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The structure and electrical properties of liquid semiconductors: II. Electron transport in liquid Ni–Te alloys

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Abstract. The resistivity and thermoelectric power of liquid Ni–Te alloys have been measured as a function of temperature over a wide range of compositions. It is shown that the resistivity of liquid Te can be halved by the addition of less than 10 at%Ni. Comparison with other liquid alloys containing Te is made and a unified model for the atomic and electronic structure is proposed.

1. Introduction

In paper I of this series (Nguyen *et al* 1982) the structural properties of liquid NiTe and NiTe₂ alloys were reported and a comparison was made with liquid CuTe. It was concluded that all three melts consisted of an anion subsystem composed of Te²⁻ ions and a cation subsystem in which the metal ions were coordinated to at least two other metal ions and three anions. In view of these data and the metallic character of NiTe₂ in the solid, the value quoted for the conductivity of liquid NiTe₂ of 1400 Ω⁻¹ cm⁻¹ (Ioffe and Regel 1960) seems rather low. Accordingly, a study of the conductivity and thermoelectric power as a function of temperature for liquid Ni_xTe_{1-x} for 0 < x < 0.67 has been undertaken. The object of this paper is to report on these data and to compare them with those of Dancy (1965) for liquid Cu_xTe_{1-x} (x < 0.5).

2. Experimental details and results

The experimental technique is similar to that first used by Howe and Enderby (1967). A four-point DC method was used to measure the resistivity ρ , and the thermoelectric power S could be measured on the same sample by observing the Seebeck EMF that developed at any two of these points in the presence of a small temperature gradient. The sample containment cell was fabricated from fused-quartz-capillary and normal wall tubing and electrical contact was made at each of four ultrasonically drilled holes via a molybdenum sheet and a graphite barrier plug. The temperatures at the four points

of contact were measured by chromel–alumel thermocouples and, in addition, the chromel lead served as the reference counter electrode in the thermopower measurements. The thermocouples and counter electrode were precalibrated in the manner described by Newport *et al* (1980); further calibration trials on post-experiment electrodes showed that no significant change had occurred. The tellurium was supplied in ingot form by Johnson–Matthey Chemicals with a batch purity of better than 99.99%, the nickel was obtained as sponge from Koch Light Laboratories with the same estimated purity, and the alloys were prepared under vacuum in sealed silica tubes. Subsequent chemical analysis indicates that the differential tellurium loss arising from the preparation and subsequent experiment amounted to less than 0.7%.

The experimental data for S and ρ are presented as function of temperature and composition in figures 1 and 2. In pure Te, both S and ρ are seen to vary non-linearly with temperature above the melting point; with the exception of $\rho(T)$ for Te–4at%Ni, the alloys exhibit a simple linear dependence over a corresponding temperature range. The resistivity of Te decreases markedly on addition of Ni and the negative temperature coefficient at the melting point has become positive at 5at%Ni. The data are summarised in table 1 where other published work on liquid Te is included for comparison.

3. Discussion

It is now generally agreed that the density of states at the Fermi energy $g(\epsilon_F)$ is substantial in pure liquid Te and is equivalent to approximately 2.5 electrons per atom (Warren

