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THE HEAT CAPACITY AND ENTHALPY OF SOME HUME—ROTHERY PHASES FORMED BY COPPER, SILVER AND GOLD. PART I. Cu + Sb, Ag + Sb, Au + Sb, Au + Bi SYSTEMS

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ABSTRACT

The heat capacity and enthalpy between 230 and 800 K have been determined by differential scanning calorimetry for several alloy compositions in the Cu + Sb, Ag + Sb, Au + Sb and Au + Bi systems. The following alloy compositions have been studied: $Cu_{0.81}Sb_{0.19}$, $Cu_{0.67}Sb_{0.33}$, $Cu_{0.75}Sb_{0.25}$, $Cu_{0.715}Sb_{0.285}$, $Ag_{0.9}Sb_{0.1}$, $Ag_{0.77}Sb_{0.23}$, $Au_{0.34}Sb_{0.66}$ and $Au_{0.67}Bi_{0.33}$, and any transition data recorded have been used to provide phase diagram information.

INTRODUCTION

These measurements of the heat capacity and enthalpy of the antimonides and bismuthide reported here were part of a larger programme to investigate the thermal properties of a wide range of Hume —Rothery phases formed by copper, silver and gold. It was hoped that such a survey would (i) reveal to what extent the structure of these phases influences the heat capacity, and (ii) provide valuable phase diagram information for the many uncertain regions of the phase diagrams of these systems.

EXPERIMENTAL

The alloys used in this study were prepared from high purity materials (99.9995%); the Cu, Sb and Bi were supplied by Preussag AG and the Ag and Au by Degussa. The two components were melted together in sealed, evacu-

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ated, silica capsules and quenched into iced water. They were homogenized 5 K below the solidus temperatures for several days and then cooled slowly to room temperature. The products were then crushed and pressed into discs. Any stored energy effects caused by the cold work were eliminated by further annealing. Further details of preparations are given elsewhere [1]. The sample was examined and identified by X-ray diffraction and metallographic analysis.

Measurements were made using a Perkin-Elmer differential scanning calorimeter (DSC) model 2. The output signal from the DSC was measured with a digital voltmeter and recorded on paper tape. The treatment of the data to yield enthalpy and heat capacity values has been described by Mills and Richardson [2]. Corrections for thermal lag in the calorimeter were made using the method due to Richardson and Burrington [3]. The apparatus was checked by measuring the heat capacity of silver; the scatter of individual points from the $C_p(T)$ curve due to Hultgren et al. [4] had standard deviations of 1% for the range 250—600 K and 2% for the range 600—1000 K. Temperatures were based on IPTS-68.

RESULTS AND DISCUSSION

In this paper, molar thermodynamic properties are for 1 mole of A_xB_{1-x}, where $x < 1$ and A is Cu, Ag or Au and B is Sb or Bi.

Cu + Sb System

There are still some uncertainties in the phase diagram [5,6] for this system; the more recent phase diagram due to Gunzel and Schubert [6] is shown in Fig. 1; this contains several differences from the phase diagram proposed by Hansen and Anderko [5]. Two phases, ϵ and 'Cu_2Sb' , are known to exist at ambient temperatures and four further phases, β, κ, η and ϵ' have been reported [6] to exist at higher temperatures. The alloy compositions were selected to investigate both high- and low-temperature phases. The temperature range of this study was limited to 773 K to minimize any vaporization of antimony from the samples, which could adversely affect the performance of the DSC.

