Charge Transfer in Liquid Semiconductors: The K-Te System

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The neutron diffraction patterns of molten $K_x Te_{1-x}$ alloys for $x = 0.12$ and $x = 0.50$ demonstrate the persistence of covalently bonded tellurium in the liquid. In the case of liquid $K_{0.12}Te_{0.88}$, the measured structure is dominated by the Te-Te contribution, and is remarkably similar to that of pure liquid tellurium. The equiatomic alloy $K_{0.50}Te_{0.50}$ is shown to contain mostly Te pairs which are identified with Zintl ions, Te_2^{2-}. The presence of these ions explains the semiconducting behavior of these alloys deduced from recent electrical transport measurements.

The chalcogen elements S, Se, and Te play a principal role in the formation of liquid semiconducting matter [1,2]. The nature of the chemical bonding in these elements, namely, their tendency to form twofold covalent bonds in the melt, appears to be central to the semiconducting behavior of their melts and many of their alloys. Of these, tellurium is perhaps the least understood. Pure liquid (l-) Te is a semimetal, whose conductivity places it between the regimes of Ziman scattering theory (metallic) and diffusive (semiconducting) behavior. Possible ambipolar conduction has made transport [3] and optical [4,5] properties of l-Te difficult to interpret in a consistent manner. Further confusion arises from diffraction measurements, where the measured radial distribution function (RDF) shows that there is no well-defined first coordination shell [1,6], leaving open the fundamental point of whether the number of bonded neighbors is two or three. This is in contrast to liquid selenium, where a well-defined first coordination peak with an area of two atoms is derived from neutron diffraction results [7].

The peculiar structure of pure l-Te has been explained by Cutler [2] as containing a high density of single-bonded ($1F$ or D^-) and threefold-bonded ($3F$ or D^+) defects in a nominally twofold network. Later on, Silva and Cutler [5] proposed that the electronic and optical properties may be explained if one assumes very short (three to four atoms) covalently bonded, electrostatically interacting chains with a nearly equal density of $1F$ and $3F$ sites. Thus, the first peak in the RDF of pure l-Te has contributions from long-lived twofold (intrachain) and short-lived $3F$ (interchain) and $1F$ (dangling bond or chain termination) sites. The $3F$ and $1F$ sites are in "fast exchange" as short chains interact, a process that results in the observed broad, asymmetric first RDF peak. This view is consistent with the rapid transition from semimetallic to semiconducting behavior observed when alloying Te with Se [3], Tl [1], or K [8]. Magaña and Lannin [4] have also suggested that threefold bonding is needed to explain the Raman spectra of pure l-Te, and their observation of a sudden qualitative change in the Raman spectra of the Se-Te system at ~ 20–30 at.% Se was interpreted as a transition from threefold to twofold bonding. These authors preferred a modified version of an earlier

model of Cabane and Friedel [9], in which the structure of pure l-Te is a continuous random network of mostly threefold bonds. Alternatively, a recent EXAFS study [10] of l-Te has attributed the broad first coordination sphere to the presence of long (3.0 Å) and short (2.8 Å) bonds, though strictly preserving twofold coordination. It is difficult, however, to reconcile their observation of increasing population in the *longer* bond as the temperature increases with the known increase in electrical conductivity, σ, with temperature [3].

Insight into the atomic and electronic structure of pure l-Te may be obtained from a better understanding of the role played by Te in liquid semiconducting alloys. Recent thermodynamic investigations of the potassium-tellurium system [11] have shown that for three compositions there is considerable "excess stability," indicative of chemical ordering. Of particular interest is the nature of this ordering at the compositions $K_{0.12}Te_{0.88}$ and $K_{0.50}Te_{0.50}$ corresponding to the local maxima in the excess stability function. Both of these compositions are characterized by liquid semiconducting behavior defined in the narrow sense by Enderby and Barnes [1], with $\partial \sigma / \partial T > 0$ and with $\sigma = 200$ and 1 $\Omega^{-1}cm^{-1}$ at $T = 450\,°C$ for $x = 0.12$ and 0.50, respectively [8]. For tellurium-rich tellurides, the tendency for Te to form covalently bonded chains, which are known to survive into the melt, is expected to be significant. At the equiatomic composition, the Zintl rule [12] suggests the formation of Te_2^{2-} anions if the charge transfer from K to Te is complete. Indeed, such dimer ions have been identified not only in the crystalline form by Böttcher [13] and others [14] but also more recently in the vapor phase of the Na-Te system [15]. This paper reports the structures of these two compositions obtained from neutron diffraction and their relation to the semiconducting properties of the alloys.

