The Specific Heat of Ag$_2$S in $\alpha$-phase

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The specific heat of Ag$_2$S has been measured from room temperature up to the melting point (838 °C). The temperature dependence of the specific heat of its $\alpha$-phase in the temperature range from the $\beta$-$\alpha$ transition point at 179 °C to 586 °C, at which temperature there occurs another crystallographic transition, is well reproduced by supposing a Schottky-type specific heat (excitation of mobile ions) in addition to the normal lattice heat capacity. The latent heat of the latter transition, where the structure of the lattice changes from bcc to fcc, is obtained to be 774 J/mol.

The specific heat of solid superionic conductors gives important information about the behaviour of the mobile ions. Measurements of the specific heat of Ag$_2$S have yet been insufficient, although many measurements have been done on AgI, whose structure in its superionic phase is similar to that of Ag$_2$S. Moreover, there exist discrepancies concerning the temperature dependence of the specific heat of Ag$_2$S [1, 2], and the measurements have been restricted to below 400 °C. This prompted us to reexamine the specific heat of Ag$_2$S and to expand the range of temperatures up to the melting point (838 °C).

The measurements at high temperature were carried out on specimens enclosed in silica tubes in vacuum in order to avoid dissociation. An adiabatic type equipment for measuring specific heats (produced by Sinku Riko Co., Japan as the type SH-3000) was used. Details of the equipment and method are published elsewhere [3].

Ag$_2$S has three phases in the solid state. The crystallographic transitions take place at 179° and 685 °C, the crystal structure changing from monoclinic to bcc and from bcc to fcc, respectively. We call these phases as $\beta$-, $\alpha_B$- and $\alpha_F$-phase in the order from lower to higher temperature. At the first transition, the superionic conduction by Ag$^+$ ions begins. In this paper we pay attention to the $\alpha_B$-phase because its crystal structure, necessary to analyse the experimental results, is well known.

Our results are shown in Fig. 1, together with those obtained by Jost and Kubaschewski [1], and by Perrott and Fletcher [2]. The results obtained were estimated to be within 3% in the accuracy. The question of the rapid increase in the specific heat after melting is still open. Below 400 °C our results coincide with those of Jost and Kubaschewski and differ from those of Perrott and Fletcher. According to Perrott and Fletcher, stoichiometric Ag$_2$S shows a $\lambda$-type anomaly after the $\beta \rightarrow \alpha_B$ transition. So, we have exactly controled the stoichiometry of the specimen within 10$^{-2}$% by Coulometric titration through a cell Pt| specimen AgI|Ag before meas-

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Fig. 1. The specific heat of Ag$_2$S. Small open circles and black ones show the specific heat obtained experimentally and calculated from (1), respectively. Arrows show the experimental accuracy.

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suring the specific heat. We did not find this anomaly, so that we support the results of Jost and Kubaschewski. The extraordinary increase in the specific heat near the phase transition $\beta \rightarrow \alpha_B$ is explained by the excess heat necessary to create the Frenkel type cationic defects [1]. Our interpretation will be limited to the behaviour of the specific heat in the $\alpha_B$-phase, since the crystal structure of the $\alpha_F$-phase is not sufficiently known.

The measured molar specific heat at constant pressure, $C_p$, can be expressed by three terms:

$$C_p = C_v + \frac{9 x_1^2 V_m T}{\chi_T} + \Delta C_p,$$

(1)

where $C_v$ is the molar specific heat at constant volume. The second term is due to the anharmonic lattice vibration of the constituent ions; $x_1$ means the linear expansion coefficient, $V_m$ the molar volume, $\chi_T$ the isothermal compressibility and $T$ the absolute temperature. $\Delta C_p$ is a Schottky-type excess specific heat caused by jumps of mobile ions from stable equilibrium positions to activated ones. If we assume that each ion vibrates independently within a harmonic well, which may be a good approximation at higher temperature, then $C_v$ becomes $3 n R$ (Dulong-Petit's law), where $R$ is the gas constant and $n = 3$. Therefore, $C_v$ of $\alpha_B$-$Ag_2S$ is equal to 74.9 J/mol K.