The hexagonal ϵ-phase has an electron/atom ratio of 21/12; the composition of the ϵ-phase studied in this investigation was $Cu_{0.81}Sb_{0.19}$. The ϵ'-phase has a modified hexagonal structure. The heat capacity and enthalpy of the ϵ-phase are given in Fig. 2. No transitions were observed between 250 and 630 K and the $C_p(T)$ relationship for this range is given by eqn. (1)

$$C_p/(\text{J K}^{-1}\ \text{mole}^{-1}) = 23.56 + 7.57 \times 10^{-3}(T/\text{K}) - 68\,631(T/\text{K})^{-2} \qquad (1)$$

The heat capacity and enthalpy of the tetragonal "Cu_2Sb" phase are given in Fig. 3. The results indicate that a transformation probably occurs just above 700 K. This transformation could indicate that the composition of the sample lies outside the copper-rich boundary of the homogeneity range for the "Cu_2Sb" at this temperature and hence contains a small amount of the

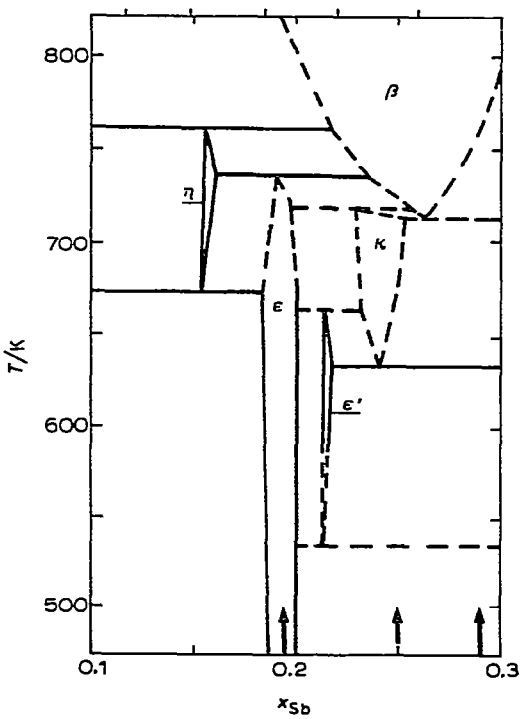

Fig. 1. The phase diagram for Cu + Sb according to Günzel and Schubert [6]; three of the four alloy compositions studied are shown by arrows.

