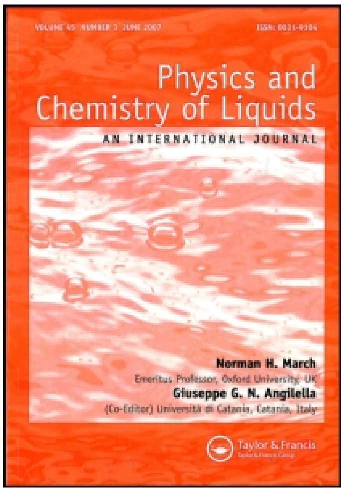

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Electrical, Magnetic, Optical, Thermodynamic, and Structural Properties of Liquid In-Te Alloys

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The paper reviews the experimental results of electrical, magnetic, optical, thermodynamic, and structural investigations of liquid In-Te alloys. The experimental results can be explained under the assumption of association—forming tendency at least for tellurium mole fractions larger than $c_{Te} \approx 0.3$. This value seems to be a limit concerning different interactions between indium atoms on the one hand and between indium and tellurium atoms on the other hand. For calculations the formation of In_2Te_3 associations is assumed.

I INTRODUCTION

In the case of simple liquids, including simple liquid metal alloys, the experimentally observed physical and chemical properties can be explained to some extent by assuming a model of randomly packed hard spheres. Such alloys do not have properties which vary distinct from those of the pure elements. On the other hand there is a lot of binary liquid alloys showing strong deviations of physical and chemical properties from ideal solution behaviour. Liquid In–Te alloys below to this type of systems. Our knowledge concerning electronic and atomic structure of such systems, especially concerning relations between electronic and atomic structure and observed deviations from ideal solution behaviour is still only weak. In the present paper electrical, magnetic, optical, thermodynamic, and structural properties of molten In–Te alloys are reviewed. The results are discussed with respect to conclusions on the electronic structure. On the basis of thermodynamic relations a consideration of the formation of associations is made and compared with conclusions from diffraction data concerning short range order.

II EXPERIMENTAL RESULTS

The phase diagram of the In–Te system is shown in Figure 1.[1,2,3] Two congruently melting compounds InTe unde In_2Te_3 are known. A miscibility gap is observed on the In-rich side. The electrical conductivity and thermoelectric power of liquid In–Te alloys have been extensively studied by Chizhevskaya and Glazov,[4] Zhuze and Shelykh,[5] Blakeway,[6] Shevshuk, Malinovski and Velikanov,[7] Nonomiya, Nakamura and Shimoji,[8] Tschirner, Popp, Wolf and Wobst[9] and Popp, Tschirner and Wobst.[10] About measurements of the Hall-coefficient in this system has been reported by Blakeway,[6] Andreev, Mamadaliev and Regel,[11] Andreev and Turgunov,[12] and Tschirner, Wolf and Wobst.[13] The Knight-shift of the alloy In_2Te_3 has been studied by Warren.[14] About measurements of the magnetic susceptibility of In–Te alloys has been reported by Fischer,[15] Fischer and Güntherodt,[16] Tsuchiya, Shibusawa and Tamaki[17] and Tsuchiya, Tamaki and Waseda.[18] The reflectance spectrum of liquid In–Te alloys has been measured by Trotter, Jr., Even and Thompson.[19] Thermodynamic investigations have been done by Maekawa, Yokokawa and Niwa,[20] Predel, Piehl und Pool[21] and Ninomiya,

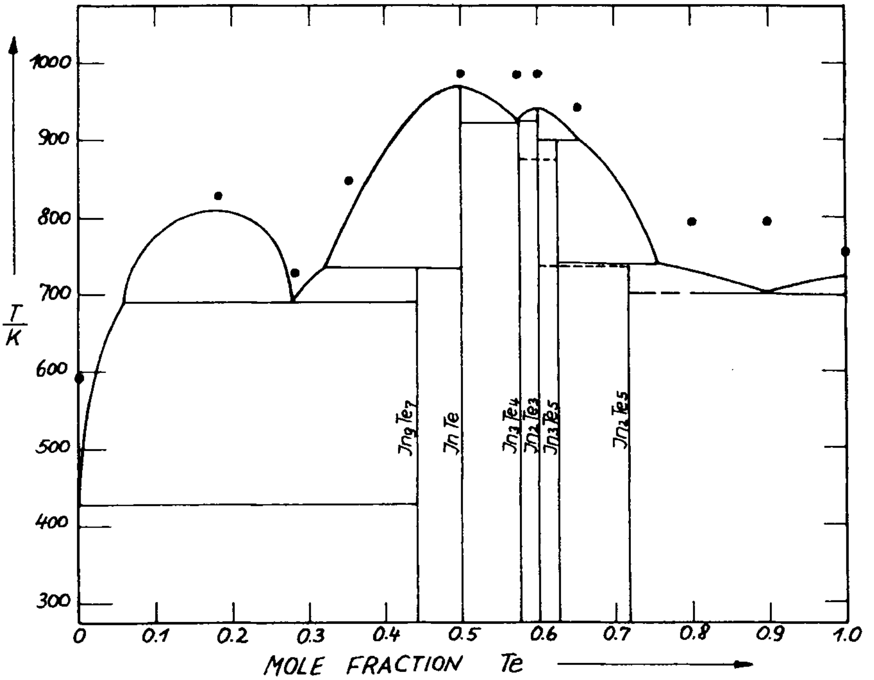
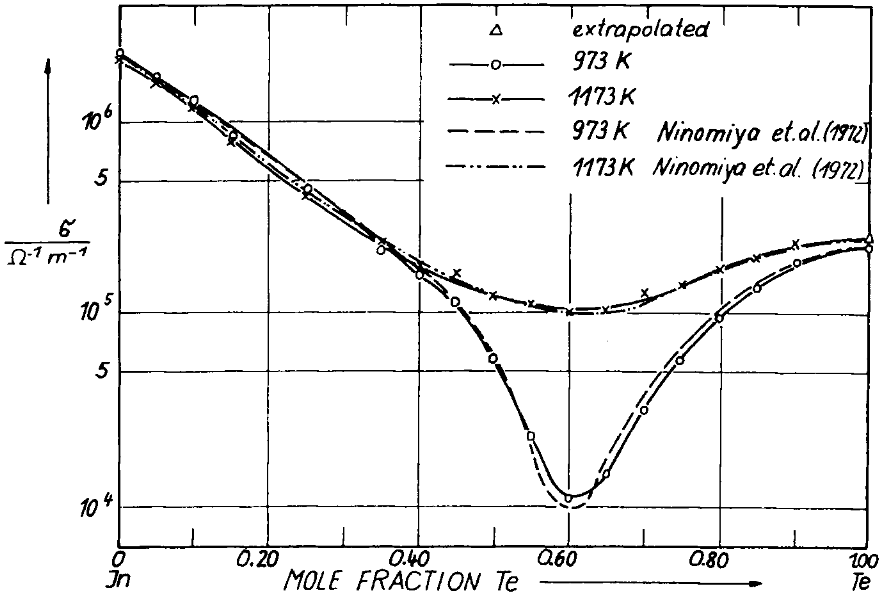


