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## The specific heat of the solid electrolyte system CuI–AgI

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**Abstract.** The specific heat for AgI-doped CuI has been measured by the method of differential scanning calorimetry. Anomalous specific heats were observed around the transition temperature from non-superionic to superionic phases. These were well explained in terms of the Schottky-type excess specific heat.

### 1. Introduction

From the thermodynamic point of view, the enthalpies, entropies and specific heats of the so-called superionic conductors around the temperature of the transition to the superionic phase have been measured by several authors (Nölting *et al* 1969, Johnston *et al* 1969, Jost and Kubaschewski 1968, Okazaki and Takano 1985). In the superionic phases, a large amount of excess specific heat has been seen in addition to the Dulong–Petit value, and also there is a tendency for  $dC_p/dT$  to be less than zero. These phenomena could be caused by a large degree of cation disorder.

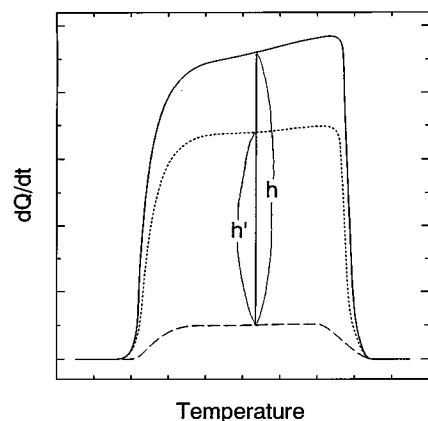
For the AgI–CuI pseudo-binary system, the ionic conductivity in the high-temperature phase or the superionic phase is very large. Because of the high degree of cation disorder, the specific heats for this system are expected to indicate an anomalous behaviour. Nölting (1964) has measured the specific heat for this system and  $dC_p/dT < 0$  was observed for the copper-rich region in its superionic phase.

In order to understand the thermodynamic properties of this system, qualitatively and quantitatively, the specific heats were measured from room temperature to the melting temperature by using differential scanning calorimetry (DSC) and the anomalous specific heats obtained were analysed in terms of a model of Schottky-type excess specific heat. The analysed results were connected with the ionic conduction mechanism.

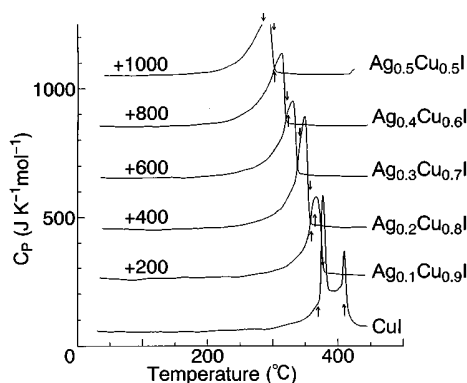
### 2. Experimental method

Specimens on which to measure specific heats were prepared by co-melting of appropriate amounts of AgI and CuI.

In the measurement of specific heat by DSC, the accuracy is not too high in comparison with that of adiabatic calorimetry and/or the AC calorimetry; however, it may be sufficient for one to obtain the essential features of the thermochemistry around the temperature of the transition to the superionic phase for the present system. Thus, we have measured specific heats of the present system by using the DSC apparatus Rigaku DSC8270B. The



**Figure 1.** The temperature dependence of the thermal absorption by an empty container (the dashed line), a specimen together with the container (the solid line) and a standard material together with the container (the dotted line).



**Figure 2.** The specific heats of  $\text{Ag}_x\text{Cu}_{1-x}\text{I}$  ( $0 \leq x \leq 0.5$ ),  $C_p$ , as functions of the temperature. The base lines are separated by  $200 \text{ J K}^{-1} \text{ mol}^{-1}$  from each other. Arrows indicate the transition temperature estimated from the phase diagram (Nöling 1964).

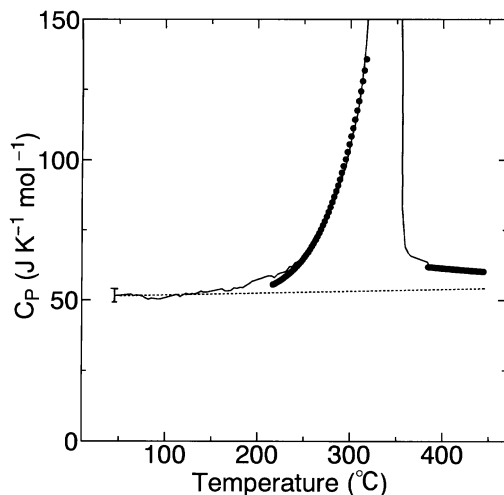
**Table 1.** The composition dependence of the energy required for the transfer,  $h_{C_p}(J)$ , in the temperature regions before and after transition. For comparison, the heats of enthalpy,  $h_\sigma(J)$ , obtained from the conductivity measurements (Kusakabe *et al* 1996a) are also listed.

