EMF Measurements on the Thermocell $Ag(T_1)/AgI/Ag(T_2)$

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Thermal emf measurements have been carried out on AgI using reversible silver electrodes between 75° and 300 °C. A sharp change in the magnitude of the thermoelectric power (Θ) has been observed at 146 °C corresponding to the β to α phase transition. The results may be represented by the equations

$$\beta\text{–AgI:}\quad \theta = -\,[(0.351 \pm 0.032)\,(10^3/T) + 0.203 \pm 0.083]\,\mathrm{mV/K},\quad 70\text{–}146\,^\circ\mathrm{C},$$
$$\alpha\text{–AgI:}\quad \theta = -\,[(0.052 \pm 0.011)\,(10^3/T) + 0.531 \pm 0.031]\,\mathrm{mV/K},\quad 146\text{–}300\,^\circ\mathrm{C}.$$

From these the heats of transport of the Ag^+ interstitials and ions respectively in the two phases have been calculated to be $(0.351-h/2)$, h being the heat of formation of a Frenkel defect pair in β–AgI, and 0.052 eV, whereas the activation energies for conduction are 0.38 and 0.051 eV respectively. These results are compared with those of previous authors.

Introduction

The electrical conductivity of silver iodide is of the order of $10^{-5}\,\mathrm{ohm^{-1}\,cm^{-1}}$ at room temperature [1]. This compound undergoes a phase transition at 146 – 147 °C above which its ionic conductivity becomes abnormally high [2], i. e. of the order of $10^{0}\,\mathrm{ohm^{-1}\,cm^{-1}}$. This high temperature modification, technically known as α-AgI, has been put to a number of applications, particularly in solid state electrochemical cells [3–5]. It could not find commercial applications because its conductivity at room temperature is relatively poor. The structural determinations [6, 7] of both phases of AgI prompted workers in the field to develop electrolytes which may have the α-AgI type structure and corresponding conductivity at room temperature. Considerable success in this direction has been achieved in investigations on Ag_3SI, Ag_2HgI_4, MAg_4I_5 (M = K, Rb and NH_4), $Ag_6I_4WO_4$, $[(CH_3)_4N]_2Ag_{13}I_{15}$ etc. besides a few other salts which are not silver ion conductors. These solid electrolytes have ionic conductivities in the range 10^{-1} to $10^{-2}\,\mathrm{ohm^{-1}\,cm^{-1}}$ at room temperature. The highest conductivity ($0.25\,\mathrm{ohm^{-1}\,cm^{-1}}$ at 27 °C) has been found in $RbAg_4I_5$. All these electrolytes are prepared starting from AgI i. e. AgI is used as the mother salt.

Therefore, in the frame of our regular studies on high conductivity solid electrolytes [8–10], it was planned to study again the electrical conductivity and thermoelectric power (θ) of solid AgI. The electrical conductivity has already been studied by many workers [1, 2, 6, 7, 11, 12]. The thermoelectric power (θ) has also been studied [13–16], but in all cases but one [15] only above the phase transformation temperature (146 °C). Previous studies of the thermoelectric power of α-AgI show some disagreement concerning the temperature dependence [13–16], and only two points are included in the previous investigation [15] on β-AgI. The authors have chosen different approaches for analysing their results.

In this work, measurements of the electrical conductivity and thermoelectric power of both phases of AgI are reported. The results on θ for β-AgI are analysed using the thermodynamical treatment of Howard and Lidiard [17]. The same treatment, modified for a pure cationic conductor [8] with a cationically disordered structure (CDS) in contact with its cationic metal electrodes, has been applied on α-AgI. It is shown that in both cases θ is a linear function of $1/T$, the slope giving $1/e$ times $(q^*_{Ag^+} + h/2)$ and $q^*_{Ag^+}$ for β- and α-AgI respectively, where $q^*_{Ag^+}$ is the heat of transport of the Ag^+ ion, h is the heat of formation of a Frenkel defect pair in β-AgI and e is the electronic charge. The reliability of the obtained heat of transport in α-AgI is checked by comparing the activation energies of electrical conduction in cationically disordered solids with their corresponding heats of transport.

Experimental

99.9 percent pure AgI was used without further purification. The powdered sample was pressed into cylindrical pellets (area = 1.8 cm², thickness ~ 5 mm) using a steel die and a hand press (AMIL, India).

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The conductivity was measured with a systronics (India) conductivity meter operating at 2 kHz. Our previous cell [8] was used for the thermoelectric measurements. The temperature of the two surfaces of the pellet was measured by a pair of iron-constantan thermocouples welded to the back of the silver electrodes. A silver wire was welded to each silver electrode to be used as the lead for the thermoelectric voltage. The temperature difference across the silver electrodes was assumed to be negligible in comparison to the $15-20\,^{\circ}C$ temperature difference across the sample. The variation of the thermal emf with the temperature difference (ΔT) was found to be linear. All voltages were measured using a vernier potentiometer (OSAW, India) and a galvanometer as a null detector.