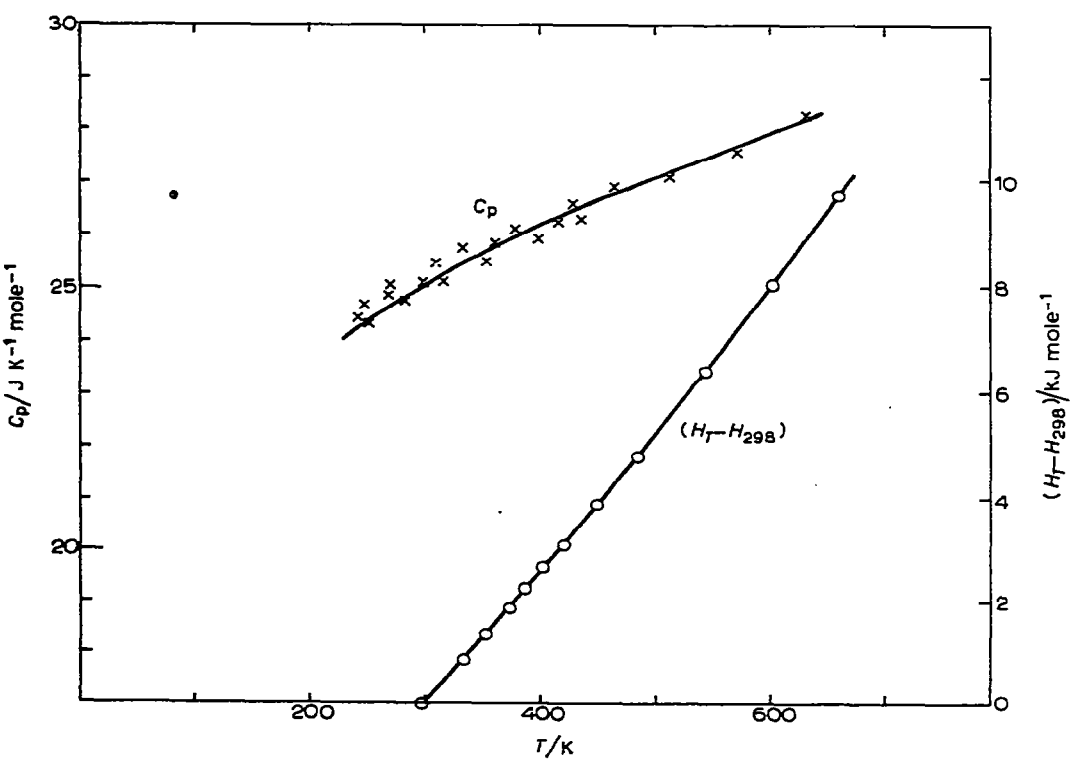

Fig. 2. The heat capacity and enthalpy of the ϵ-phase, $Cu_{0.81}Sb_{0.19}$. ×, ○ Experimental values for C_p and $(H_T - H_{298})$, respectively.

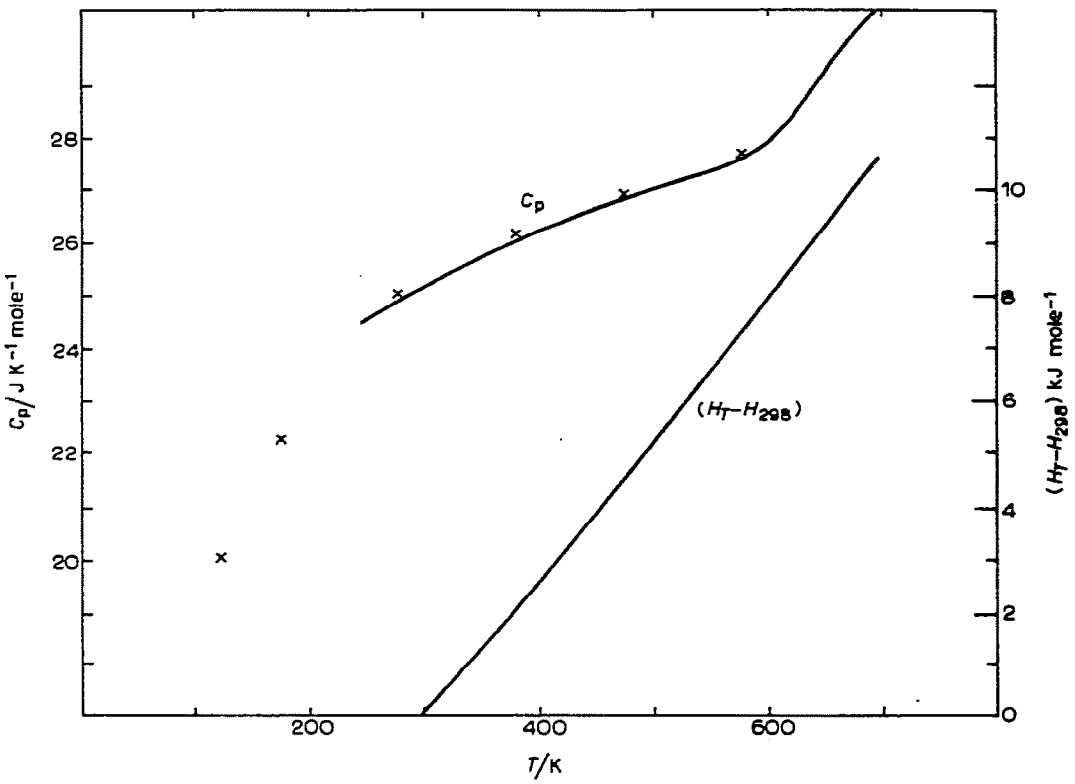

Fig. 3. The heat capacity and enthalpy of the "Cu_2Sb" phase, $Cu_{0.67}Sb_{0.33}$. ×, Ref. 7.

κ-phase. The thermal effect could thus be due to the transformation of the κ-phase into the β-phase around 710 K.