$x$ in $\text{Ag}_x\text{Cu}_{1-x}\text{I}$	0	0.1	0.2	0.3	0.4	0.5
Before transition						
$h_{C_p}$ ( $10^{-19}$ J)	2.7	3.0	2.6	2.4	2.7	2.6
$h_\sigma$ ( $10^{-19}$ J)	2.7	2.7	2.7	2.6	2.6	2.6
After transition						
$h_{C_p}$ ( $10^{-19}$ J)	0.38	0.32	0.27	0.22	0.16	0.14
$h_\sigma$ ( $10^{-19}$ J)	0.43	0.41	0.38	0.35	0.32	0.29

principle for measuring specific heat is described elsewhere (O'Neil 1966). Figure 1 shows the temperature dependence of the thermal absorption by an empty container (the dashed line), a specimen together with the container (the solid line) and a standard material together with the container (the dotted line). In these measurements, the specific heat  $C_p$  for the specimen is given by

$$C_p = \frac{m'h}{mh'} C'_p \quad (1)$$

where  $m$  and  $m'$  are the mass of the specimen and that of a standard material,  $h$  and  $h'$  are the net energy fluxes counted from the dashed line, and  $C'_p$  is the specific heat of the standard material.  $\alpha\text{-Al}_2\text{O}_3$  is used as the standard material because its specific heat can be measured with a high accuracy. The  $C_p$ -value of  $\alpha\text{-Al}_2\text{O}_3$  (Castanet *et al* 1985) was used for the calculation of the specific heats. The difference in mass between the specimen container and the reference one has been corrected for. Before measurement, the specimen in the sealed container was annealed. All measurements were performed via a heating process. In addition, to achieve the high accuracy for the specific heat, it was measured by a stepwise heating method (Katayama *et al* 1986). The present DSC instrument is designed so as to avoid thermal delay by ensuring that the heat capacity of the heater and



**Figure 3.** The observed specific heat of  $\text{Ag}_{0.2}\text{Cu}_{0.8}\text{I}$  (the solid line). The solid circles indicate the specific heats estimated by using the parameters listed in table 1 and equations (4) and (5). The dotted line shows the specific heat extrapolated from the specific heat at lower temperature where there is no excess specific heat.

the thermal resistivity are very small. The thermal delay due to the thermal conductivity must be affected if the bulk size is large, and if the heating rate is too fast such a delay is inevitable. However, the present experiment was carried out under the condition of a slow heating rate of  $5\text{ }^\circ\text{C min}^{-1}$  and the error bar based on the above delay is quite small. The accuracy is within about 5% as was determined by comparing the two known standard samples and is also recognized by repeating measurements.

### 3. Results and discussion

Figure 2 shows the specific heat obtained for  $\text{Ag}_x\text{Cu}_{1-x}\text{I}$  ( $0 \leq x \leq 0.5$ ). The specific heats obtained for CuI are in good agreement with the literature values (Nölting 1964). The features of the result obtained are that anomalous excess specific heats are seen before the transition temperature is reached ( $\gamma \rightarrow \gamma + \alpha'$ ) and  $dC_p/dT < 0$  is seen after the transition temperature has been passed ( $\gamma + \alpha' \rightarrow \alpha'$ ).

Although these transitions are of first order, the contribution of enthalpy to the  $C_p$  at temperatures far from the transition ones should be small, so the  $C_p$  that we obtained is expressed as

$$C_p = C_p^0 + \Delta C_p \quad (2)$$

where  $C_p^0$  and  $\Delta C_p$  are given by the contribution from the lattice vibration and by the cation disorder, respectively. Values of  $C_p^0$  for this system are not exactly determined; however, we assume roughly that the  $C_p^0$  can be represented by values linearly extrapolated from the  $C_p$  around the room temperature as indicated in figure 3.