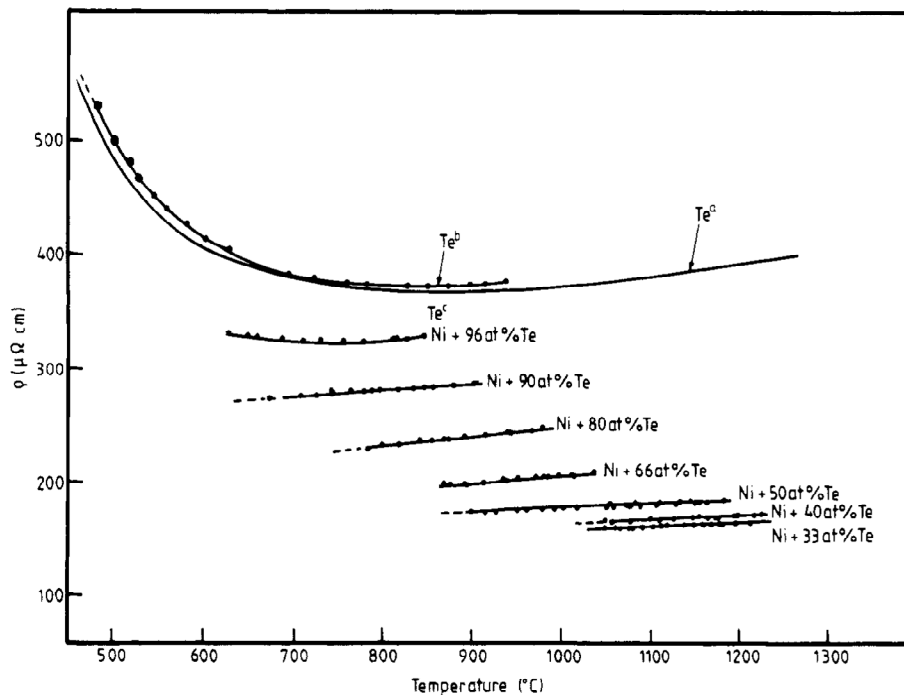


Figure 1. The resistivity of liquid Ni–Te alloys as a function of temperature. References are to (a) Baker and Webb (1974) (at 25 atmospheres), (b) present work and (c) Perron (1967).

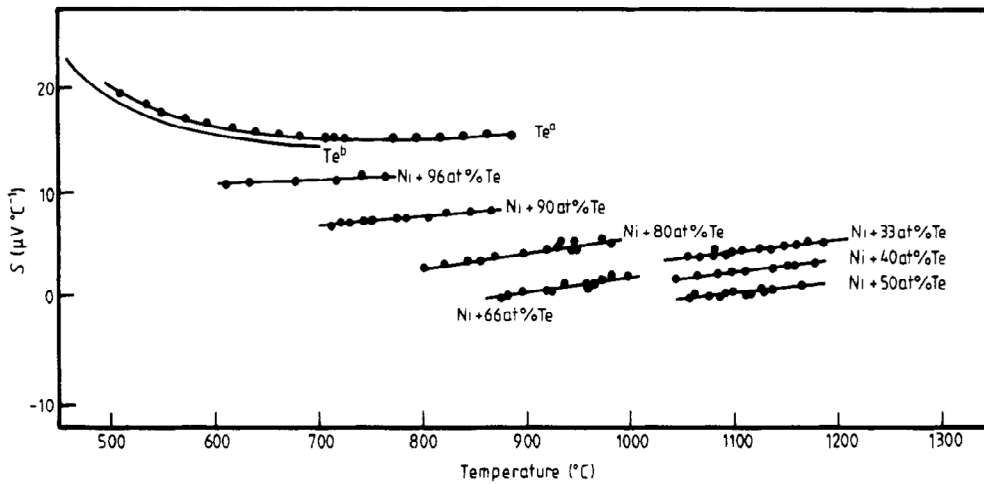


Figure 2. The thermoelectric power of liquid Ni-Te alloys as a function of temperature. References are to (a) present work, (b) Perron (1967).

1972). The precise origin of these states is controversial (Cutler 1977) but is intimately connected with over-coordination in liquid tellurium. According to Kastner *et al* (1976) for example, the density of defect states of the form C_3^+ is sufficiently high to give rise to the near-metallic nature observed in liquid Te at temperatures close to the melting point.

When the electropositive elements Ni and Cu are added to liquid Te, the structural evidence described in I shows that a radical change in the bonding characteristics occurs and that Te^{2-} ions are formed. The coordination number changes from 3 to 10 as

Table 1.

Sample composition (at %)	Liquidus temperature, T_L (°C) (f)	Resistivity at $T_L \pm 2\%$ ($\mu\Omega$ cm)	Resistivity at 900 °C ($\mu\Omega$ cm)	$(d\rho/dT)$ at $T_L \pm 0.07$ ($\mu\Omega$ cm K^{-1})	Thermopower at $T_L \pm 3\%$ ($\mu V K^{-1}$)	Thermopower at 900 °C ($\mu V K^{-1}$)
Pure Ni	1452	85.8		0.01	-38	
$Ni_{67}Te_{33}$	1022	162.7		0.03	4.2	
$Ni_{60}Te_{40}$	1015	168.5		0.03	2.3	
$Ni_{50}Te_{50}$	875	174.4	177	0.04	-1.7	-1.5
$Ni_{34}Te_{66}$	862	201.3	202	0.06	0.5	0.7
$Ni_{20}Te_{80}$	780	235.1	243	0.08	3.0	4.4
$Ni_{10}Te_{90}$	680	277.4	290	0.05	7.2	8.9
Ni_4Te_{96}	630	334.0	340	-0.13	11.2	12.1
Pure Te	449.5	570.0	376	-1.88	22.7	15.9
a		520.0			26.0	
b					23.0	
c		580.0			25.0	
d		565.0			23.0	
e		570.0	390.0			

(a) Epstein *et al* (1957).