FIGURE 1 Phase diagram of the In-Te alloy system. The points mark the temperature and concentration of X-ray scattering experiments from Hoyer *et al.*[25]

Nakamura and Shimoji.[22] About scattering experiments has been reported by Poltavtsev,[23] Waseda, Tsuchiya and Tamaki[24] and Hoyer, Müller, Thomas and Wobst.[25]

The electrical conductivity, the Hall-coefficient and the thermoelectric power of liquid In–Te alloys are plotted versus tellurium concentration in Figure 2. For comparison some results from the literature are given. The electrical conductivity and the Hall-coefficient show a deep minimum and a maximum, respectively, at a mole fraction Te of $c_{Te} = 0.60$ corresponding to the congruently melting solid state compound In_2Te_3. In contrast, the thermoelectric power exhibits a strong maximum at a concentration between $c_{Te} = 0.65$ and $c_{Te} = 0.70$ and a weak maximum at about $c_{Te} = 0.43$.[7,8,10] This behaviour of the thermoelectric power significantly differs from that which has been observed in the liquid Ga–Te system (compare e.g. Ref. 26). The concentration dependence of the magnetic susceptibility shows a departure from a linear interpolation between the values of the two pure constituents, most striking near the composition In_2Te_3. This and a weak anomaly near $c_{Te} = 0.4$ can be seen from the measurements by Fischer[15] presented in Figure 3.



(a)

FIGURE 2 Electrical conductivity, Hall-coefficient and thermoelectric power of liquid In-Te alloys.

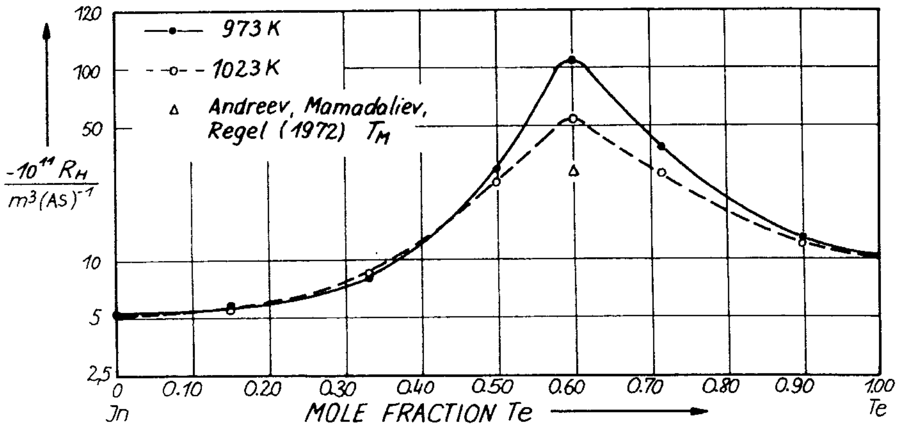


FIGURE 2(b)

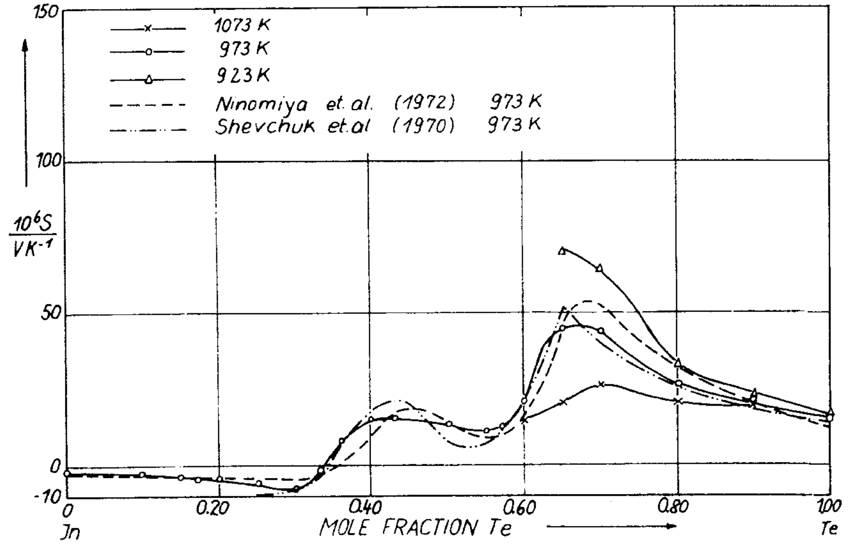


FIGURE 2(c)

The alloys with tellurium concentrations lower than $c_{Te} = 0.35$ show electrical conductivities in the range of $2 \cdot 10^6\ \Omega^{-1}m^{-1}$ to $2 \cdot 10^5\ \Omega^{-1}m^{-1}$. The temperature coefficient of the specific resistivity $d\rho/dT$ is weak positive. The magnitudes of the negative thermoelectric powers are comparable to those of typical metals. The temperature coefficient of the absolute thermoelectric powers $d|S|/dT$ are positive. At the melting point the Hall coefficient of the alloy $In_{0.85}\,Te_{0.15}$ is $R_H = -7.1 \cdot 10^{-11}\ m^3(As)^{-1}$. This value is higher by 1.3 times than that calculated from the model of nearly free electrons. In this