Results and Discussion

a) Electrical Conductivity

It was measured on the same pellet as the thermal emf. Table I gives the conductivity at a few temperatures. The activation energy as calculated from the linear plot of $\log\sigma$ vs $1/T$ has been found to be 0.38 eV for conduction of Ag^+ ion in β-AgI. According to recent measurements of Takahashi et al. [1], silver iodide is a mixture of the γ and β phases at room temperature. They obtained 0.33 eV and 0.41 eV for the activation energies of the Ag^+ ions in the γ and β phases respectively, and these values are thus compatible with our result. Since we did not have facilities for accurate measurements of the conductivity of α-AgI, we must in this case rely on literature data. While Takahashi et al. [18] report an activation energy of 0.025 eV, both Tubandt and Lorenz [2] and Kvist and Josefson [12] obtain 0.051 eV (mistakenly quoted as 0.10 eV by Rice and Roth [19] from Ref. [2] for the activation energy of the Ag^+ ion in α-AgI). Since these two studies show excellent agreement for both α-AgI and the melt, we consider their results as more reliable. These activation energies have been compared with heats of transport in Table II.

Table I. Electrical conductivity of AgI pellets (pressed at 2800 kg/cm²) at different temperatures.

Temperature [°C]	Conductivity [$Ohm^{-1}\,cm^{-1}$]
50	1.74×10^{-5}
70	$3.89\times-$
90	$7.94\times-$
110	1.51×10^{-4}
130	$2.69\times-$
150 (α-AgI)	~1.18

b) Thermoelectric Power

The final expressions for the homogeneous and heterogeneous thermoelectric power obtained by Howard and Lidiard [17] reduce, for pure cationic conductors in contact with their cationic metals (for example AgI in contact with Ag metal), to

$$\theta_{\mathrm{hom}} = -\frac{k\,T\,\mathrm{grad}\,n_{Ag^+}}{e\,n_{Ag^+}\,\mathrm{grad}\,T} - \frac{q^{*}_{Ag^+}}{e\,T} \tag{1}$$

and

$$\theta_{\mathrm{het}} = \frac{1}{e}\frac{\partial g_{Ag^+}}{\partial T} + \frac{k\,T\,\mathrm{grad}\,n_{Ag^+}}{e\,n_{Ag^+}\,\mathrm{grad}\,T} + \frac{k}{e}\ln(n_{Ag^+}/N) + (1/e)\,s^{Ag}_{Ag} \tag{2}$$

respectively, where T is the absolute mean temperature of the sample, n_{Ag^+} and N are the numbers of mobile Ag^+ ions and normal sites per unit volume respectively, $q^{*}_{Ag^+}$ is the heat of transport of the Ag^+ ion, g_{Ag^+} is the work required to bring a cation from a state of rest at infinity into a particular (but arbitray) interstitial position in the crystal at constant temperature and pressure and $s^{Ag}_{Ag^+}$ is the partial entropy of the Ag^+ ion in silver metal.

Adding Eqs. (1) and (2), we get the following expression for total thermoelectric power (θ)

$$\theta = \theta_{\mathrm{hom}} + \theta_{\mathrm{het}} = -\frac{q^{*}_{Ag^+}}{e\,T} + H \tag{3}$$

where

$$H = (1/e)\,[(\partial g_{Ag^+}/\partial T) + k\ln(n_{Ag^+}/N) + s^{Ag}_{Ag^+}]\,. \tag{4}$$

(a) θ of α-AgI: Equation (3) shows that thermoelectric power ($-\theta$) is linear in T^{-1} if H is independent of temperature. Concerning the second term in H, the low activation energy indicates that the number of Ag^+ ions (n_{Ag^+}) per unit volume in α-AgI is almost temperature independent. Also, the first and third terms in the expression for H are small and such that an increase of one of them is nearly compensated by a decrease of the other [8]. Thus the term H can be considered as temperature independent, though it is an approximation.

