Transport Processes in TlI and in the AgI-TlI-System

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The transport properties of TlI and of the system AgI–TlI were investigated by measuring the electrical conductivity, σ, and the electronic and ionic transport numbers.

A particularly high electronic conductivity was detected in β-TlI, while the α phase showed a predominant anionic contribution, as in TlCl and TlBr.

The intermediate compounds, $AgTl_2I_3$ and $AgTlI_2$, are silver ion conductors, but they exhibit low σ values.

A comparison with other poliiodides, with a high silver ion conductivity, is suggested on the basis of the crystal bond ionicity.

A number of physico-chemical properties of Tl and Ag halides were already studied and compared by Tubandt and Lorenz[1] and by Friauf[2]. The similarity observed between these two families of salts, noticeably pronounced in the case of the iodides (which also exhibit the common feature of allotropic modifications affectable by mechanical pressure[3–5] does not extend to the transport properties.

This is particularly true for AgI and TlI, as proved by the transport measurements reported in the present paper.

Experimental

A pellet obtained by pressing the yellow β-TlI powder (Fluka p. a.; impurities <20 ppm) showed a reddish surface colour corresponding to a partial $\beta \rightarrow \alpha$ transition and exhibited time dependent electrochemical properties; however, after two days annealing at 50 °C, it turned to the yellow colour and to the stable electrochemical properties of β-TlI. Therefore specimens were always annealed before use.

The electrical conductivity was measured on pellets obtained by pressing TlI powder between two silver powder layers. A recorder connected to an autobalancing Wayne Kerr bridge, mod. B 331, allowed to follow the signal change over the annealing period until stabilization and then to detect the conductivity behaviour with increasing temperature.

The electronic contribution was determined by suppressing the ionic part of the total electrical conductivity[6, 7] in a way quite similar to that employed by Vest and Tallan[8]: the pellet was adjusted between two graphite electrodes, to which a dc voltage (from an Amel mod. 551 potentiostat) lower than the decomposition potential of the salt, was established, while the current flow detected through a high sensitivity galvanometer Amel mod. 668 was recorded until a steady value, I_∞, was reached. Owing to the very low current signal an accurate screening of the experimental arrangement was required mainly for α-TlI specimens.

Measurements of the ionic transport numbers in TlI, t_{Tl} and t_I, were carried out by the Tubandt method on a three pellets arrangement clasped between two silver discs.

Results and Discussion

Transport Properties of TlI

The conductivity data on TlI samples were obtained either at stepwise stabilized temperatures or with a 2 °C/min rising temperature. Both methods gave closely similar and reproducible results, fitted by the empirical equation

$$\sigma = A \exp\{-B/T\}$$

where σ is the specific conductivity: for the α and β phase regions, $A = 1288$ and $0.992\ \mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, $B = 8600$ and 6500 K were respectively obtained.

Figure 1 shows the present results along with those by Phipps and Partridge[9] and by Morlin[10], the latter referring to single crystal samples. A satisfactory agreement is observed in the α-phase region, where the relatively small deviations may be due to an uncertainty in the cell constant values and to differences in the contact resistances. On the contrary wider discrepancies between our and Morlin's results are evidenced in the β phase region.

The $\beta \longleftrightarrow \alpha$ transition was recently proved to be not instantaneous by Samara[5] and Morlin[10],

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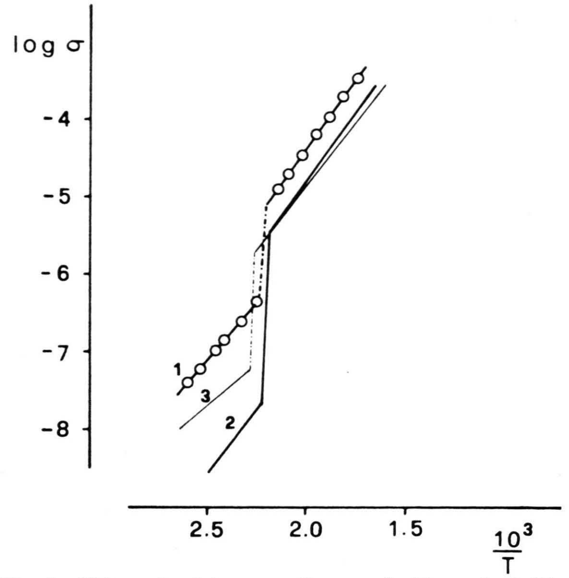

Fig. 1. Tl I conductivity according to: 1 this work, 2 Morlin, 3 Phipps and Patridge.

through dielectric constant measurements and TTT analysis respectively.