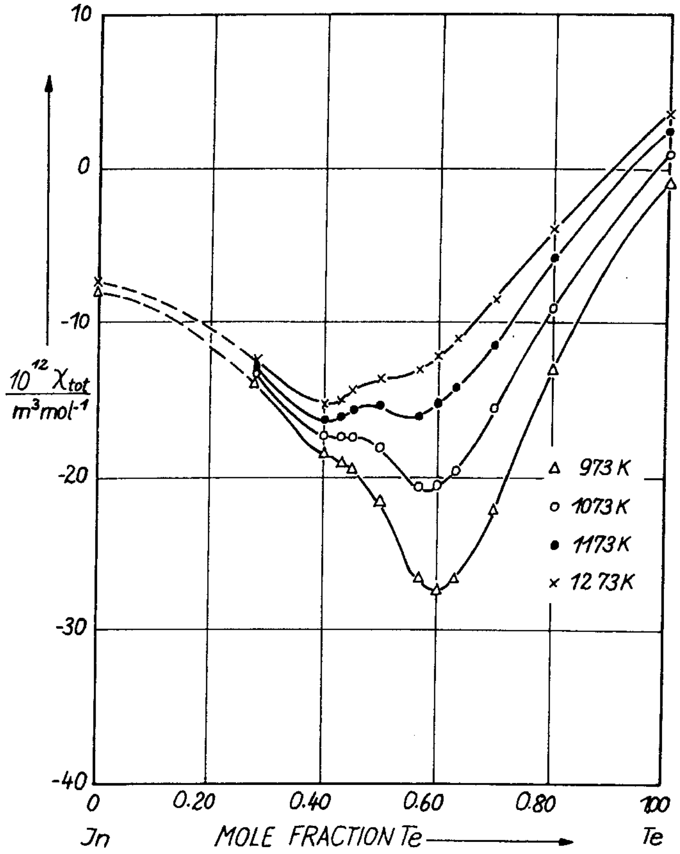


FIGURE 3 Magnetic susceptibility of liquid In-Te alloys at four temperatures (Fischer[15]).

concentration range the temperature coefficients of the magnetic susceptibility are comparable to those of pure indium. The thermoelectric power changes its sign near a mole fraction of $c_{Te} = 0.34$. In the concentration range between $c_{Te} = 0.35$ and $c_{Te} = 0.50$ the alloys exhibit electrical conductivities between $15 \cdot 10^4\ \Omega^{-1}m^{-1}$ and $5 \cdot 10^4\ \Omega^{-1}m^{-1}$. The values of the thermoelectric power are lower than $20 \cdot 10^{-6} VK^{-1}$ and the corresponding temperature coefficients $d(S)/dT$ are negative. The Hall-coefficient of the alloy $In_{0.50}$ was estimated to be $R_H = -31 \cdot 10^{-11}\ m^3(As)^{-1}$ at the melting point. With increasing temperature it decreases linearly. The temperature coefficient of the magnetic susceptibility $d(\chi)/dT$ shows a steep rise in the concentration range between $c_{Te} = 0.43$ and $c_{Te} = 0.50$.[15] In the concentration range between $c_{Te} = 0.55$ and $c_{Te} = 0.80$ the alloys exhibit typical liquid semiconductor behaviour, characterized by a linear dependence of $\ln\sigma$, $\ln R_H$

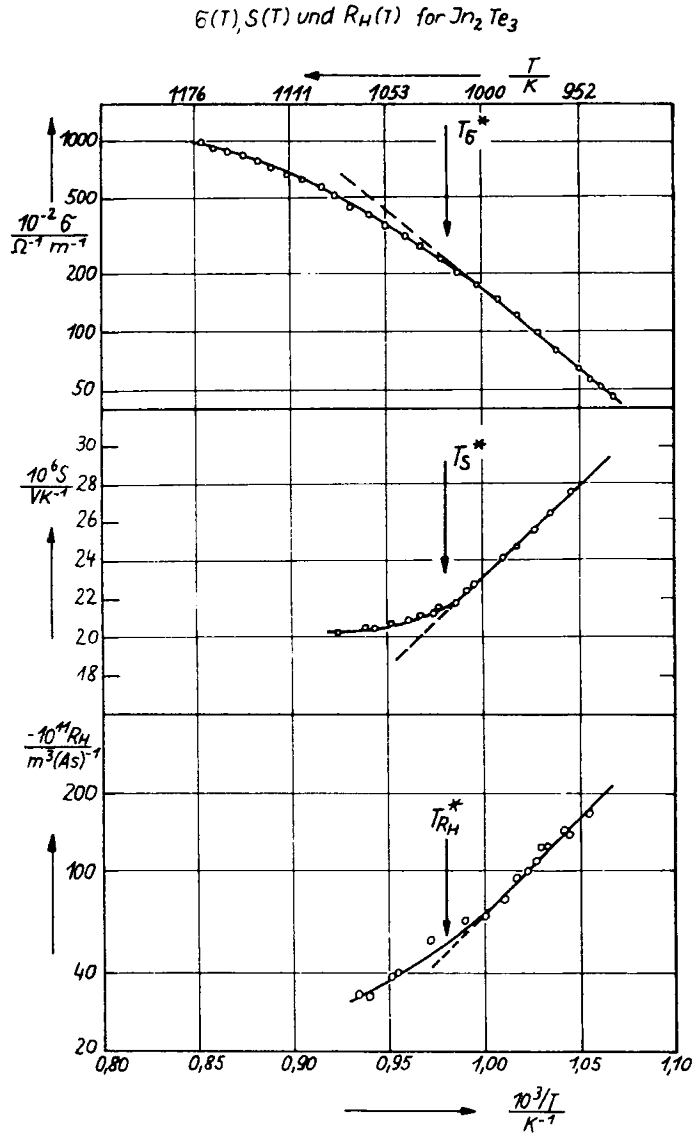


FIGURE 4 Conductivity, thermoelectric power and Hall-coefficient for the In_2Te_3 alloy according to Tschirner.[27]