Our experimental plot of ($-\theta$) vs. $1/T$ (Fig. 1) is within experimental error a straigth line represented by the equation

$$-\theta = [0.052\,(10^3/T) + 0.531]\ \mathrm{mV/K}\ \text{ for } \alpha\text{-AgI}$$

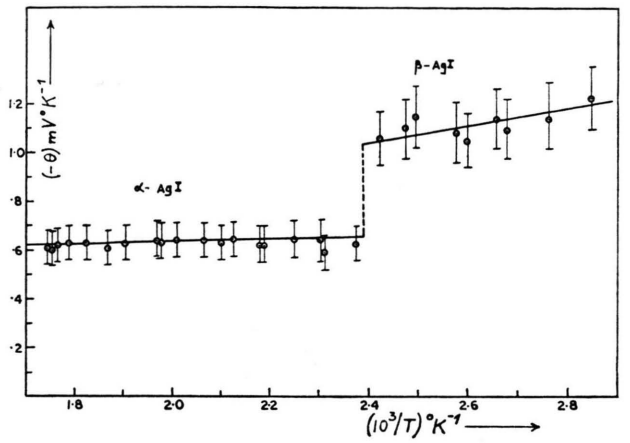

Fig. 1. Thermoelectric power of AgI as a function of inverse of absolute temperature.

which on comparision with Eq. (3) gives 0.052 eV for the heat of transport ($q^*_{Ag^+}$) of the Ag^+ ions in α-AgI. An inspection of Fig. 1 shows that the value of the thermoelectric power sharply changes from ~ 0.66 to 1.04 mV/K at 146 °C corresponding to the large change in activation energies for Ag^+ ion conduction in the two phases.

Earlier studies of α-AgI have given the following results:

Reinhold [13]: $\theta = -0.56$ mV/K, no detectable temperature dependence,

Kvist [14, **]: $-\theta = 0.144\,(10^3/T) + 0.346$ mV/K,

Mogilevski et al. [15]: $-\theta = 0.06\,(10^3/T) + 0.52$ mV/K

Magistris et al. [16]:

$$-\theta = 0.125\,(10^3/T) + 0.370 \text{ mV/K}.$$

The coefficient of the first term (indicating the slope of θ vs. $1/T$ plot) corresponds to $q^*_{Ag^+}$. The result, $q^*_{Ag^+}$, of Mogilevskii et al. is in good agreement with ours and that of Reinhold is in confirmity with these two studies, while the other two [14, 16] give considerably higher values for $q^*_{Ag^+}$.

The thermoelectric properties for a number of double salts possessing pure cationic conduction and 'CDS' have been studied, besides us, by Takahashi et al. [20] and Magistris et al. [16]. The only clear deviation from a linear $1/T$ relation for θ is found for α-Ag_3SI, which is known to possess appreciable electronic conduction at higher temperatures. In Table II experimental heats of transport are compared with the activation energies (ε) of electrical

** The recalculation done by the referee from Kvist's original data is gratefully acknowledged.

Table II. Heat of transport and activation energy for electrical conduction in some solid silver ion conductors.

Ionic conductor	Heat of transport (eV)	Arrhenius activation energy (eV)	Reference to data
α-AgI **	0.052 (this work) 0.144 (Ref. 14) 0.06 (Ref. 15) 0.125 +	0.051	2, 12
$RbAg_4I_5$	0.078 0.086 * 0.093 +	0.098	
KAg_4I_5	0.092 0.088 * 0.078 +	0.095	20
$NH_4Ag_4I_5$	0.093 0.058 +	0.095	
$Ag_6I_4WO_4$	0.14	0.16	8
Ag_2HgI_4	0.61 0.402 *	0.69	unpublished result of Takahashi et al.
$[(CH_3)_4N]_2^-$ $Ag_{13}I_{15}$	0.115 0.090 +	0.17	Shahi et al. *

* The values are taken from unpublished results of the authors.

\+ The values are taken from Reference 16.

** The heat of transport in α-AgI quoted from other references are those obtained according to analysis of the present work.

conductivity. These two entities tend to be equal. This is to be expected if the mobile cations are in a 'free ion like state' [19]. Rice and Roth [19] have recently developed a theory for 'super ionic conductors' which predicts that $-e\theta_{hom} = \varepsilon/T$. As can be seen from the relations quoted here, our study and three previous ones [14–16] agree fairly well at low temperatures (150 – 200 °C). At high temperatures (>200 °C) there is good agreement between Mogilevskii et al. and our values, extrapolated while two other studies give lower values for the thermoelectric power.

b) Thermoelectric Power of β-AgI

β-AgI can be considered as a normal salt much similar to AgCl and AgBr, therefore the term H in Eq. (4) will be temperature dependent as considerable energy is required to form a Frenkel defect pair. The number of interstitial silver ions (n_{Ag^+}) in β-AgI may be given by

$$n_{Ag^+} = (N N')^{1/2} \exp\{-h/2\,kT\}, \qquad (5)$$

where h is the heat of formation of a Frenkel defect pair and N' is the number of interstitial sites per unit volume available to an Ag^+ ion. Since N and

N' are of the same order of magnitude, one can obtain

$$(k/e)\ln(n_{Ag^+}/N) = -(h/2eT) \qquad (6)$$

from Eq. (5) for the second term in the expression of H [Eq. (4)], and consequently the expression for thermoelectric power [Eq. (3)] of β-AgI becomes

$$\theta = -\frac{1}{eT}(q^*_{Ag^+} + \tfrac{1}{2}h) + S, \qquad (7)$$

where

$$S = \frac{1}{e}\left[\left(\frac{\partial g_{Ag^+}}{\partial T}\right) + s^{Ag}_{Ag^+}\right]. \qquad (8)$$

