

The structure and electrical properties of liquid semiconductors: I. The structure of liquid NiTe₂ and NiTe

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Abstract. The structure of liquid NiTe₂ and NiTe has been investigated by applying the technique of neutron diffraction to isotopically enriched samples. The three partial structure factors relating to Ni-Ni, Te-Te and Ni-Te correlations have been successfully extracted from the experimental data. It is concluded that tellurium exists in these liquids as a dense assembly of Te²⁻ ions. The average coordination of Ni²⁺ is characterised by approximately three Ni²⁺ ions at 2.54 Å with four Te²⁻ ions at 2.56 Å for NiTe and approximately two Ni²⁺ ions at 2.81 Å with four Te²⁻ ions at 2.56 Å for NiTe₂. Comparison is made with the results of a new analysis of earlier data taken on liquid CuTe.

1. Introduction

The electronic and structural properties of pure liquid tellurium have received considerable attention in recent years. In terms of the general classification of conducting materials developed by Mott and co-workers (Mott 1971, Mott and Davis 1979) the electrical properties are intermediate between the metallic and the semiconducting regimes. Structurally liquid Te is characterised by a structure factor $S(k)$ and a pair correlation function $g(r)$ which are quite different from those for metallic liquids, even those with a short electronic mean free path (e.g. liquid Bi). Although there has in the past been some controversy about the detailed structure of liquid Te (Waseda and Tamaki 1975) our most recent measurements (figures 1 and 2) agree very well with those of Bellissent and Tourand (1980). Both sets of data show that the coordination number \bar{n} defined by

$$\bar{n} = 4\pi\rho \int_0^{r_1} g(r)r^2 dr \quad (1)$$

is 3.1. In (1) ρ is the total number density and r_1 is the position of the first minimum in $r^2g(r)$.

The fact that liquid Te is over-coordinated as compared with solid Te (or indeed

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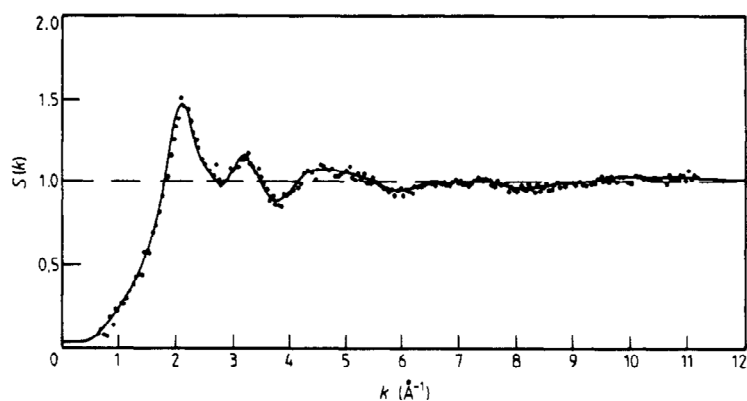


Figure 1. The structure factor for liquid Te at 520 °C.

with liquid Se) suggests, in the language of defect configurations (Street and Mott 1975, Kastner *et al* 1976), that C_3^+ defects are widespread in the melt. These defects will produce states in the gap in sufficient numbers to give rise to the near-metallic nature of liquid Te at temperatures close to the melting point.

Apart from the interest of liquid Te in its own right, Te frequently forms one element in a wide range of liquid semiconductors (Cutler 1977). When Tl, Ag or Cu are added to liquid Te, a variety of electrical behaviour occurs at low concentration. The addition of copper to tellurium hardly changes the conductivity until the concentration CuTe is reached, whereas silver decreases it by $\approx 35 \Omega\text{cm}^{-1}/\text{at}\%$ over most of the composition range up to Ag_2Te . The behaviour of Tl is intermediate between Cu and Ag. All three systems show a sharp minimum in the conductivity at the stoichiometric compositions Tl_2Te , Cu_2Te and Ag_2Te (Cutler 1977).