and S as functions of the reciprocal absolute temperature $1/T$. Above the melting point they show conductivities lower than the minimum metallic conductivity of approximately $(2 \ldots 3) \cdot 10^4 \Omega^{-1} m^{-1}$. In Figure 4 these typical dependences of the transport properties are given for the alloy In_2Te_3.[27] The T^*-temperatures indicate the beginning of deviations from a linear dependence. They should be also a rough indication for the onset of the delocalization of states in the pseudogap. It should be noted that the estimation of T^*-temperatures cannot be done without a certain degree of arbitrariness. The temperature $T^*_{\sigma, R_H, S}$ of the In_2Te_3-alloy was estimated to be $T^*_{\sigma, R_H, S} = (1025 \pm {}^{40}_{25})$ K. Tsuchiya *et al.*[17] mentioned that there is the possibility to get some information about electron localization from the temperature at which the electron susceptibility vanishes. From their experimental data they obtained $T^*_\chi = 1118$ K. In comparison the temperature for the beginning of the delocalization of states at the Fermi level calculated from the NMR-measurements by Warren[12] is $T^*_K = 1075$ K.

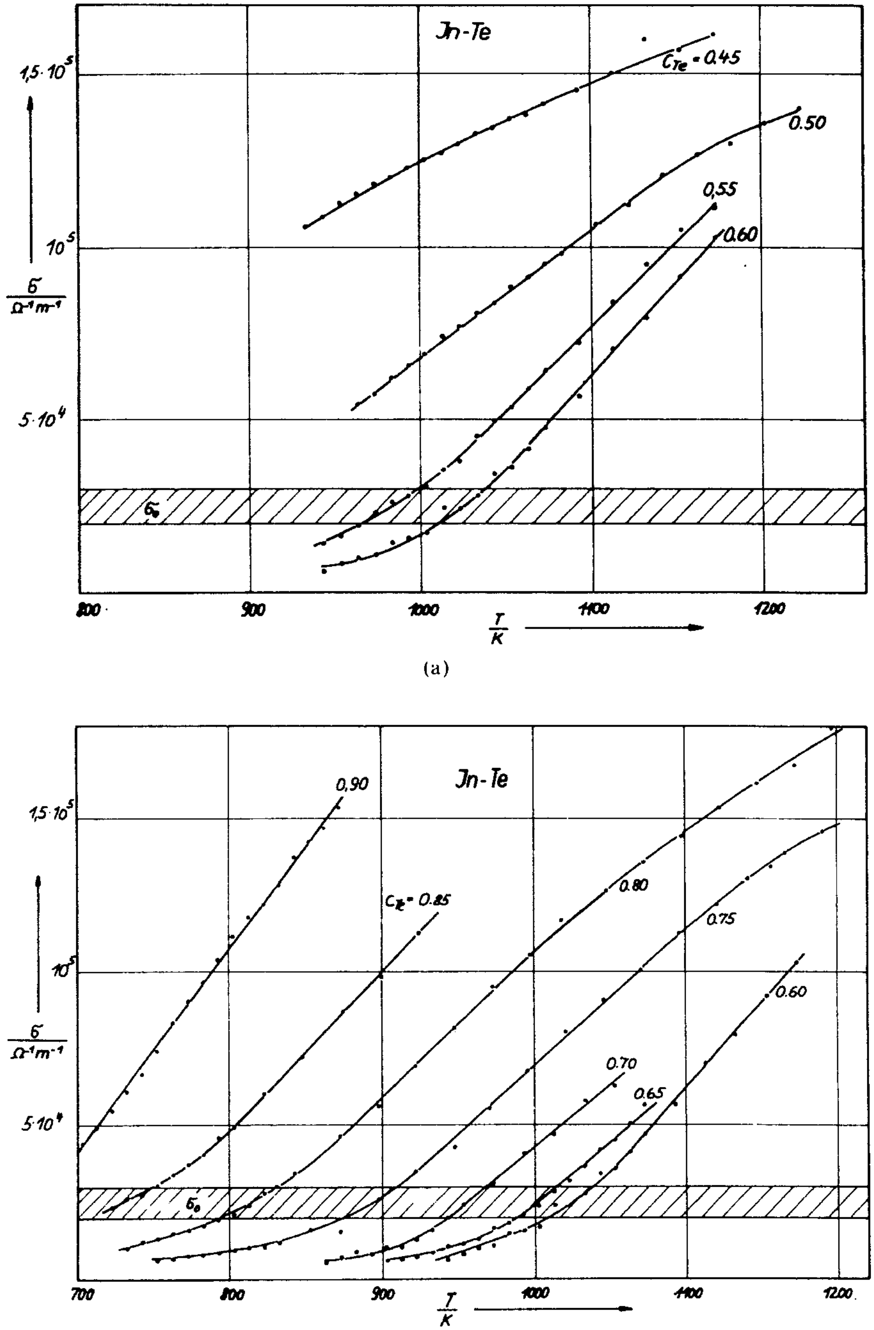
At the melting point the observed change of the Knight shift is only weak, but it shows a strong temperature dependence in the liquid state.[14] The temperature coefficient of the magnetic susceptibility of liquid In_2Te_3 is also large, e.g. in comparison to that of liquid Tl_2Te.[17]

The calculation of activation energies yields the values $E_\sigma(0) = (1.67 \pm 0.05)$ eV, $E_{R_H}(0) = 1.46 \pm 0.05)$ eV, and $E_S(0) = (0.10 \pm 0.05)$ eV. The value $E_\sigma(0) = 1.67$ eV does not agree with an activation energy published in a previous paper (Popp *et al.* Ref. 10). Recent measurements of σ both by means of an electrodeles field method and by means of a four probe method have yielded the higher activation energy $E_\sigma(0)$ and they confirm the result obtained by Ninomiya *et al.*[8] The Hall-coefficient of the composition In_2Te_3 at the melting point is $-200 \cdot 10^{-11} m^3 (As)^{-1}$ and it is not consistent with the value measured by Blakeway.[6]

The thermoelectric power depends weakly on temperature. At the melting point a value of $24 \cdot 10^{-6} VK^{-1}$ is found. The relatively low thermoelectric power can be explained assuming bipolar conduction.[27]

At all temperatures liquid pure Tellurium and tellurium rich alloys show conductivities higher than the estimated minimum metallic conductivity limit. At the liquidus temperature the Hall-coefficient of the alloy $In_{0.10}Te_{0.90}$ is $-10 \cdot 10^{-11} m^3 (As)^{-1}$ and the thermoelectric power was found to be $67 \cdot 10^{-6} VK^{-1}$, respectively.