The thermoelectric power in this case again is linear in T^{-1}, the slope of the θ vs. $1/T$ plot giving $1/e$ times $(q^*_{Ag^+} + h/2)$. Thus the considerable energy required for the formation of a defect increases the slope of the θ vs. $1/T$ plot by $h/2$. Our result for β-AgI (Fig. 1) is, within the experimental error, a straight line expressed by the equation

$$-\theta = [(0.351 \pm 0.032)\,10^3/T + 0.203 \pm 0.083]\ \mathrm{mV\,K^{-1}}$$

which on comparison with Eq. (7) gives $q^*_{Ag^+} = (0.351 - h/2)$ eV for the heat of transport of Ag^+ interstitials in β-AgI. Using the data of Lieser [21] for the heat of formation, $h = 0.68$ eV in β-AgI, $q^*_{Ag^+} = 0.011$ eV is obtained, which is very low in comparison to $\varepsilon_+ \cong 0.15$ eV [11, 21], the activantion energy of motion of Ag^+ interstials.

The only previous measurement of θ on β-AgI is due to Mogilevskii et al. [15]. They reported $Q^*_{Ag^+} = 0.45$ eV for the overall cation heat of transport in β-AgI (the overall cation heat of transport, $Q^*_{Ag^+}$, appearing in Holtan's treatment [16a] is related with the heat of transport, $q^*_{Ag^+}$, by the equation in its simplest form, $Q^*_{Ag^+} = q^*_{Ag^+} + h/2$). Thus the slope of the θ vs. $1/T$ plot [Eq. (7)] is directly $Q^*_{Ag^+}$, and our result is $Q^*_{Ag^+} = 0.351$ eV, which is 22% lower than their [15] value (0.45 eV), primarily because they have measured θ about 17% higher than we, and secondly because of the different methods of analysis. They [15] obtain $Q^*_{Ag^+}$ from Eq. (7) by substituting the calculated value for the sum S [Eq. (8)] and using the observed value of θ at a particular temperature T while we obtained it from the slope of the θ vs. $1/T$ plot. Thus our result seems likely to be more reasonable even when the absolute value of θ is not so accurate. However, the result of Mogilevskii et al. [15] ($Q^*_{Ag^+} = 0.45$ eV) for β-AgI would lead to $q^*_{Ag^+} = 0.11$ eV.

There have been extensive measurements [22–24] on the thermoelectric power of AgCl and AgBr. In AgBr Patrick and Lawson [22] and also Christy et al. [24] have found $\theta = -1.24$ and $-0.56\ \mathrm{mV\,K^{-1}}$ at 200 °C and 400 °C respectively, and in AgCl Christy [23] found $\theta = -1.50$ and $-0.75\ \mathrm{mV\,K^{-1}}$ respectively at the same temperatures. Thus in β-AgI $\theta = -1.04\ \mathrm{mV\,K^{-1}}$ at 146 °C, and its temperature coefficient (Fig. 1) obtained by us seems reasonable. Whereas the original calculation [22] gave $q_i^* = 0.017$ eV and $q_+^* = -0.385$ eV, a recalculation by Haga [25] gives $q_i^* = +0.07$ eV and $q_+^* = -0.52$ eV respectively for the heats of transport of Ag^+ ion interstitials and vacancies in AgBr. These heats of transport can be compared with the activation energies of electrical conductivity [26] $\varepsilon_i = 0.15$ and $\varepsilon_+ = 0.37$ eV. According to Christy [23] and Christy et al. [24] the heats of transport are strongly temperature dependent and it is difficult to get the individual heats of transport (interstitials and vacancies) without a knowledge of the entropy contribution from the change in lattice vibrational frequencies around the interstitials and vacancies.

Thus, the comparison of the results on β-AgI with those on AgCl and AgBr seems difficult, perhaps due to the fact that in AgCl and AgBr, though also containing Frenkel defects in their lattices, the mobilities of the interstitial cations and cation vacancies are comparable while in β-AgI the Ag^+ interstitials mobility is dominant [27, 30].

Note added in proof:

The authors became aware of the recent work of Cochrane and Fletcher [30] on β-AgI. They give somewhat different results to usuals although they also obtain $\varepsilon = 0.39$ eV, from σ measurements on thin β-AgI films, in good agreement, as expected, with ours (0.38 eV). They report the heat of formation $h = 0.60$ eV which gives $q^*_{Ag^+} = 0.051$ eV (a more reasonable value as compared to that of AgBr [22, 25]) for the heat of transport of Ag^+ interstitial in β-AgI.

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