(b) Cutler and Mallon (1962).

(c) Tièche and Zareba (1963), Busch and Tièche (1963).

(d) Perron (1967).

(e) Baker and Webb (1974).

(f) Klepp and Komarek (1972).

$x \rightarrow 0.5$ and the Te-Te separation increases from 2.91 to 3.56 Å. The mechanism by which the threefold 'defect' structure goes over to the close-packed assembly of tellurium anions is not understood but the essential point for this paper is that the localisation of electrons to form Te^{2-} ions together with the gradual elimination of the C_3^+ (or equivalent) sites would, all else being equal, increase the electrical resistivity by $\approx 10 \mu\Omega \text{ cm/at\%}$. In paper III of this series we shall show that when liquid Te is alloyed with electropositive metals in which the d band is well away from ϵ_F (as, for example, in Tl) this is precisely what happens. However, for metals like nickel and copper, d band effects become very significant. We believe that the model we now propose exposes the essential physics of liquid alloy semiconductors in which one component is a transition metal.

Consider figures 3 and 4 which compare the behaviour of the electrical resistivity and thermoelectric power when Ni and Cu is added to liquid Te. At first sight the effect of Ni and Cu on the electrical properties of Te seems very different; but we should first note that if Te^{2-} ions are indeed present in NiTe and CuTe, both cations have, in effect, reduced the resistivity (table 2). Moreover the presence of the d band is known to influence strongly the sign of the thermoelectric power in both of the current theories: directly through $g(\epsilon_F)$ (Mott 1972, Enderby and Dupree 1977) or indirectly through the scattering phaseshifts associated with the d levels (Dreirach *et al* 1972). The significant point of comparison is that the thermoelectric power of liquid copper is positive and that for liquid Ni is negative. In other words, the concentration dependence of S in both

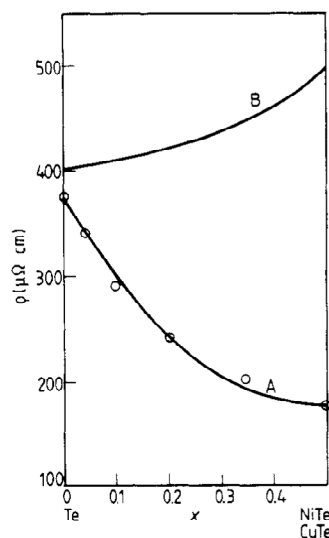


Figure 3. The resistivity of liquid (A) $\text{Ni}_x\text{Te}_{1-x}$ at 900 °C and (B) $\text{Cu}_x\text{Te}_{1-x}$ at 600 °C (Dancy 1965) for $0 \leq x \leq 0.5$.

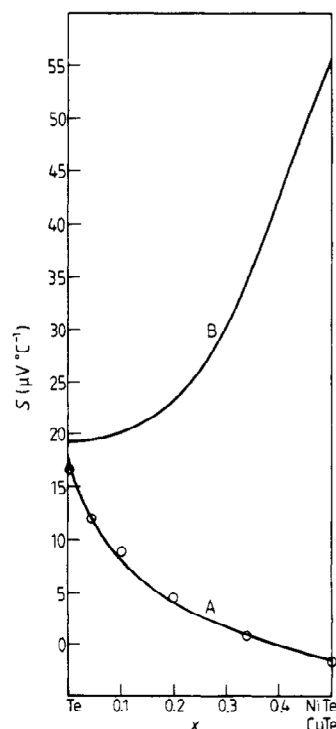


Figure 4. The thermoelectric power of liquid (A) $\text{Ni}_x\text{Te}_{1-x}$ at 900 °C and (B) $\text{Cu}_x\text{Te}_{1-x}$ at 600 °C (Dancy 1965) for $0 \leq x \leq 0.5$.