Our conductivity and DTA results allowed to state that the transition occurs at 182 – 185 °C and that, whenever a TlI sample undergoes a $\beta \longleftrightarrow \alpha$ transition, thermal annealing is compulsory in order to obtain a single phase specimen.

In fact it was possible to follow the transition process by observing the variation of the electronic contribution to the electrical conductivity, which is quite large for β-TlI, but negligible for the α phase.

In a typical experiment, a β-TlI sample showed at 160 °C a high and at 200 °C (after thermal stabilization) a negligible electronic conductivity: in the same sample, cooled down again to 160 °C, the electronic conductivity was initially still low, but slowly reassumed, after some hours annealing, a constant value as large as at the beginning of the cycle.

By plotting I_∞ vs V (the latter never exceeding 100 mV) straight lines were obtained, the slope of which corresponded to the electronic conductance, C_e. The ratio between C_e and the total conductance, C_t, obtained in a. c. with a 10^4 rad/sec frequency, gave the electronic transport number, t_e, with a good approximation.

Figure 2 shows some typical results from which it is apparent that $t_e = 0.6 \pm 0.1$ for β-TlI at $100 \div 185$ °C, whilst for the α-phase $t_e \approx 0$ at 200 °C.

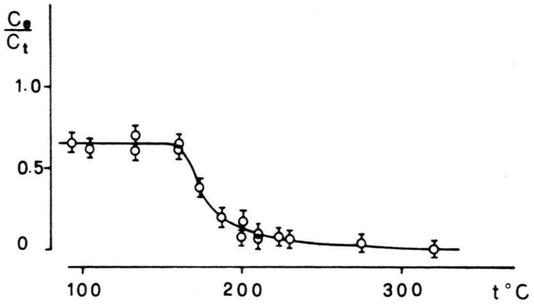

Fig. 2. $\beta - \alpha$ transition of Tl I detected by electronic conductance determinations; the ratio, C_e/C_t, between electronic and total conductance gives the electronic transport number.

As for ionic transport numbers in TlI, Table 1 reports the results of several determinations in α-TlI in the temperature range 206 – 255 °C. Measurements at higher temperatures were not reliable owing to the sublimation of TlI.

The t_{Tl} values were calculated on the basis of $\Delta P_{\text{cathodic}}$ and ΔP_{anodic}, which refer to the total weight variation of the compartement, i. e., electrode + adjacent pellet.

The data fluctuation and the narrow temperature range did not allow to recognize a particular dependence on temperature.

Taking into account the experimental difficulties of Tubandt transport number determinations on Tl halides [11], the given values of t_{Tl} must be considered correct within ± 15%.

Tab. 1. Tubandt transport numbers determinations on the cell +Ag/Tl I/Tl I/Tl I/Ag–. ΔP values are referred to 10 coulombs flowed through the cell.

Compartement	$T = 206$ °C	$T = 212$ °C	$T = 224$ °C	$T = 225$ °C	$T = 255$ °C
ΔP_{anodic}	+4.05 mg	+3.86 mg	+2.61 mg	+2.89 mg	+3.40 mg
$\Delta P_{\text{cathodic}}$	–4.21 mg	–3.51 mg	–3.44 mg	–2.65 mg	–2.10 mg
t_{Tl} from anode	26.5%	27.1%	30.7%	29.9%	28.4%
t_{Tl} from cathode	26.0%	28.1%	28.3%	30.6%	32.2%

The table figures show that in α-TlI, as well as in TlCl and TlBr, the principal carrier is the anion, although the Tl^+ contribution to the ionic conductivity, amounting to about 30%, is not negligible.

The ionic transport numbers in β-TlI, which should attain about 40%, could not be determined because the high electrical resistance would require too long periods or too high voltages for an electrolytic process to become able to give detectable weight variations.

The AgI-TlI System

The phase diagram, as determined by Berg and Lepeshkov [12], was substantially confirmed.

In Fig. 3 $\log \sigma$ vs $1/T$ is plotted for TlI, AgI and the peculiar compositions $X_{\text{AgI}} = 0.33$ and $X_{\text{AgI}} = 0.5$, corresponding to the two known intermediate compounds [13, 14].