In order to throw further light on the basic physics of liquid semiconductors, a series of structural and electrical measurements have been undertaken on a wide range of alloy systems. This paper deals with the structure of two liquid alloys, of composition NiTe_2 and NiTe in the Ni-Te system; the companion paper (part II in the series) reviews the electrical properties of the same alloy system. The reasons for the choice of nickel as an additive to liquid Te will become apparent as the two papers are read. We have also

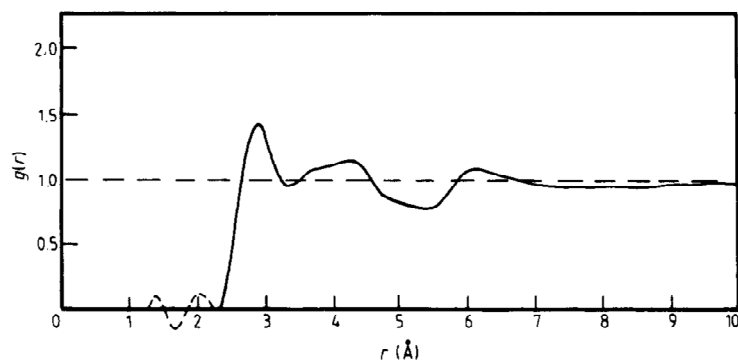


Figure 2. The pair correlation function for liquid Te.

Table 1

Isotope	Scattering length (10^{-12} cm)
^{Nat} Ni	1.03
⁶² Ni	-0.87
⁰ Ni (⁶² Ni/ ^{Nat} Ni mixture)	0.00
^{Nat} Cu	0.77
⁶³ Cu	0.67
⁶⁵ Cu	1.11
Te	0.54

re-evaluated some earlier data for liquid CuTe and have included new results in this present paper for the purposes of comparison.

2. Experimental method and results

The quantity that can be obtained from a single diffraction experiment on a liquid containing two species a, b (Enderby *et al* 1966) is the total structure factor $F(k)$ defined by

$$F(k) = c_a^2 f_a^2 (S_{aa}(k) - 1) + c_b^2 f_b^2 (S_{bb}(k) - 1) + 2c_a c_b f_a f_b (S_{ab}(k) - 1) \quad (1)$$

where c_a and c_b are the atomic fractions of the two species, f_a and f_b are the relevant scattering lengths and S_{aa} , S_{bb} and S_{ab} are the partial structure factors related to the pair correlation functions $g_{\alpha\beta}(r)$ by

$$S_{\alpha\beta}(k) = 1 + \frac{4\pi\rho}{k} \int (g_{\alpha\beta}(r) - 1) r \sin kr \, dr \quad (2)$$

where $\alpha, \beta = a$ or b and ρ is the total number density. It is now widely accepted that the crucial structural information about binary systems is contained in $S_{\alpha\beta}(k)$ (or some combination of them, like for example the $S_{CC}(k)$, $S_{NN}(k)$ and $S_{NC}(k)$ of Bhatia and Thornton (1970)) and that $F(k)$ itself may conceal some important physics.

To separate out $S_{\alpha\beta}(k)$ from $F(k)$, f must be changed systematically and the method we favour, neutron diffraction experiments on isotopically enriched samples, is particularly favourable for liquids that contain Ni. The method and its application have been fully described in the literature (Enderby *et al* 1966, Enderby and Neilson 1980) and need not detain us here.

The isotopes used in this work with their scattering lengths are shown in table 1. The negative scattering length for ⁶²Ni has two important consequences. Firstly it yields a set of well conditioned equations with a normalised determinant of $|A_n|^\dagger$ of 0.94 (see Edwards *et al* (1975) for a full explanation of the importance of conditioning). Secondly, it allows one to make a null mixture of Ni (the 'zero' nickel referred to in table 1) and thereby obtain $S_{TeTe}(k)$ directly from equation (2). The partial structure factors and the pair correlation functions for the two liquid alloys investigated are shown in figures 3–6.

† For molten NaCl where an excellent separation was achieved by isotopically changing the chloride ions, $|A_n|$ was only 0.03.

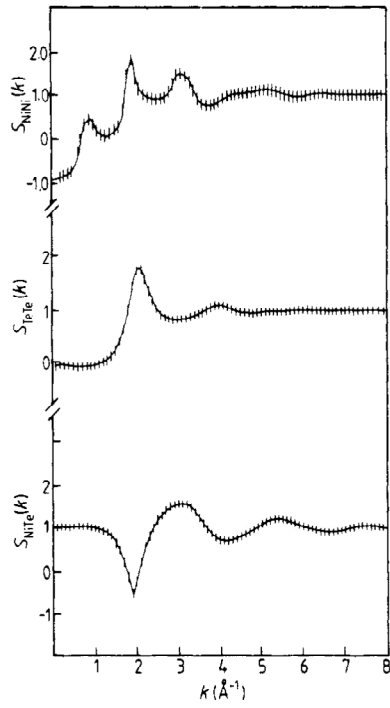


Figure 3. The partial structure factors for liquid NiTe_2 at 930°C .