The conductivity of the alloys plotted as a function of temperature is shown in Figure 5. It can be seen that the curves for the alloys in the concentration range between $c_{Te} = 0.55$ and $c_{Te} = 0.80$ and for conductivities lower than the minimum metallic conductivity depart significantly from linearity. The linear dependence of the conductivity on temperature in the range of metallic conduction with strong scattering can be described by the



(a)

(b)

FIGURE 5 Temperature dependence of conductivity of liquid In-Te alloys.

relation:

$$\sigma = \sigma_{\mathrm{In},(\mathrm{Te})}\,(T - T_0) \tag{1}$$

where σ_{In} is proportional to $(3.5c_{\mathrm{Te}} - 1)$ in the range of tellurium concentration $0.40 \leq c_{\mathrm{Te}} \leq 0.55$. This result confirms the proportionality calculated by Cutler.[28] The value σ_{Te} is proportional to $(1 - 1.0c_{\mathrm{Te}})$ for tellurium rich alloys. This result differs from the concentration dependence $(1 - 0.55c_{\mathrm{Te}})$ calculated by Cutler.[28]

Trotter, Even and Thompson[19] investigated the reflectance spectrum of four In–Te alloys with 0.33, 0.50, 0.60 and 0.70 mole fractions Te. The reflectance of In_2Te_3 yielded the lowest value and increased with increasing photon energy, contrarily to the other alloys.

The enthalpies of mixing of Indium and Tellurium in the liquid state have been measured by Maekawa, Yokokawa and Niwa.[20] The enthalpy goes steeply and almost linearly downwards, turning at a minimal value of $H_m = -33.5\ \mathrm{Jmol}^{-1}$ and a mole fraction Te $c_{\mathrm{Te}} = 0.60$. Predel, Piehl and Pool[21] estimated the integral molar free energy of mixing from vapour pressure measurements, and the enthalpy of mixing from calorimetric studies. Their data of ΔH_m differ greatly from those of Maekawa, Yokokawa and Niwa.[20] Predel, Piehl and Pool[21] have got a more flat minimum of enthalpy at about $c_{\mathrm{Te}} = 0.5$ mole fractions Te. The free energy and entropy of mixing in this system have been determined by means of the electromotive force method by Naoi, Nakamura and Shimoji.[22] Both the free energy and enthalpy of mixing show deep minima around the stoichiometric composition In_2Te_3 and a marked reduction of the entropy of mixing was found at the same concentration. Their data of the free energy of mixing also differ greatly from those of Predel, Piehl and Pool.[21] Poltavtsev[23] reported about X-ray diffraction experiments on the alloy $In_{50}Te_{50}$ at 1023 K. The radius of the first coordination shell was found to be 0,32 nm and the corresponding coordination number was determined to be 6.3. There is relatively poor agreement with the results given by Hoyer, Müller, Thomas and Wobst.[25] In Table I are given their results concerning the position of nearest neighbours (r^I) and the number of neighbours in the first coordination shell (N^I).

The measuring temperatures are indicated in Figure 1. On the Te-rich side the r^I-values show only weak concentration dependence, nearest neighbours are located at nearly the same distances. These distances are distinctly smaller compared with the position of nearest neighbours of alloys having In content higher than $c_{\mathrm{In}} = 0.65$. A similar behaviour can be seen for the corresponding coordination numbers.

Unfortunately Waseda, Tsuchiya and Tamaki[24] in their paper did not give values for N^I and r^I and therefore there is no possibility to compare qualitatively with the results from Hoyer *et al.*[25]

TABLE I

Position and coordination number of nearest neighbours r^I and N^I for liquid In-Te alloys according to Hoyer *et al.*[25]

c_{Te} mole fraction	r^I nm	N^I
1.00	0.295	3.0
0.90	0.290	3.0
0.80	0.295	3.6
0.65	0.290	3.4
0.60	0.287	3.4
0.57	0.290	3.5
0.50	0.295	4.6
0.35	0.312	6.1
0.28	0.315	6.6
0.18	0.320	8.1
0.00	0.320	8.6

In the case of the alloy $In_{0.40}Te_{0.60}$ Waseda, Tsuchiya and Tamaki[24] determined partial structure factors. A remarkable fact is the disappearing of the second peak in the partial structure factor S_{TeTe} (Q), (Q-length of the diffraction vector), raising the temperature. A similar distinct change is found in the corresponding partial pair correlation function g_{TeTe} (r), the peak near the distance of 0.37 nm disappears at 1353 K. Both peaks are characteristically for the structure of pure liquid tellurium.

III DISCUSSION

The observed small change of the Knight shift at the melting point of In_2Te_3 suggests that the local atomic arrangement is preserved to a large degree. The strong temperature dependence of the Knight shift indicates a temperature-dependent density of states. From the NMR-measurements and conductivity data Warren[14] has concluded that the liquid In_2Te_3-alloy must be called a liquid semiconductor in a certain temperature range above the melting point.