The heat capacity values obtained by Schubel [7] for "Cu_2Sb" are in excellent agreement with those of the present investigation (see Fig. 3). The $C_p(T)$ curve for the temperature interval 250—600 K obtained in this investgation is given by eqn. (2)

$$C_p/(\text{J K}^{-1}\text{ mole}^{-1}) = 23.67 + 7.18 \times 10^{-3}(T/\text{K}) - 54\,620(T/\text{K})^{-2} \qquad (2)$$

The β-phase was investigated by the C_p measurements for two alloys, $Cu_{0.75}Sb_{0.25}$ and $Cu_{0.715}Sb_{0.285}$; the results of these studies are given in Figs. 4 and 5, respectively. The $C_p(T)$ curves for these alloys indicate that at least three transformations occur between 600 and 800 K. Uncertainties in the phase diagram prevent an unequivocal interpretation of the various endotherms recorded. However, the following observations can be made from an inspection of Figs. 4 and 5:

(i) there is no evidence of any thermal effect around 540 K which could be associated with the $\epsilon \rightarrow \epsilon'$ transformation;

(ii) the significant increase in the slope of the $C_p(T)$ curve above 630 K is probably caused by the formation of the κ-phase. The C_p peak at 660 K in Fig. 4 could be due to either the decomposition of the ϵ'-phase or the combined effects of the sluggish nature of the $\epsilon' \rightarrow \kappa$ transformation and the dynamic nature of the measurement technique. If the latter conditions

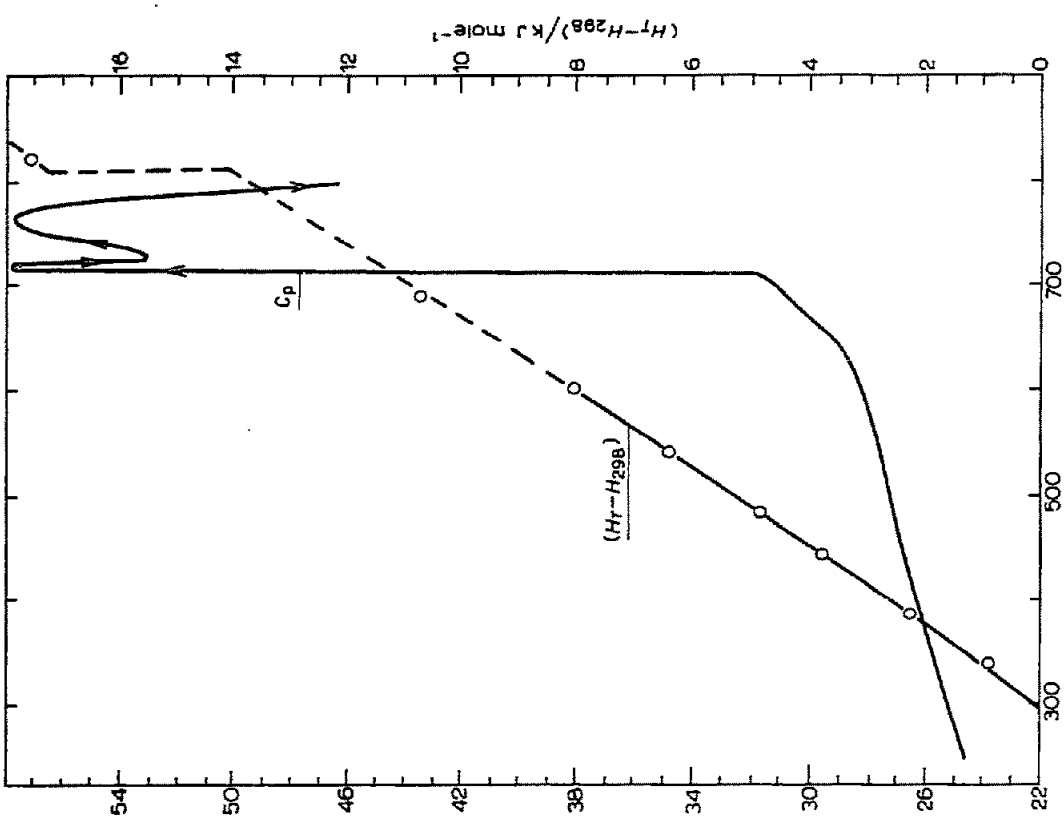

Fig. 4. The heat capacity and enthalpy of the phase, $Cu_{0.75}Sb_{0.25}$. X, ref. 7; O, this investigation.