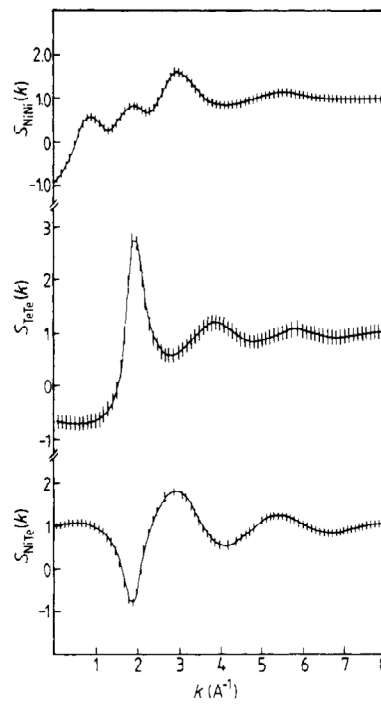


Figure 4. The partial structure factors for liquid NiTe at 930°C .

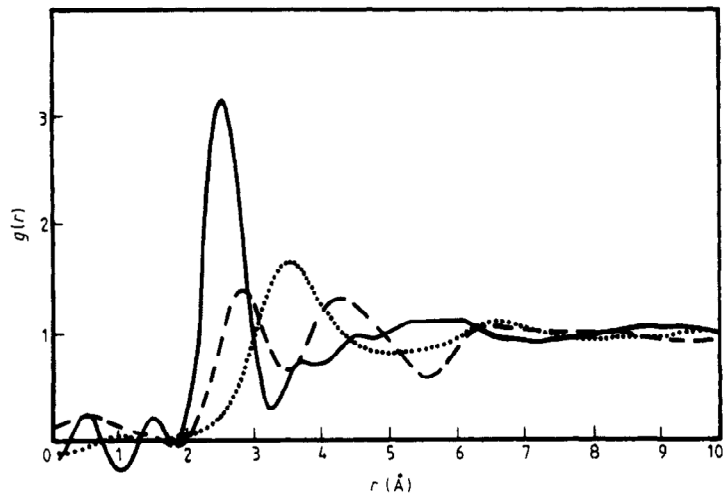


Figure 5. The pair correlation functions for liquid NiTe_2 . Full curve: g_{NiTe} ; broken curve: g_{NiNi} ; dotted curve: g_{TeTe} .

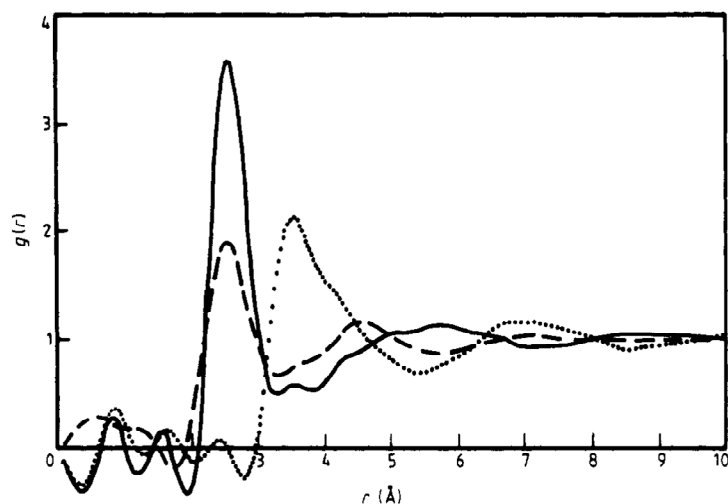


Figure 6. The pair correlation functions for liquid NiTe. Full curve: g_{NiTe} ; broken curve: g_{NiNi} ; dotted curve: g_{TeTe} .

