occurs at low values of σ. The resulting correction is small and not critically dependent on $\sigma(E)$. The value of A obtained for the valence band provides new information, and leads to a quantitative expression for $N(E)$ in that band. The rough value of A obtained for the conduction band is in good agreement with the value previously found from transport studies.

ACKNOWLEDGMENT

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