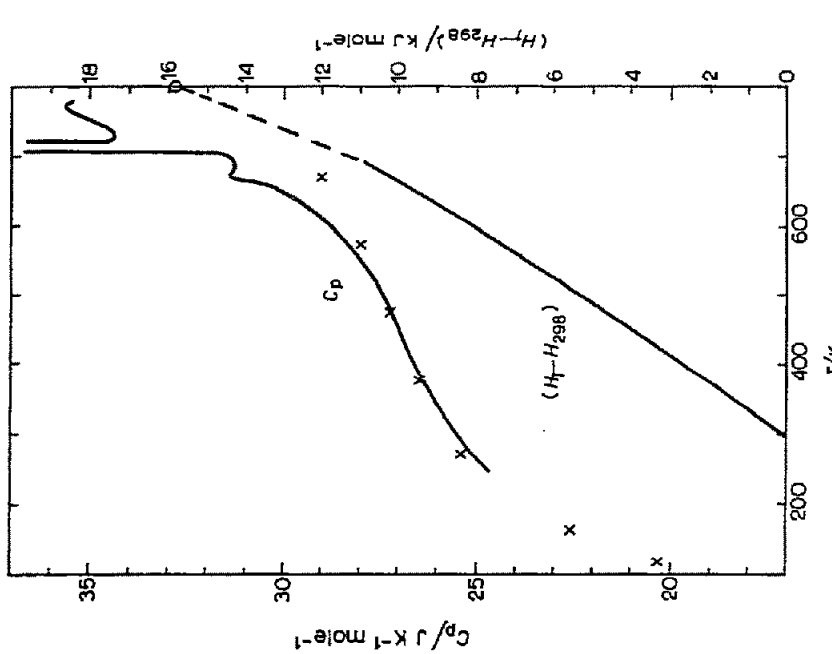

Fig. 5. The heat capacity and enthalpy of the phase, $Cu_{0.715}Sb_{0.285}$. O, Experimental points for $(H_T - H_{298})$.

obtain, then the value for the enthalpy of transition (ca. 130 J mole^{-1}) derived from the hump in the $C_p(T)$ curve for Fig. 4 may not refer to equilibrium conditions for the $\epsilon' \rightarrow \kappa$ transformation;

(iii) the endotherm at 710 K can be assigned to the formation of the β-phase;

(iv) the endotherm at 760 K could be assigned to the decomposition of the η-phase for $Cu_{0.75}Sb_{0.25}$ and to the $(Cu_2Sb + \beta) \rightarrow \beta$ transformation for $Cu_{0.715}Sb_{0.285}$. If these interpretations are correct, the tentative boundaries of the β-phase for copper-rich compositions should be reassigned to higher temperatures.

It was not possible to ascribe individual ΔH_{tr} values to the various transformations from the results obtained. However, extrapolation of the enthalpy curve in Fig. 5 suggests that the total ΔH_{tr} for all three transitions has a value around 3.2 kJ mole^{-1}. It will also be noted from Fig. 4 that the C_p values obtained by Schubel [7,8] for "Cu_3Sb" are in excellent agreement with those obtained in the present investigation. The $C_p(T)$ curve for $Cu_{0.75}Sb_{0.25}$ for the temperature range 250—570 K obtained in this investigation is given by eqn. (3).

$$C_p/(\text{J K}^{-1}\ \text{mole}^{-1}) = 24.17 + 7.07 \times 10^{-3}(T/\text{K}) - 76\,418(T/\text{K})^{-2} \qquad (3)$$