For the second term on the r.h.s. of (1) we need the knowledge of $x_1$, $V_m$ and $\chi_T$ as a function of temperature. For the compressibility of Ag$_2$S we use the value at room temperature ($2.9 \times 10^{-12}$ cm$^3$/dyne [4]). If the second term on the r.h.s. of (1) is written as $LC_2^2 T$ with $L = 9 x_1^2 V_m / \chi_T C_p$, then $L$ turns out to be almost constant for a wide range of temperatures (Nernst-Lindemann relation). Using the $\beta$-phase value of $x_1 = 2.0 \times 10^{-5}$/K [5] and $V_m = 34$ cm$^3$ (density 7.3 g/cm$^3$), we have $L = 0.69 \times 10^{-6}$ mol/J. We assume $L$ to be constant throughout the $\beta$- and $\alpha_B$-phase, then we obtain the values of $9 x_1^2 V_m T / \chi_T$ shown in Table 1*.

The last term in (1) may be derived from the following considerations. In $\alpha_B$-$Ag_2S$, sulphur ions form a bcc lattice and silver ions are distributed randomly over tetrahedral 12 (h) sites. If a silver ion occupies a 12 (h) site, however, other silver ions may not occupy neighbouring sites at the same time because the diameter of the silver ion (2.32 Å) is larger than the distance of the neighbouring 12 (h) sites (1.72 Å). According to the recent study on the crystal structure of $\alpha_B$-$Ag_2S$ by neutron diffraction by Cava et al. [6], who have used a single crystal, the silver ions are delocalized along the $\langle 100 \rangle$ directions. This fact suggests that silver ions prefer to move in the $\langle 100 \rangle$ direction, i.e. a silver ion moves from a tetrahedral site (referred to as A-site hereafter) to one of its next nearest A-sites via the octahedral 6 (e) site (referred to as B-site hereafter) as illustrated in Figure 2. This situation is remarkably different to that in $\alpha$-AgI, where mobile ions prefer to move along the $\langle 100 \rangle$ direction from a 12 (h) site to one of its neighbouring 12 (h) sites via the 24 (j) site [7]. The ionic conductivity of $\alpha_B$-$Ag_2S$ increases with increasing temperature, which means that the population of the conducting Ag$^+$ ion on B-sites increases with increasing temperature. If $\Delta h$ is the enthalpy difference between A- and B-sites, the Gibbs free energy associated with the promotion of $N_B$ ions from A- into B-site, $\Delta G$, is written as

$$\Delta G = N_B \Delta h - T \Delta S,$$

where $\Delta S$ is the entropy change, which consists of the configurational entropy $\Delta S_c$ and the entropy change associated with the change of the vibrational frequency of ions on B-sites, $\Delta S_f$. For a highly disordered system, such as $\alpha_B$-$Ag_2S$, $\Delta S_f$ will be small and may therefore be neglected. $\Delta S_c$ may be calculated by the equation

$$\Delta S_c = k_B \ln (W_A W_B),$$

(3)

where $W_A$ and $W_B$ are the numbers of possibilities to distribute $N_A$ ions on $j_A N_A$ A-sites ($j_A > 1$) and

* The values of $9 x_1^2 V_m T / \chi_T$ estimated by Perrott and Fletcher are about four times larger than our values. Probably they have used the value of $x_1$ in the $\alpha_F$-phase, which is about two times larger than that in the $\beta$-phase.