The excess specific heat  $\Delta C_p$  before the transition seems to be attributable to the cation disorder which is produced by a distribution of cations located at the two different energy levels. In fact, the magnitude of the ionic conductivity in this region is comparable to that in the superionic phase; in other words, the cation disorder may be considerable in this

region (Kusakabe *et al* 1996a). High ionic conductivity of cations appears in  $\gamma$ -CuI from 300 °C to the transition temperature. This high conductivity might be caused by cation disorder, and such a cation disorder can be produced by the fact that a proportion of the tetrahedral cations move to the octahedral site (Boyce *et al* 1981) by absorbing the thermal energy which is equal to the excess specific heat. This situation may also be applicable for the case of Ag-doped CuI.

The excess specific heat caused by cation disorder is analysed by two alternative methods. One approach is that used by Hall *et al* (1985) for the solid electrolyte  $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ . This consists in examining the cation disorder of the solid electrolyte by comparison of its heat capacity with the sum of those of its constituent components (AgI and  $\text{Ag}_2\text{WO}_4$ ) and discussing the cation disorder. This method may be useful for a specimen of uncertain structure and also for a qualitative estimation of cation disorder. It is, however, difficult to apply this method for the CuI–AgI system, because the cation disorder does, more or less, exist for the whole of the observed temperature range for CuI and AgI.

The other method for analysis of the excess specific heat for cation disorder,  $\Delta C_P$ , modelled by Wiedersich and Geller (1970), is useful for analysing our data. Their simple model essentially involves a Schottky-type specific heat with two different energy levels for mobile cations. The crystal contains  $N_A$  and  $N_B$  cation sites of the types A and B, respectively, for a total of  $n$  cations. Under the assumption that the energy required to migrate one cation from a site of type A to a site of type B scarcely varies with the distribution of cations on the site types, the total Gibbs free-energy difference  $\Delta G$  associated with  $n_A$  and  $n_B$  cations on site types A and B, respectively, may be written as follows:

$$\Delta G = n_B g_{AB} - kT \ln \frac{N_A!}{(N_A - n_A)! n_A!} \frac{N_B!}{(N_B - n_B)! n_B!} \quad (3)$$

where  $g_{AB}$  is equal to  $\Delta G/n$ . In addition, introducing the multiplicity of the set of sites  $m_i \equiv N_i/n$ , the Schottky-type specific heat  $\Delta C_P$  is given by

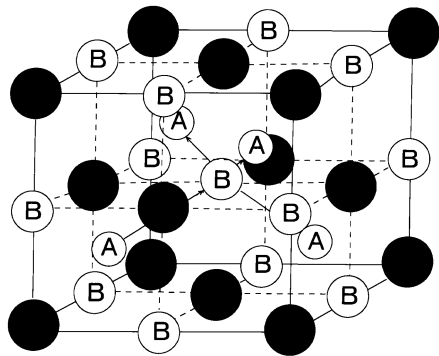
$$\Delta C_P = \frac{N_0 h_{AB}^2}{kT^2} \frac{Q}{1 - Q} \frac{m_B - (m_A + m_B) f_B}{\sqrt{\{m_A - 1 + Q(m_B + 1)\}^2 + 4Q(1 - Q)m_B}} \quad (4)$$

where  $N_0$  is the Avogadro's number,  $h_{AB}$  the energy required for the transfer from a site A to another site B—i.e. the enthalpy for the transfer,  $f_B$  the fraction of cations on the B sites, and  $Q = \exp(-g_{AB}/kT)$ .

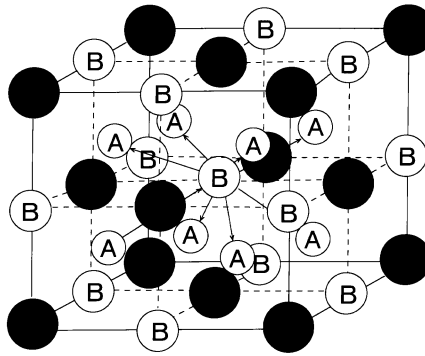
In the case of the present system near the transition temperature ( $\gamma \rightarrow \gamma + \alpha'$ ), if A and B sites are allocated to the lattice site (tetrahedral site) and the interstitial site (octahedral site), respectively,  $m_A$  and  $m_B$  are taken as unity as shown in figure 4. Moreover, the condition  $kT \ll h_{AB}$  can hold in this phase. Under these circumstances, equation (4) is simplified and rewritten as

$$\Delta C_P = \frac{1}{2} N_0 k \left( \frac{h_{AB}}{kT} \right)^2 \exp\left(-\frac{g_{AB}}{2kT}\right). \quad (5)$$