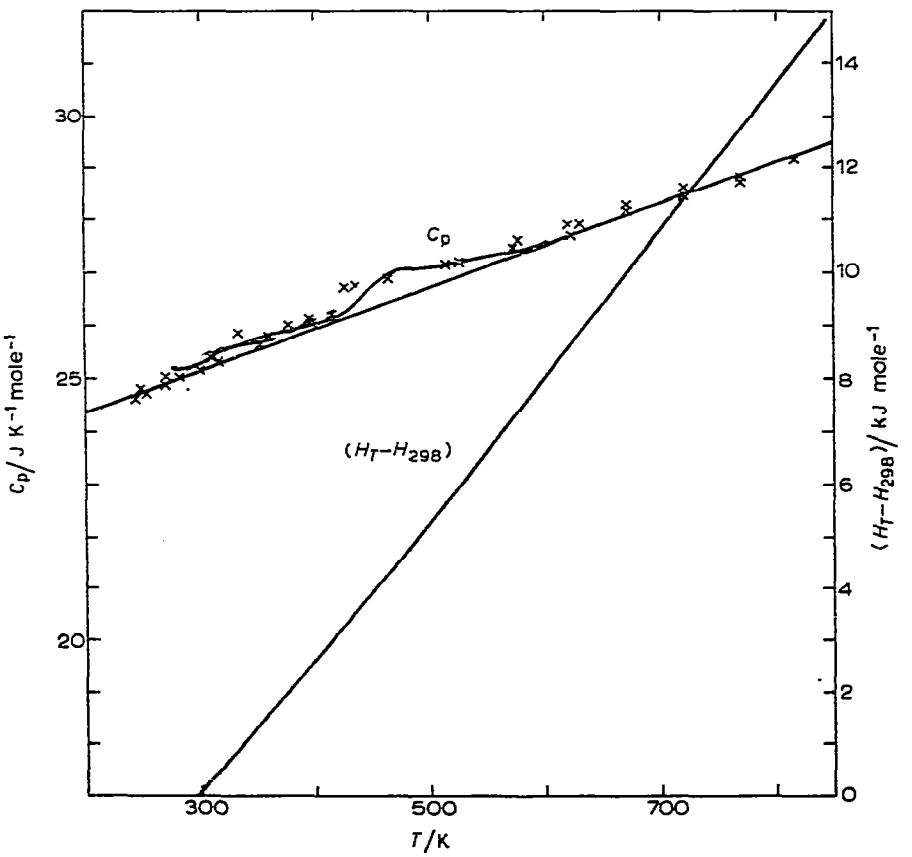

Fig. 6. The heat capacity and enthalpy of the ζ-phase, $Ag_{0.9}Sb_{0.1}$. ×, Experimental points for C_p.

Ag + Sb System

The phase diagram due to Hansen and Anderko [5] shows the existence of two intermetallic phases, ζ and ϵ'. Both of these phases exhibit a large range of non-stoichiometry. The composition $Ag_{0.9}Sb_{0.1}$ was selected for a study of the ζ-phase, which has an electron/atom ratio of 21/14 and has a hexagonal close-packed structure. The heat capacity and enthalpy measurements are shown in Fig. 6, and the $C_p(T)$ relationship is given by eqn. (4). A small hump in the $C_p(T)$ curve was observed in the temperature range 450—550 K; it is not known if this is associated with a transformation; if so, it must mean that the ζ-phase homogeneity range above 450 K is not as extensive as that indicated by Hansen and Anderko [5].

$$C_p/(\text{J K}^{-1}\text{ mole}^{-1}) = 22.69 + 8.01 \times 10^{-3}(T/\text{K}) + 1705(T/\text{K})^{-2} \quad (4)$$

