The Specific Heat of Ag_2S in α-phase

Hideo Okazaki
General Education Department, Niigata University, Niigata, Japan

Akio Takano
Department of Physics, Faculty of Science, Niigata University, Niigata, Japan

Z. Naturforsch. **40 a**, 986–988 (1985); received May 14, 1985

The specific heat of Ag_2S has been measured from room temperature up to the melting point (838 °C). The temperature dependence of the specific heat of its α-phase in the temperature range from the β-α 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_2S have yet been insufficient, although many measurements have been done on AgI, whose structure in its superionic phase is similar to that of Ag_2S. Moreover, there exist discrepancies concerning the temperature dependence of the specific heat of Ag_2S [1, 2], and the measurements have been restricted to below 400 °C. This prompted us to reexamine the specific heat of Ag_2S 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_2S 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 β-, α_B- and α_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 α_B-phase because its crystal structure, necessary to analyse the experimental results, is well known.

Reprint requests to Prof. H. Okazaki, Physics Laboratory, General Education Department, Niigata University, Niigata 950-21, Japan.

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_2S shows a λ-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 mea-

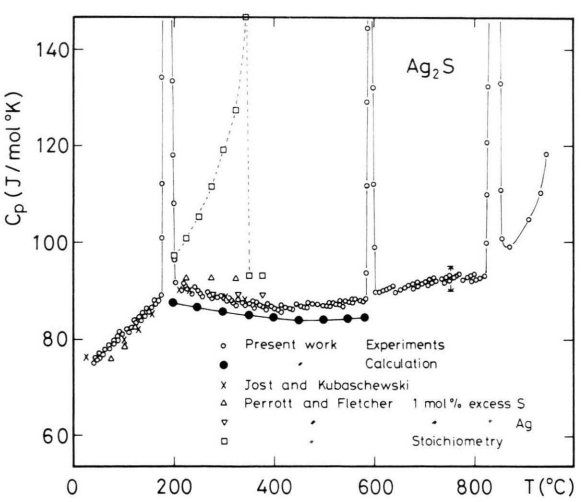

Fig. 1. The specific heat of Ag_2S. Small open circles and black ones show the specific heat obtained experimentally and calculated from (1), respectively. Arrows show the experimental accuracy.

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

T(°C)	200	250	300	350	400	450	500	550	585
$9\alpha_l^2 V_m T/\chi_T$	2.72	2.85	3.01	3.26	3.43	3.64	3.89	4.39	4.66
ΔC_p	9.12	8.29	7.49	6.78	6.11	5.48	4.98	4.52	4.81

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 creat the Frenkel type cationic defects [1]. Our interpretation will be limited to the behaviour of the specific heat in the α_B-phase, since the crystal structure of the α_F-phase is not sufficiently known.

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

$$C_p = C_v + \frac{9\alpha_l^2 V_m T}{\chi_T} + \Delta C_p , \qquad (1)$$

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; α_l means the linear expansion coefficient, V_m the molar volume, χ_T the isothermal compressibility and T the absolute temperature. ΔC_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 $3nR$ (Dulong-Petit's law), where R is the gas constant and $n = 3$. Therefore, C_v of α_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 α_l, V_m and χ_T as a function of temperature. For the compressibility of Ag_2S we use the value at room temperature (2.9×10^{-12} cm^2/dyne [4]). If the second term on the r.h.s. of (1) is written as $LC_p^2 T$ with $L = 9\alpha_l^2 V_m/\chi_T C_p^2$, then L turns out to be almost constant for a wide range of temperatures (Nernst-Lindemann relation). Using the β-phase value of $\alpha_l = 2.0 \times 10^{-5}$/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 in the β- and α_B-phase, then we obtain the values of $9\alpha_l^2 V_m T/\chi_T$ shown in Table 1*.

The last term in (1) may be derived from the following considerations. In α_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 α_B-Ag_2S by neutron diffraction by Cava et al. [6], who have used a single crystal, the silver ions are delocalized along the ⟨100⟩ directions. This fact suggests that silver ions prefer to move in the ⟨100⟩ 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 α-AgI, where mobile ions prefer to move along the ⟨100⟩ direction from a 12 (h) site to one of its neighbouring 12 (h) sites via the 24 (j) site [7]. The ionic conductivity of α_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 Δh 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, ΔG, is written as

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

where Δs is the entropy change, which consists of the configurational entropy Δs_c and the entropy change associated with the change of the vibrational frequency of ions on B-sites, Δs_f. For a highly disordered system, such as α_B-Ag_2S, Δs_f will be small and may therefore be neglected. Δs_c may be calculated by the equation

$$\Delta s_c = k_B \ln (W_A W_B) , \qquad (3)$$

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

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

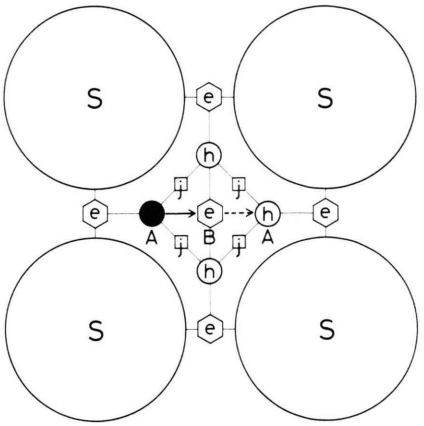

Fig. 2. Three kinds of positions on the (100) plane of α_B-Ag_2S. Big circles show sulphur ions. Small circles, hexagons, and squares mean 12 (h), 6 (e), and 24 (j) sites, respectively. A cation (black circle) on a 12 (h) site (an A site) prefers to move to one of its second neighbouring A sites in the ⟨100⟩ direction via the 6 (e) site (B site) like shown by arrows.

N_B ions on $j_B N$ 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 Ag^+ ions may not occupy neighbouring A-sites at the same time, W_A is given by

$$W_A = \frac{(j_A N - N_A + 1)!}{N_A!\,(j_A N - 2N_A + 1)!}. \tag{4}$$

W_B is similarly given by

$$W_B = \frac{(j_B N)!}{N_B!\,(j_B N - N_B)!}. \tag{5}$$

The equilibrium value of N_B at a temperature is obtained as

$$\frac{f(1+2f)^2}{(1-f)(2+f)(\frac{3}{2}-f)} = \exp(-\Delta h/k_B T) \tag{6}$$

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

$$\Delta C_p = \frac{2N_0(\Delta h)^2}{k_B T^2}\frac{1}{F}, \tag{7}$$

where $2N_0$, k_B and F are the number of mobile ions in 1 mol Ag_2S (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

$$F = \frac{1}{f} + \frac{4}{1+2f} + \frac{2}{1+f} + \frac{1}{1-f} + \frac{1}{2+f} - \frac{9}{2+3f}, \tag{8}$$

respectively. The evaluated values of the excess specific heat using (7) are also shown in Table 1 for the case of $h = 0.11$ 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 χ_T of the α_B-phase and have assumed L 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.

Authors express their thanks to Professor Tamaki for valuable discussion. One of the authors (A. T.) is grateful to Drs. S. Takeda and S. Harada for their helpful discussions.

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