Table 2. $(\partial\rho/\partial c)_{c\rightarrow 0}$ for several solutes in liquid Te.

Solute	Temperature (°C)	$(\partial\rho/\partial c)_{c\rightarrow 0}$ ($\mu\Omega$ cm/at%)	Reference
Cr	800	+13	a
Mn	800	+13	a
Cu	800	-1	a
		+1	b
Fe	800	-4	a
Co	800	-4	a
Ni	800	-9	a
	800	-11	c

(a) Takeda *et al* (1976).

(b) Dancy (1965).

(c) Present work.

Cu–Te and Ni–Te reflects the electronic structure of the cation. A further point to note is that the temperature coefficient of resistivity is very small for both NiTe (figure 1) and CuTe (Dancy 1965). We therefore conclude that the coordination that characterises both Ni^{2+} and Cu^{2+} in the melt is sufficient to give an unfilled d band and, in accordance with the principles set out by Wilson (1972), electrons in this band are on the delocalised side of the Mott transition[†]. In this sense both liquid NiTe and CuTe are ‘metallic’ and the sign of the thermopower simply reflects the location of the Fermi energy with respect to the hybridised d band.

The model proposed above will not apply for $x \leq 0.2$ because the Ni–Ni overlap is insufficient to produce a d band of significant width. Evidence will be presented in a later paper to show that for small x , C_3^+ (or equivalent sites) coexist with those associated with Te^{2-} and the Te–Te near-neighbour distance is close to that for pure Te. It follows that the rapid changes in S and ρ must reflect an enhanced value of $g(\epsilon_F)$, presumably associated with a nickel resonance close to ϵ_F . We are unable to give a detailed description of this effect. It is, however, relevant to note that ‘ligand/metal mixing’ (Wilson 1972) is important in determining the width of the d band and hence the Mott boundary between conductors and insulators. (A striking example of this is afforded by metallic NiSe_2 and insulating NiS_2 ; the Ni–Ni distance is actually shorter in the latter, but the $p \rightarrow s$ band gap closes through the sequence $\text{O} \rightarrow \text{S} \rightarrow \text{Se} \rightarrow \text{Te}$ so that sufficient d/p mixing is possible in NiSe_2 to delocalise the electrons.)

For $x > 0.5$, ρ increases rapidly for Cu–Te and becomes a maximum at Cu_2Te . By contrast, Ni–Te continues its gradual progression to metallic behaviour. The presence of monovalent Cu^+ in the d^{10} configuration implied by the stoichiometry of Cu_2Te will lead to low conductivities; no such behaviour will occur for Ni–Te and the model therefore gives a natural explanation of the contrasting behaviour for $x > 0.5$.

Consider now the addition of Mn to liquid Te. According to the model, Te^{2-} ions will be created while the Mn^{2+} ions may overlap and form a d band. However, MnTe (in the solid) is a hard Mott insulator and it is unlikely that any small decrease in the Mn–Mn distance, or an increase in the coordination number, would be sufficient to

[†] In the solid state CuTe and NiTe are metallic (Hulliger 1968). For NiTe the cation–cation distance in the liquid is smaller than in the solid (2.54 Å compared with 2.68 Å). The reverse is true for CuTe (2.82 Å compared with 2.63 Å) and this probably accounts for the higher resistivity.

delocalise the d electrons. We therefore predict that liquid MnTe will have a low conductivity. On the same basis we predict that liquid CoTe and FeTe should have a conductivity comparable with liquid NiTe but that their thermoelectric powers should be considerably less negative. We also expect that liquid MgTe will have a low conductivity even though Mg^{2+} and Ni^{2+} are almost exactly equal in size. All these predictions will be tested in due course. Meanwhile it should be noted that Takeda *et al* (1976) have investigated the resistivity of dilute solutions ($x < 0.05$) for a range of transition metals in liquid Te. Their results, which are shown in table 2, are, as far as they go, in accordance with these predictions.

4. Conclusions

We have shown that nickel reduces the electrical resistivity of liquid Te and makes the thermoelectric power more negative. We believe that the d^8 configuration of Ni^{2+} , and its position with respect to the Mott transition is the basic explanation of these facts.

An extension of this approach to include Mott insulators and electropositive elements in which the d band can be safely neglected will form the basis of future work.

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