The composition $Ag_{0.77}Sb_{0.23}$ lies just inside the silver-rich boundary of the reported homogeneity range for the ϵ'-phase; this phase has an orthorhombic structure and has an electron/atom ratio of 21/14. The heat capacity and enthalpy for the ϵ'-phase are given in Fig. 7 and the $C_p(T)$ relationship for temperatures between 250 and 600 K are given in eqn. (5)

$$C_p/(\text{J K}^{-1}\text{ mole}^{-1}) = 32.83 + 8.42 \times 10^{-3}(T/\text{K}) + 2013(T/\text{K})^{-2} \quad (5)$$

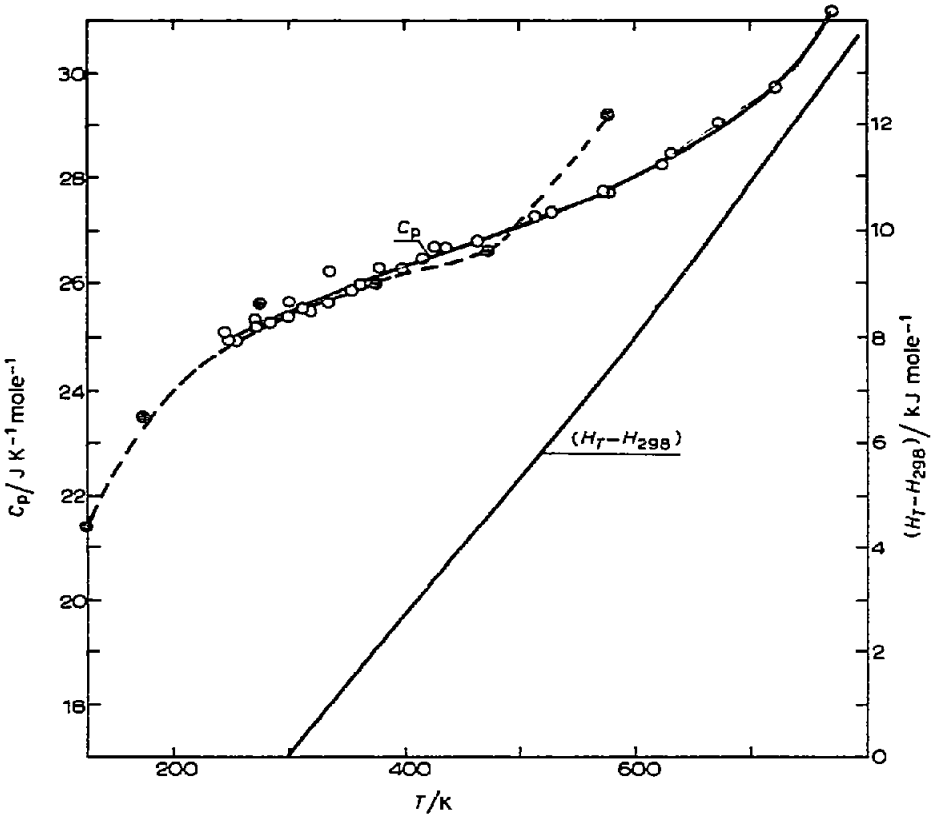

Fig. 7. The heat capacity and enthalpy of the ϵ'-phase, $Ag_{0.77}Sb_{0.23}$. — — — —, ●, Ref. 4; ———, ○, this investigation.

A transformation $\epsilon' \rightarrow \epsilon$ has been reported to occur at ca. 720 K for this phase and the data were interpreted as evidence for an order → disorder reaction [9]. However, Burkhardt and Schubert [10] were unable to find this transition. No transitions were observed to occur around 720 K, as can be seen from Fig. 7. However, the shape of the $C_p(T)$ curve suggests that a transformation probably occurs around 800 K. Three possible explanations can be forwarded for the existence of a transformation: (i) that the $\epsilon' \rightarrow \epsilon$ transformation occurs around 800 K for this composition, (ii) that the $\epsilon' \rightarrow \epsilon$ transition is a very sluggish transformation and that the thermal effect is displaced to higher temperatures when dynamic techniques (e.g. DSC) are used, (iii) that this is associated with the transformation $\epsilon \rightarrow \epsilon$ + liquid which probably occurs around 820 K. Obviously, further phase studies are required to explain this behaviour.