Alkali metals and tellurium are known to react violently even at temperatures close to the low melting points of the alkali metals. Consequently, the synthesis of potassium tellurium alloys was carried out by adding very small amounts of Te to melted potassium contained in a high-purity alumina crucible. The alumina crucible containing the partly reacted K-Te mixture was then sealed in a stainless-steel vacuum nipple and annealed above the

liquidus ($\sim$450 °C). The $K_{0.50}Te_{0.50}$ obtained was a dark purple crystalline material. Some of this was mixed with pure Te to produce $K_{0.12}Te_{0.88}$. The samples were sealed under vacuum in thin-walled (0.5 mm) fused silica ampoules, with one empty ampoule for container subtraction. With the exception of the sealing procedure, all operations were conducted inside a very-high-purity helium-filled glovebox.

Time-of-flight neutron diffraction was carried out in the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source. Powder diffraction patterns were obtained at room temperature, and liquid diffraction was performed at $\sim$450 °C. Standard programs for intensity, background, absorption, multiple scattering, and inelastic scattering were used to analyze and refine the data. The measured total structure factors are shown in Fig. 1. There are major differences in the structures as shown by the presence of the first peak located at about 1.2 Å^{-1} for $K_{0.50}Te_{0.50}$ (which occurs only as a weak shoulder in the case of $K_{0.12}Te_{0.88}$), and the alternating positions of the first three extrema thereafter, i.e., the minimum in one composition corresponds to the maximum observed in the $S(Q)$ of the other composition. The peak at 1.2 Å^{-1} is referred to as the "first sharp diffraction peak," a well-known signature of intermediate-range order in similar liquid alloys [16] and amorphous systems [17]. The total
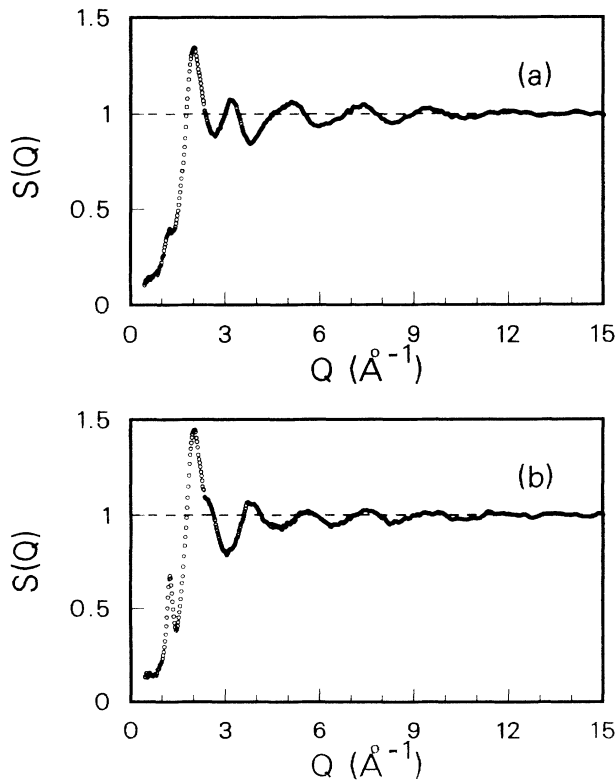

FIG. 1. The total structure factor obtained by neutron diffraction: (a) l-$K_{0.12}Te_{0.88}$ and (b) l-$K_{0.50}Te_{0.50}$.