Tsuchiya *et al.*[17, 18] have supposed that the large temperature coefficient of the magnetic susceptibility is a distinct hint for the "dissociation" of "molecules". The delocalisation of electrons is connected with a change of the short range order. The disappearing of peaks in S_{TeTe} (Q) and g_{TeTe} (r) (Waseda *et al.* Ref. 24) for In_2Te_3 at approximately 1353 K seems to confirm this conclusion. Comparison of the measured susceptibility with the calculated values for ionic bonding and covalent bonding, respectively, leads to the conclusion that the interaction of atoms in liquid In_2Te_3 is determined by covalent bonding, at least in a temperature range above the melting point.[15] Cutler[28] assumed that the strong temperature dependence of the electrical properties is caused rather from the "dissociation" of "molecules" than from excitation of electrons. For Te concentrations lower than $c_{Te} = 0.33$ he supposed the bonding being ionic, for In_2Te_3 being covalent near the melting point. With increasing deviation from the stoichiometric composition In_2Te_3 or with raising temperature the bonding becomes more ionic. This model seems to confirm the concentration dependence of the factors $\sigma_{In,(Te)}$ in Eq. (1) as calculated by Cutler.[28] However it is not clear why $\sigma(T)$ should be linear in T rather than follows the usual Arrhenius formula. As Cutler suspected, the reason for that can be related to a strong effect of the configurational entropy on the bond equilibrium.

The results of the reflectance spectrum measurements from Trotter, Jr. *et al.*[19] tend to support the conclusion that in liquid In-Te alloys "molecular clusters" are present. The bonding system associated with these clusters leads to the existence of energy bands and a band gap. Trotter, Jr. *et al*[19] have assumed that the alloys with tellurium concentrations higher than $c_{Te} = 0.33$ behave as liquid semiconductors. Their results suggest also that the alloy $In_{0.30}Te_{0.70}$ being slightly "more semiconducting" than the alloy $In_{0.40}Te_{0.60}$. This behaviour seems to be noteworthy with respect to the concentration dependence of the thermoelectric power. Trotter, Jr. *et al.*[19] proposed that the valence band is composed of π_{Te} nonbonding states, but the conduction band is built up from σ^*_{In-Te} anti-bonding states only at temperatures near the liquidus and for $c_{Te} > 0.33$. At higher temperatures or smaller concentrations c_{Te}, the conduction band is built up from In p and s atomic states, lying at about the same energy as the σ_{In-Te} antibonding states.

The results and conclusions support the assumption that In-Te alloys form molecule-like associates in the liquid state. Up to now we have no experimental evidence, e.g. by means for far-infrared reflectivity or small-angle X-ray scattering, that molecule-like associates in the liquid state exist. But the results of thermodynamic studies and X-ray scattering allow us to show in a more indirect way that the assumption of In_2Te_3 associates is not in contrast to the experiments.

A strong indication for phase separation or formation of associates can be provided by the aid of the concentration dependence of the structure factors $S_{cc}(0)$ (zero wave-vector limit) introduced by Bhatia and Thornton.[29] Thompson, Ichikawa and Granstaff, Jr.[30] calculated $S_{cc}(0)$ from thermodynamic data. The minimum in $S_{cc}(0)$ is rather broad and somewhat displaced from the stoichiometric composition In_2Te_3. This displacement could be caused by the possible influence of molecule-like associations with different stoichiometry. Bhatia and Hargrove[31] and McAlister and Crozier[32] made an attempt to relate the concentration dependence of $S_{cc}(0)$ to simple models of association forming binary alloys based on conformal solution theory. A limiting case of this theory refers to situations with very strong tendency to form associations. Following Bhatia and Hargrove,[31] at the stoichiometric composition c_c the free energy of mixing must be $(G_M\ (c_c)) > 3$ RT for this case. The experimental value $(G_M\ (c_c)) \approx 4.4$ RT at the temperature $T = 1073$ K published by Naoi, Nakamura and Shimoji[22] fulfills this conditon. Therefore, we consider the liquid In–Te system consisting of two pseudobinary systems: In – In_2Te_3 and In_2Te_3 – Te. The free energy of mixing was calculated using Flory's approximation[33] for the entropy of mixing. A further simplifaction was made by assuming that the atomic volume of In- and Te-atoms is nearly the same and that the volume of In_2Te_3 associations is five times larger. The resulting expression for the free energy of mixing is:

$$G_M = -n_3g + RT(n_i \ln n_i + n_3 \ln 5n_3) + v_{i3}n_in_3, \qquad (2)$$

where the first term $(-n_3g)$ represents the lowering of the free energy due to the formation of the associations. The n_i $(i = 1, 2)$ are the mole fractions of "free" In- or Te-atoms. The mole fraction In_2Te_3 is n_3 and v_{i3} are the interaction energies. The mole fraction n_3 was calculated from the mole fraction of Te-Atoms:

$$n_3 = \frac{c_{Te}}{3} \quad \text{for} \quad 0 < c_{Te} \leq 0.6$$

$$n_3 = \frac{1 - c_{Te}}{2} \quad \text{for} \quad 0.6 \leq c < 1. \qquad (3)$$

The variation of the mole fraction n_3 as a function of tellurium content is shown in the upper part of Figure 6. For comparison, the cross indicates the mole fraction of associates calculated with the assumption that the interaction energies between the different species are zero. In the lower part of Figure 6 the calculated values of the free energy of mixing G_M (points) are compared with the experimental data. In order to estimate the unknown constants g, v_{13} and v_{23} the free energy of mixing G_M from Eq. (2) was fitted to the experimental data at tellurium concentrations 0.3, 0.6 and 0.8. This procedure yielded to $g = 196.4 \cdot 10^3$ J mol^{-1}, $v_{13} = -94.3 \cdot 10^3$ J mol^{-1}, and $v_{23} = -97.5 \cdot 10^3$ J mol^{-1}. The agreement between calculated curve and observed data is remarkably good as can be seen from Figure 6.