The composition dependence for the heat of transfer,  $h_{AB}$ , which is determined under the condition of minimum difference between the observed result and equation (5), is shown in table 1. In this table, the heats of transfer, determined by fitting conductivity data to an Arrhenius-type equation in the region between the transition temperature and below 50 °C from the transition temperature, are also shown for comparison.  $C_P$  is measured virtually under thermal equilibrium, and the measurement of the conductivity was also carried out at constant temperature; therefore the two results can be compared. The heats of transfer are in good agreement with each other. Therefore, the excess specific heat for the present system in the  $\gamma$ -phase could be explained in terms of the cation disorder.



**Figure 4.** A proposed crystal structure for  $\text{Ag}^+$ -doped CuI near the transition temperature ( $\gamma \rightarrow \gamma + \alpha'$ ). In this figure, solid circles indicate iodine ions, A sites indicate cations on tetrahedral sites, and B sites indicate cations on octahedral sites, respectively.



**Figure 5.** A crystal structure for  $\text{Ag}^+$ -doped CuI in the  $\alpha'$ -phase (Kusakabe *et al* 1996b). In this figure, solid circles represent iodine ions, A sites represent cations on tetrahedral sites, and B sites represent cations on octahedral sites, respectively.

It is emphasized, from these results, that the highly ionic conduction near the transition temperature ( $\gamma \rightarrow \gamma + \alpha'$ ) may be induced by a special path for the cation's migration, i.e. either 'from the lattice site to the Frenkel defect' or 'from the Frenkel defect to the lattice site'.

The anomalous specific heat for  $dC_p/dT < 0$  is observed after the transition temperature has been passed ( $\gamma + \alpha' \rightarrow \alpha'$ ). In most superionic phases, it is observed that the specific heat is given by  $dC_p/dT < 0$ ; this is again attributable to the jumps of mobile ions between two different energy sites. Recently, x-ray diffraction measurements were performed (Kusakabe *et al* 1996b); the present system is well explained in terms of the model in which negative ions form a f.c.c. lattice and positive ions are located at eight tetrahedral and four octahedral sites as shown in figure 5. Then the Schottky-type excess specific heat is given by equation (4) with  $m_A = 2$  and  $m_B = 1$ . The enthalpy for the transfer was determined by least-squares fitting with the observed specific heat and the calculated specific heat. The enthalpies obtained for the transfer are listed in table 1.

Under the assumption that the steady ionic conduction is only attained by the flow from a tetrahedral site to an octahedral one although the ratio of the occupation of the octahedral site to that of the tetrahedral one is uniquely determined by temperature, the enthalpies obtained by the two different methods agree well with each other.

However, a discrepancy between the enthalpies obtained by the two methods on increasing the Ag-ion concentration should arise, because cation–cation interactions are not taken into account in equation (4). For a high ionic conduction, it may be necessary to adopt a change of the sum of interionic potentials due to the change of ionic configuration, in order to discuss rigorously the temperature dependence of  $C_p$ . However, this method is not well established at the present stage except for in the investigations by Wiedersich and Johnston (1969) and Himba (1977). We assumed that the main effect for a large change of  $C_p$  in the present system may be caused by an ionic configuration or an entropy change, although proving this is difficult at the present stage. However, the enthalpy decreases with increasing Ag-ion concentration. This qualitative behaviour agrees well with the results obtained from conductivity measurements.

In any case the composition dependence of the specific heat can be roughly explained

by using equation (4). Originally, equation (4) was derived under the assumption that the energy required to promote one cation from a site of type A to a site of type B is independent of the distribution of cations on the site types, and all cation–cation interactions are neglected. However, if we assume that  $g_{AB}$  and in due course  $h_{AB}$  are meant to be ‘averaged’ quantities, then equation (4) may again be applicable for the system containing such effects.

It is worth mentioning that the enthalpies before and after the phase transition are quite different; that is,  $h_{AB}$  after the transition temperature has been passed is almost ten times smaller than that before the transition temperature is reached. This is because the cation migration in the superionic phase is caused by a collective motion of cations, which may drastically diminish the  $h_{AB}$ . In fact, such a collective motion has been discussed theoretically on the basis of the caterpillar mechanism (Yokota 1966), in which the Haven ratio is smaller than unity and a computer simulation has provided additional evidence (Okazaki and Tachibana 1987).

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