3. Discussion

We begin by focussing attention on the k -space data for NiTe_2 shown in figure 3. At a k -value of $\approx 2 \text{ \AA}^{-1}$ the dip in the cross terms, $S_{\text{NiTe}}(k)$, corresponds to maxima in $S_{\text{NiNi}}(k)$ and $S_{\text{TeTe}}(k)$. This behaviour is a clear signal (Enderby and Neilson 1980) that electron transfer from the Ni to the Te has taken place and is a characteristic feature of ionicity in liquids (Edwards *et al* 1975, Evans and Telo da Gama 1980). We shall from now on refer to the nickel as the cation and the tellurium as the anion because this designation indicates the direction of electron transfer (Hulliger 1968). Ionicity is also evident in the structure factors for liquid NiTe but here, on account of the increased conductivity (see paper II in this series) the effect is partially damped out through electron screening (figure 4).

We now consider the structure in real space (figures 5 and 6); whereas ionicity tends to show itself at *large* distances in the form of charge cancellation and thereby gives rise to the characteristic *small-k* behaviour, short-range chemical effects are most evident in

Table 2. Average coordination numbers[†] and distances (M = Ni or Cu).

	Average coordination numbers			Distances (\AA)		
	M-M	Te about M	Te-Te	M-M	Te-M	Te-Te
NiTe	2.9 ± 0.4	4.5 ± 0.5	10 ± 3	2.54 ± 0.03	2.56 ± 0.03	3.56 ± 0.04
NiTe ₂	1.6 ± 0.4	4.6 ± 0.3	11 ± 3	2.81 ± 0.03	2.56 ± 0.03	3.55 ± 0.04
CuTe	3.6 ± 0.4	2.9 ± 0.3	10 ± 3	2.82 ± 0.03	2.55 ± 0.03	3.66 ± 0.05

[†] The apparent coordination number, particularly for ionic liquids, depends strongly on the method of calculation (Ohno and Furukawa 1981). The numbers reported here are the *average* obtained from methods (c) and (a) in the paper by Ohno and Furukawa which respectively yield high and low values for \bar{n} . The error reflects the spread in values derived by the two methods.

$g_{\alpha\beta}(r)$ for $r < 4 \text{ \AA}$. Of particular significance therefore are the coordination numbers, $\bar{n}_{\alpha\beta}$, and the position of the first peak, $\bar{r}_{\alpha\beta}$, and these quantities are summarised in table 2.

The first observation to make on these data is that both the Te–Te structure factor and pair correlation function are very different from those characteristic of pure liquid Te. At NiTe₂, for example, all traces of the unusual structural properties of liquid Te have been lost. It is particularly significant that \bar{r}_{TeTe} for the alloy is some 20% greater than in the pure liquid and \bar{n}_{TeTe} has changed from 3 to 11. These facts strongly support the notion that tellurium in Ni–Te alloys does indeed behave as an anion; in molten NaCl, for example, \bar{n}_{ClCl} is 13 and \bar{r}_{ClCl} is 3.8 Å. The sum of the conventional ionic radii $r_{\text{Ni}^{2+}} + r_{\text{Te}^{2-}}$ is 2.80 Å which is in reasonable agreement with \bar{r}_{NiTe} (2.56 Å). A final point to note is that $g_{\text{TeTe}}(r)$ is somewhat longer-ranged in liquid NiTe than in NiTe₂, the first minimum moving out of 5.40 Å from 5.10 Å. This behaviour is to be expected if tellurium exists in nickel-rich metals as Te²⁻.

If we focus attention on $g_{\text{NiTe}}(r)$ and $g_{\text{NiNi}}(r)$ we conclude that a nickel ion is, on average, surrounded by ≈ 4 Te²⁻ ions at 2.56 Å and ≈ 3 Ni²⁺ ions at 2.54 Å for NiTe. This local order provides the essential clue to the electrical behaviour to be reported in paper II of the series. The Te²⁻ ions form a close-packed structure in much the same way as Cl⁻ does in a range of molten chlorides (Biggin and Enderby 1981). However, in the molten-salt case once the radius ratio r_-/r_+ exceeds ≈ 2.4 essentially no cations can penetrate the first coordination shell (Biggin and Enderby 1981). By contrast, the cations in these alloys clearly do penetrate the first coordination shell and are able to form a threefold-coordinated structure with a Ni–Ni spacing sufficiently short to allow significant d band overlap. It is our view that the d character of nickel (and copper, see below) plays a crucial role in determining the bonding and electrical characteristics of these liquid tellurides.