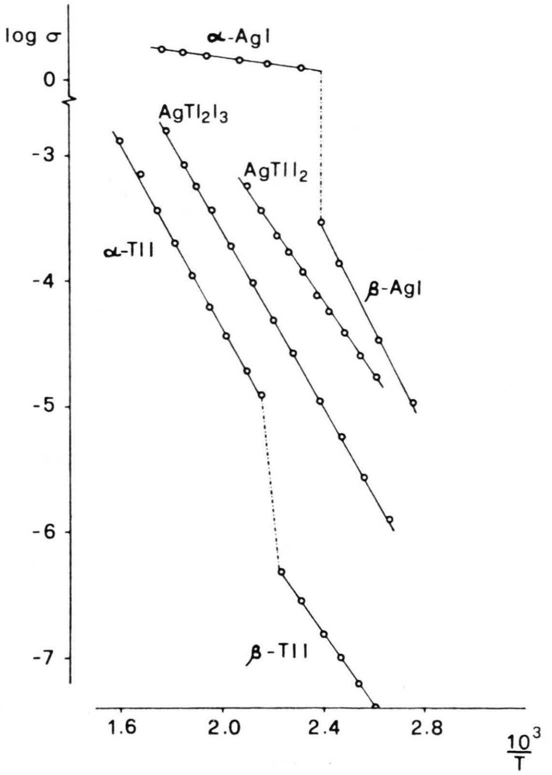

Fig. 3. Arrhenius plots of the specific conductivity for TlI, $AgTl_2I_3$, $AgTlI_2$ and AgI.

The latter were prepared by: either 150 hours annealing of proper powder mixtures at 190 °C; or coprecipitation with excess KI from aqueous solutions containing $AgNO_3$ and $TlNO_3$ in the ratios 1 : 2 and 1 : 1; or slow cooling of the melts and some hours rest at the freezing temperatures.

As for the first procedure, X rays analysis showed that the annealing time at 190 °C was critical for the complete formation of $AgTl_2I_3$ and $AgTlI_2$: e. g., only after a previous 150 hours annealing of the $X_{\text{AgI}} = 0.5$ powder mixture the peaks of AgI and $AgTl_2I_3$ vanished and a diffraction pattern was obtained showing only the $AgTlI_2$ peaks.

The not reported plots $\log \sigma$ vs $1/T$ showed a conductivity knee respectively at 145 °C (AgI $\beta \rightarrow \alpha$ transition) for $AgTlI_2$ and at 185 °C (TlI $\beta \rightarrow \alpha$ transition) for $AgTl_2I_3$, when the compounds were obtained by the first and second procedure, while such knees were completely absent (see Fig. 3) when the third procedure was followed.

In the latter case the intermediate compounds can be considered sufficiently pure for transport phenomena investigations.

Transport number determinations with the Tubandt method showed that in both compounds the silver ions must be considered as the only carriers; the results at 160 °C and 162 °C are reported in Table 2.

Tab. 2. Tubandt transport number determinations on the cells $Ag/AgI/AgTl_2I_3/AgI/Ag$ and $Ag/AgI/AgTlI_2/AgI/Ag$.

Compartement	$AgTl_2I_3$ $T = 160$ °C	$AgTlI_2$ $T = 162$ °C
ΔP_{anodic}	−21.20 mg	−11.80 mg
central pellet	+ 0.60 mg	+ 0.65 mg
$\Delta P_{\text{cathodic}}$	+19.05 mg	+12.25 mg
flowed charge	18 coul.	10.8 coul.
weigth variation in coulometer silver electr.	20.12 mg	12.07 mg
t_{Ag}	1	1

Final Remarks

The experimental results lead to the conclusion that the type of conductivity markedly varies passing from TlI to $AgTl_2I_3$, $AgTlI_2$ and AgI: the electronic conductivity, significant in β-TlI, vanishes in the intermediate compounds as well as in AgI; α-TlI shows a predominant anionic conductivity which is totally absent in the other compounds; the ionic transport number of Tl^+ falls to zero in $AgTl_2I_3$ and $AgTlI_2$ where the silver ions are the only carriers.

Furthermore, the latter compounds show a much lower conductivity than other silver ion conducting poliiodides.

This is consistent with the crystal structure of $AgTlI_2$ and $AgTl_2I_3$ [14] which is by no means an "open lattice" structure, as it seems to be required for a good ionic conductivity in solids.

The low conductivity of these salts can also be related to the theories for the crystal bond ionicity by Phillips and Van Vechten [15, 16] and by Tubbs [17], which predict in M^nX^{8-n} salts a 4-fold or a 6-fold coordination for the cations according to the fact that ionicities of the crystal bonds lie below or above a critical value (0.785 according to Phillips or 0.51 according to Tubbs). For both theories AgI performs ionicity just below and quite close to the critical value, so that on adding to AgI a highly ionic salt such as RbI, NH_4I or KI one obtains compounds where either coordination is possible; this results in many energetically equivalent positions for a silver ion and consequently in a very good conductivity [18].

This may not occur when TlI (whose ionicity is very low) is added to AgI.

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