Based on equation for r' and N' Lamparter, Steeb, and Knoll[34] and Gabathuler, Steeb and Lamparter[35] developed a method to distinguish statistical distribution, preferred like or unlike arrangement of different atoms

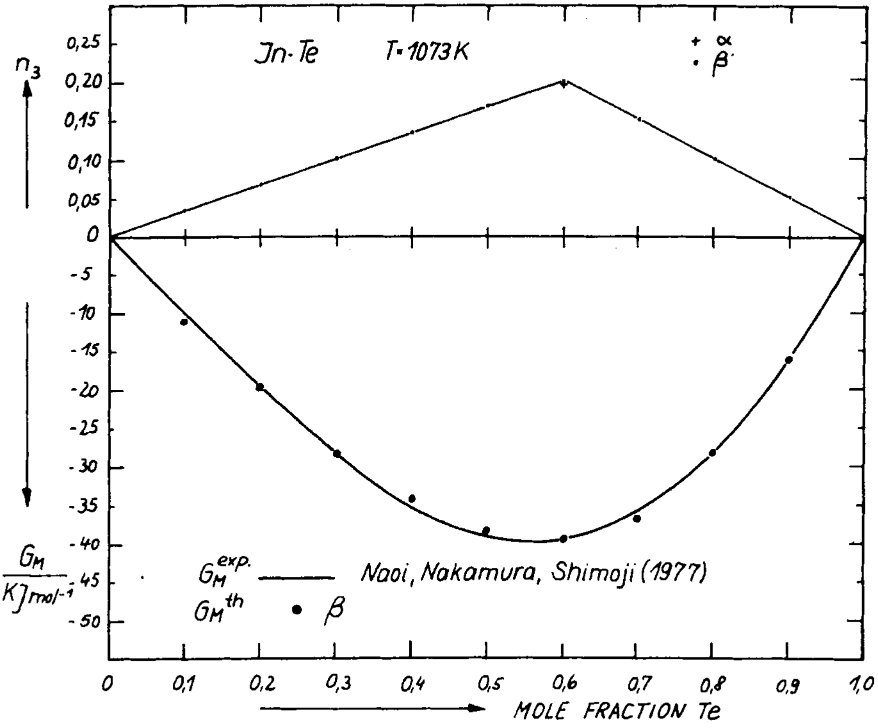


FIGURE 6 Concentration dependence of the mole fraction n_3 and of the free energy of mixing G_M.

in a binary metallic alloy melt. Following this way and using similar equations Hoyer *et al.*[25] compared the experimentally determined values r^l and N^l with calculated model values r^l_{St}, r^l_S, N^l_{St} and N^l_S. The subscripts St and S refer to model melts with statistical mutual distribution of A and B atoms and to model melts with preferred like coordination (segregation), respectively. From Figure 7 and Figure 8 it can be seen, that at low tellurium concentrations preference for like atoms pairs occurs. Above approximately $c_{\mathrm{Te}} = 0.3$ the alloys show association-forming tendency.

The electrical properties and the concentration dependence of the free energy of mixing lead to the assumption of the formation of $\mathrm{In_2Te_3}$ associations. We assume the alloys to be built up from two structures. One part of the atoms having short range order with atomic distances and coordination numbers as the solid state compound $\mathrm{In_2Te_3}$ and a second part showing statistical mutual distribution of the two atom types. Neglecting correlations between atoms arranged in "associates" and atoms arranged in the "free" part the mole fraction of associates has been estimated by Hoyer *et al.*[25].

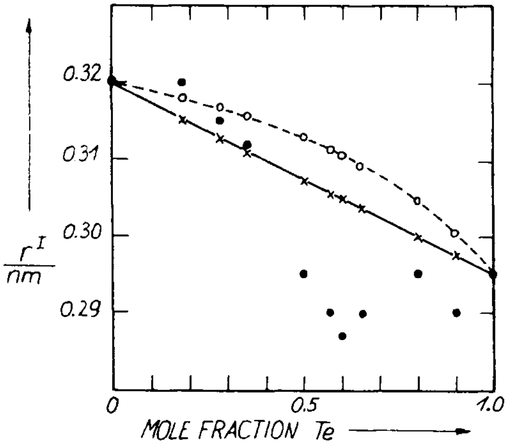


FIGURE 7 Experimentally determined values r^I and calculated values (Hoyer *et al.*[25]). × = r^I_{ST}—model value for statistical distribution; ○ = r^I_S—model value for segregation. ● = r^I—experimental values.

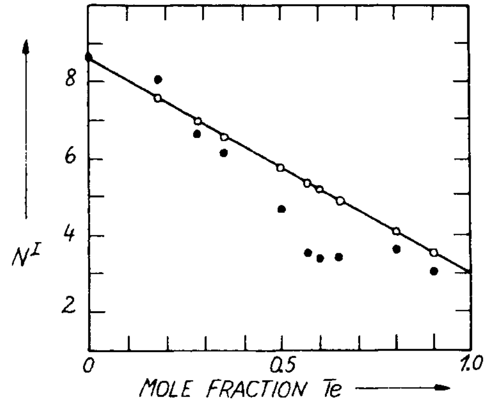


FIGURE 8 Experimentally determined values N^I and model coordination numbers (Hoyer *et al.*[25]) ○ = N^I_S, N^I_{St}—straight line. ● = r^I—experimental values.

The basis of this estimation are equations relating r^I and N^I to the assumed model. In Figure 9 the result is shown. Both, the values calculated from N^I and r^I, show a maximum association forming tendency at a mole fraction $c_{Te} = 0.6$. Considering the experimental uncertainties of r^I and especially the greater ones of N^I the calculated mole fractions agree well. Moreover there is reliable agreement between the results from thermodynamic considerations on the one hand and those from the structural results and estimations on the other hand at least in the neighbourhood of the stoichiometric composition In_2Te_7 and for tellurium rich alloys. However the thermodynamic models

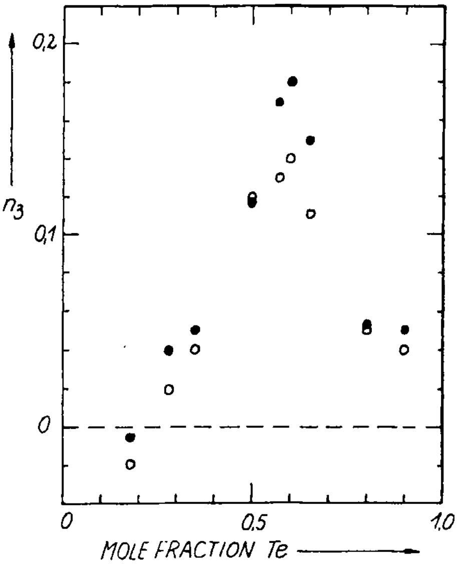


FIGURE 9 Mole fraction n_3 of associates (Hoyer *et al.*[25]). ● = n_3 calculated with the help of N'; ○ = n_3 calculated with the help of r'.

assume association forming tendency in the whole concentration range, from the diffraction experiments such tendency is only occurring at mole fractions tellurium higher than about $c_{Te} = 0.3$.