4. Comparison with liquid CuTe

Enderby and Hawker (1972) reported the first preliminary results for liquid CuTe (see

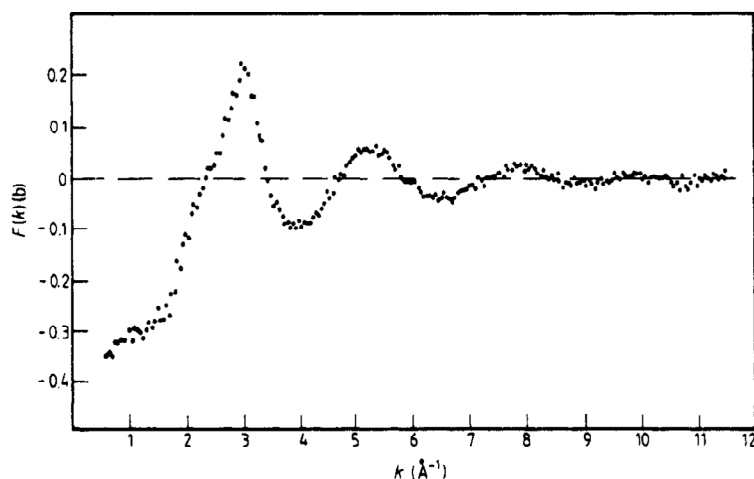


Figure 7. $F(k)$ for liquid ^{natural}CuTe at 800 °C.

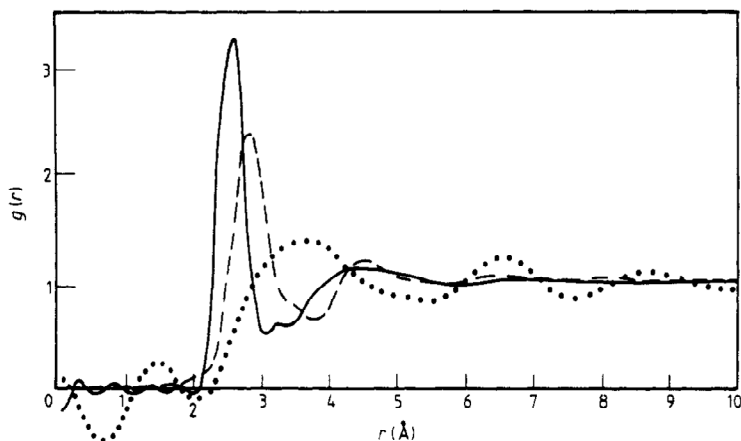


Figure 8. The pair correlation functions for liquid CuTe. Full curve: g_{CuTe} ; broken curve: g_{CuCu} ; dotted curve: g_{TeTe} .

also Hawker *et al* 1973, 1975). We have remeasured $F(k)$ for $^{\text{nat}}\text{CuTe}$ (figure 7) and have redetermined $g_{\alpha\beta}(r)$ by combining these new data with those obtained in the earlier studies. Although our numerical procedures for extracting $g_{\alpha\beta}(r)$ from $F(k)$ have become more refined over the years, the new results shown in figure 8 are in broad agreement with those reported earlier. These data confirm the tentative conclusions reached by Hawker *et al* (1973) and supported by the NMR measurements of Warren (1973) that charge transfer takes place in this alloy system. The form of $g_{\text{TeTe}}(r)$, though determined with less accuracy than the corresponding quantity in Ni–Te alloys, is consistent with a dense assembly of Te^{2-} ions. The structural parameters given in table 2 show that the structures of NiTe and CuTe are broadly similar. It follows that an explanation of the apparent differences in electrical behaviour must be sought in the electronic structure of the cation and this problem will be addressed in paper II of the series.

5. Conclusions

We have carried out a full structural analysis of liquid NiTe and NiTe_2 and have reconsidered the structure of liquid CuTe in the light of new experimental data and methods of numerical analysis. We conclude that in all three cases, substantial electron transfer takes place with the result that Te^{2-} ions exist as a close-packed assembly of anions. However, unlike the corresponding molten-salt case, direct cation–cation interactions are observed. We believe that these are manifestations of d band effects and allow a qualitative account of the electrical properties of these liquid alloys to be given.

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