structure factors, $S(Q)$, are related to the three partial functions by the following relation:

$$S(Q) = \frac{1}{(c_A b_A + c_B b_B)^2} [c_A^2 b_A^2 S_{AA}(Q) + c_B^2 b_B^2 S_{BB}(Q)$$
$$+ 2c_A c_B b_A b_B S_{AB}(Q)], \quad (1)$$

where c and b are the concentration and cross-section scattering of A and B, respectively. Thus we obtain

$$S(Q) = 0.847 S_{Te\text{-}Te}(Q) + 0.007 S_{K\text{-}K}(Q)$$
$$+ 0.146 S_{K\text{-}Te}(Q) \quad (2)$$

for $K_{0.12}Te_{0.88}$ and

$$S(Q) = 0.375 S_{Te\text{-}Te}(Q) + 0.152 S_{K\text{-}K}(Q)$$
$$+ 0.473 S_{K\text{-}Te}(Q) \quad (3)$$

for $K_{0.50}Te_{0.50}$. In the former case, the K-K contribution is negligible and the K-Te contribution is small, whereas for the latter case each partial pair distribution is substantial. This, coupled with the large difference between Te-Te covalent ($\sim$2.8 Å) and K-Te ionic ($\sim$3.6 Å) bond lengths, results in the total scattering as almost exclusively representative of the Te interactions with Te or the alkali atom.

The real-space functions complement the reciprocal-space information. The average radial distribution function $n(r)$ is given by

$$n(r) = 4\pi r^2 \rho + r D(r), \quad (4)$$

with

$$D(r) = \frac{2}{\pi} \int_0^{Q_{max}} Q[S(Q) - 1]\sin Qr \, dQ, \quad (5)$$

where ρ is the average atomic density and Q_{max} is the experimental cutoff, in our case 15 Å^{-1}.

In Fig. 2(a), $n(r)$ for the molten $K_{0.12}Te_{0.88}$ alloy is shown. Of significance here is the clear separation of the first peak in the RDF from the rest of the neighbors. A Gaussian fit to this first peak in $T(r)$, at a distance of 2.78 ± 0.04 Å and having an area of 1.7 atoms, indicates Te chains (about 5 to 10 atoms long) persisting into the melt. This distance corresponds, within experimental error, to the separation 2.74 Å of the molecular ion $(Te_2)^{2-}$ found by Hastings, Elliot, and Corliss [18] in solid $MnTe_2$ (an antiferromagnetic semiconductor). It is interesting to note, additionally, that otherwise the RDF is quite similar to that of pure liquid Te, suggesting that the increased order is achieved with only subtle changes to the local environment. A shoulder at 3.6 Å, matching the sum of the K^+ and Te^{2-} ionic radii, can by analogy with the analysis of comparable data on the liquid Tl-Te system [19] be attributed to the K-Te first coordination sphere.

The role of the potassium appears to be that of nearly complete charge transfer, stabilizing the short chains as
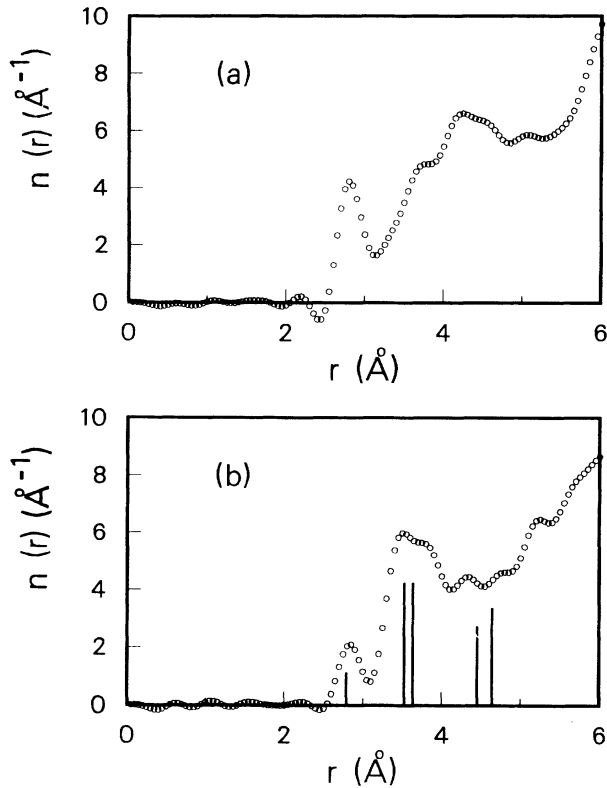
FIG. 2. The total reduced radial distribution function for (a) l-$K_{0.12}Te_{0.88}$ and (b) l-$K_{0.50}Te_{0.50}$. The vertical bars in (b) represent the position of coordination shells in the crystalline phase of KTe from Ref. [13]. These shells and their coordination (in parentheses) are, from left to right: Te-Te (1), K-Te (3), K-Te (3), K-K (6), and Te-Te (3).