Table 1. Calculated values of $9 x_1^2 V_m T / \chi_T$ and $\Delta C_p$ in units of J/mol K.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>585</th>
</tr>
</thead>
<tbody>
<tr>
<td>$9 x_1^2 V_m T / \chi_T$</td>
<td>2.72</td>
<td>2.85</td>
<td>3.01</td>
<td>3.26</td>
<td>3.43</td>
<td>3.64</td>
<td>3.89</td>
<td>4.39</td>
<td>4.66</td>
</tr>
<tr>
<td>$\Delta C_p$</td>
<td>9.12</td>
<td>8.29</td>
<td>7.49</td>
<td>6.78</td>
<td>6.11</td>
<td>5.48</td>
<td>4.98</td>
<td>4.52</td>
<td>4.81</td>
</tr>
</tbody>
</table>
Fig. 2. Three kinds of positions on the (100) plane of \( \alpha \)-phase \( \text{Ag}_2\text{S} \). Big circles show sulphur ions. Small circles, hexagons, and squares mean 12 (h), 6 (e), and 24 (j) sites, respectively. A cation (black circle) on a 12 (h) site (an A site) prefers to move to one of its second neighbouring A sites in the (100) direction via the 6 (e) site (B site) like shown by arrows.

\( N_B \) ions on \( j_B \) B-sites (\( j_B > 1 \)), respectively. Here, \( N = N_A + N_B \) is the total number of cations and \( j_X \) the mole ratio of X-sites in the unit cell (\( j_A = 12/4 = 3 \) and \( j_B = 6/4 = 3/2 \)). Since two \( \text{Ag}^+ \) ions may not occupy neighbouring A-sites at the same time, \( W_A \) is given by

\[
W_A = \frac{(j_A N - N_A + 1)!}{N_A!(j_A N - 2N_A + 1)!}.
\]  

(4)

\( W_B \) is similarly given by

\[
W_B = \frac{(j_B N)!}{N_B!(j_B N - N_B)!}.
\]  

(5)

The equilibrium value of \( N_B \) at a temperature is obtained as

\[
\frac{f (1 + 2f)^2}{(1-f)(2+f)(3-f)} = \exp(-\Delta h/k_B T)
\]  

(6)

from the condition of \( (\partial G/\partial N_B)_T = 0 \). Here, \( f \) is the ratio \( N_B/N \). The excess heat, \( \Delta Q \), which is shared by \( N_B \) ions is then expressed as \( \Delta Q = N_B \Delta h \), and the excess specific heat \( \Delta C_p \) is calculated by differentiating \( \Delta Q \) with respect to temperature. The following relation is accordingly obtained for \( \Delta C_p \):

\[
\Delta C_p = \frac{2 N_0 (\Delta h)^2}{k_B T^2} \frac{1}{F},
\]  

(7)

where \( 2 N_0 \), \( k_B \), and \( F \) are the number of mobile ions in 1 mol \( \text{Ag}_2\text{S} \) (\( N_0 \) means the Avogadro number), the Boltzmann constant and a numerical constant depending on the configurational distribution of \( N \) ions on A- and B-sites as expressed by

\[
F = \frac{1}{f} + \frac{4}{f + 2f} + \frac{2}{1+f} + \frac{1}{1-f} + \frac{1}{2+f} - \frac{9}{2 + 3f},
\]  

(8)

respectively. The evaluated values of the excess specific heat using (7) are also shown in Table I for the case of \( h = 0.11 \text{ eV} \), which corresponds to the activation enthalpy evaluated from the ionic conductivity [8]. The calculated values of the specific heat are also shown in Figure 1. The agreement with the experiments is satisfactory in view of the fact that we have no knowledge on \( \chi_T \) of the \( \alpha \)-phase and have assumed \( \chi \) to be constant in spite of the phase transition.

Finally, we have obtained a latent heat 774 J/mol for the transition taking place in the superionic phase where the anion lattice changes from a bcc to a fcc arrangement. The entropy associated with the phase transition is estimated to be 0.92 J/mol K, which is fairly small. It is an interesting problem to understand the change of the anion lattice from bcc with a lower packing density to fcc with the highest one, retaining the superionic property. This problem is now being studied.

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[5] Unpublished. The method of lamp and scale was used.