The macroscopic densities of the liquid alloys exhibit a significant departure from ideal solution behaviour (Thurn and Ruska[36]). In Figure 10 are shown macroscopic density values according to the paper of Thurn and

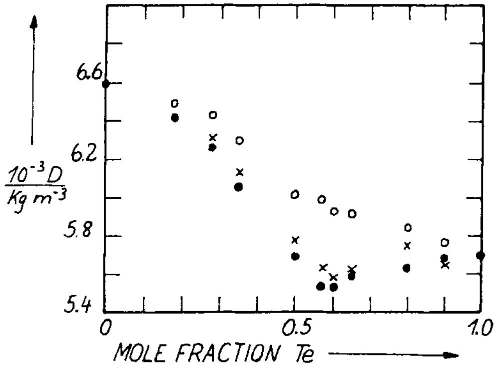


FIGURE 10 Experimentally determined densities (Thurn and Ruska[36]) in comparison with values averaged from the constituents and model densities assuming the formation of In_2Te_3 associates. ● = experimental values; ○ = average from the pure liquid elements; × = model values.

Ruska[36] in comparison to values averaged from the densities of the constituents. (The temperatures correspond to those of the scattering experiment from Hoyer *et al.*[25]). The deviation between these averaged values and the experimentally determined ones is rather large and reaches a maximum at In_2Te_3. Figure 10 also includes model densities calculated with the help of n_3 values estimated from N^I (according to Figure 9). For the calculation of the model densities we assumed the alloys to consist of two parts, one part having the density D^f and the second having the density D^a. The relative amounts are determined by the concentrations c^f and c^a of "free" atoms and atoms in "associations", respectively. c^f and c^a have been determined with the help of the relations:

$$\begin{aligned} c^f &= c^f_{\mathrm{Te}} + c^f_{\mathrm{In}} \\ c^a &= c^a_{\mathrm{Te}} + c^a_{\mathrm{In}} \\ n^3 &= \frac{c^a}{5} \\ c^a_{\mathrm{Te}} &= 1{,}5\, c^a_{\mathrm{In}} \end{aligned} \tag{4}$$

The last two relations follow from the stoichiometry of the assumed In_2Te_3-type associates.

The density D^f is the average from the densities of the pure liquid elements:

$$D^f = \frac{D_{\mathrm{In}} D_{\mathrm{Te}} (c^f_{\mathrm{Te}} A_{\mathrm{Te}} + c^f_{\mathrm{In}} A_{\mathrm{In}})}{c^f_{\mathrm{Te}} A_{\mathrm{Te}} D_{\mathrm{In}} + c^f_{\mathrm{In}} A_{\mathrm{In}} D_{\mathrm{Te}}} \tag{5}$$

$A_{\mathrm{Te,In}}$ – relative atomic mass

D^a was approximated from the density of the solid state compound In_2Te_3 (Zaslavskij and Sergeeva[37]) extrapolated to the temperature of the experiment. For this extrapolation we used the coefficient of linear expansion α given by Glazov and Regel[38] and the relation $\gamma \approx 3\alpha$ (γ-coefficient of volume expansion).

The model density D is then:

$$D = \frac{D^f D^a (c^f A^f + c^a A^a)}{c^f A^f D^a + c^a A^a D^f} \tag{6}$$

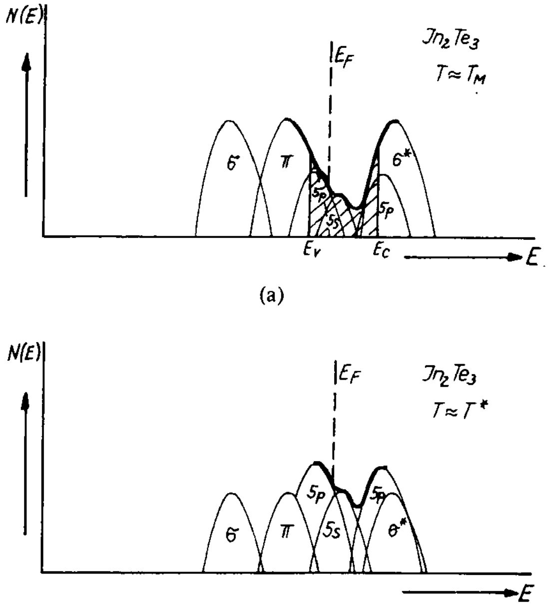
$A^{f,a}$ = average atomic mass of the "free" part and the associates, respectively

The much better agreement between the densities from this model and those from experiment supports the assumption of association-forming tendency in liquid In–Te alloys.

IV CONCLUDING REMARKS

The electrical, magnetic, optical, thermodynamic, and structural properties of liquid In_2Te_3 can be explained with the assumption that the melt contains In_2Te_3-associates. The interaction between the atoms of the associate is covalent. With increasing temperature the portion of these molecule-like associations decreases. This implies a distinct change of the density of electronic states and a transition to metallic conduction at strong scattering at higher temperatures.

A schematic representation of the energy bands and the density of states as a function of energy E is given in Figure 11. The dissociation rises the density both of In p and s and Te p atomic states in the pseudogap. At a temperature T^* all states at the Fermi energy are delocalised. For temperatures between the liquidus temperature and T^* the electrical and optical properties are governed by this pseudogap and the strong temperature dependence of the density of states. For all neighbouring alloys the portion of 'free' atoms increases and the electrical properties and their temperature dependence suggest the assumption that a pseudogap with localized states only exists between $c_{Te} \approx 0.55$ and $c_{Te} = 0.75$. It should be pointed out, that the existence of InTe associates was only excluded for simplicity not from physical



(a)

(b)

FIGURE 11 Schematic representation of the electronic density of states for liquid In_2Te_3.

points of view, although the experimental results give no hints for a such molecule-like association.

The results and conclusions support the assumption that liquid In-Te alloys with tellurium contents higher than $c_{Te} = 0.33$ contain already In_2Te_3 associates.

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VI Literature

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