Te_n^{2-} ions ($n \sim 5$-10). These charged chains in a dilute K^+ matrix will certainly interact much more weakly than the equivalent chains in the pure system, which is believed to contain a high density of $1F$ and $3F$ defects. The potassium thus enables the valence of Te to be satisfied by either twofold covalent bonds to other Te or by creating ionic bonding to the terminating K^+, thus greatly reducing the number of $3F$ defects. This explains the apparent formation of a pseudogap in the electronic density of states leading to semiconducting behavior [1,2] and the observed decrease in electronic conductivity by more than an order of magnitude (from 2500 to 200 $\Omega^{-1}cm^{-1}$) upon alloying [8]. Indeed, such a large decrease in conductivity in an alloy dilute in K is inconsistent with the formation of isolated Te_2^{2-} ions in a Te matrix, where scattering theory would predict much smaller conductivity changes.

The $n(r)$ for liquid $K_{0.50}Te_{0.50}$ [Fig. 2(b)] shows that there is again a first Te-Te coordination peak at 2.8 Å, having in this case a coordination of 0.96. This virtually complete pairing of tellurium atoms is in sharp contrast to the heterocoordination of liquid CuTe and the partial

pairing of selenium in liquid CuSe (Se-Se coordination of ~ 0.6) [20]. It is informative to compare this liquid structure with that of crystalline KTe [13,14], whose peaks are indicated in the figure by the vertical bars with heights determined by the coordination number weighted by the appropriate prefactors from Eq. (3). The covalent "Zintl" pair, present in both the solid and the liquid, proves to be quite stable, while the ionic structure is loosely preserved, typical of strongly interacting liquids. The large, broad, and asymmetric second peak at about 3.5 Å corresponds to the Te-K shell, providing the expected heterocoordination in an ionic melt. No evidence of ordering at the next-nearest-neighbor level of Te (correlation between Te_2^{2-} ions) is apparent. The vertical bars in Fig. 2(b) represent the first five coordination shells of the crystalline phase of KTe [14].

The unusual asymmetric shape of the Te-K peak at 3.5 Å precluded any reasonable fitting with Gaussians. This shape is likely due to the K^+ ions arranging themselves about a "dumbbell-shaped" Te_2^{2-} polyanion [13-15]. As the interionic Te neighbors are so strongly correlated in position, the position of the K^+ will depend on an effective three-body interaction, and the usual symmetric structure of the $T(r)$ peak will not be produced. The absence of ordering among the Te_2^{2-} indicates effective screening by the K^+. Finally, the pronounced first sharp diffraction peak at $Q \sim 1.2$ Å^{-1} arises from the high concentration of the complex Zintl ions, similar to that found in other ordered liquid systems [16]. Its weaker presence in the $K_{0.12}Te_{0.88}$ alloy (and complete absence in pure l-Te) [6] is presumably due to the lower concentration of Te_n^{2-} ions.

In conclusion, neutron diffraction from molten $K_{0.12}Te_{0.88}$ and $K_{0.50}Te_{0.50}$ indicates a high degree of structural ordering in these two liquid semiconducting alloys. These results, particularly for the dilute ($x = 0.12$) system, support the picture of Silva and Cutler for the structure of pure liquid tellurium. Also, the first evidence for the appearance of Zintl polyanions of tellurium is observed as the K concentration is increased. This is consistent with a simple charge-transfer scheme, whereby the Te bonds according to the 8-N rule with N, the number of valence electrons, determined assuming complete charge transfer from the K. The apparent removal of defects in the dilute system may be of considerable importance to the semiconducting behavior. We are unaware of any other example of Te pairing in liquid alloys. The most likely candidate for this effect is liquid $MnTe_2$. However, Te pairing which occurs in the solid and which was referred to earlier was shown to be absent in the liquid directly by structure studies and indirectly by the observed conductivity and thermopower [21].

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