Schubel [7,8] has reported C_p values for temperatures between 123 and 573 K for an alloy of composition $Ag_{0.75}Sb_{0.25}$. Up to 500 K the C_p values are in excellent agreement with those of the present investigation; however, the C_p values due to Schubel increase markedly above 500 K, as can be seen from Fig. 7. No explanation can be suggested for this behaviour as no transformation has been reported to occur around 600 K.

Au + Sb System

The phase diagram [5] shows only one phase to be present, $AuSb_2$; this compound has a cubic structure and melts at 733 K. The composition $Au_{0.34}Sb_{0.66}$ was used in this examination. The results of this study are shown in Fig. 8. The $C_p(T)$ curve shows two peaks corresponding to the

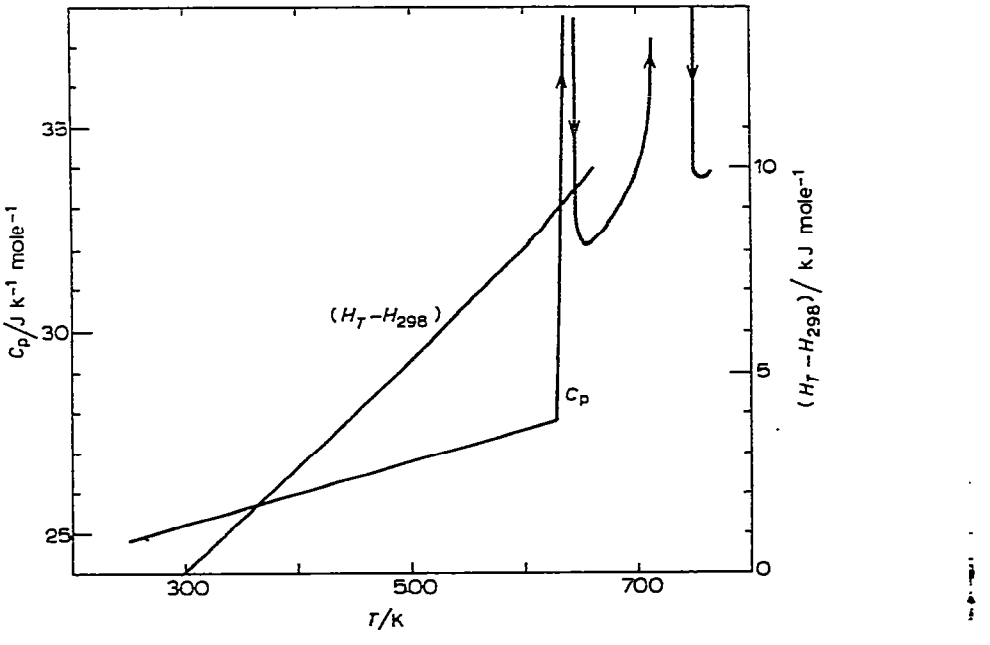

Fig. 8. The heat capacity and enthalpy of the "$AuSb_2$" phase, $Au_{0.34}Sb_{0.66}$.

transformations Au + $AuSb_2$ → eutectic liquid + $AuSb_2$ → liquid, which occurred at 634 and 740 K, respectively, in reasonable agreement with the reported phase diagram which shows the eutectic temperature at 633 K. This behaviour suggests that the sample composition, $Au_{0.34}Sb_{0.66}$, may be outside the goldrich limit of the homogeneity range of $AuSb_2$.

The $C_p(T)$ relationship for the temperature range 250—630 K is given by eqn. (6)

$$C_p(\text{J K}^{-1}\text{ mole}^{-1}) = 22.94 + 7.96 \times 10^{-3}(T/\text{K}) - 9162(T/\text{K})^{-2} \quad (6)$$

Values of C_p obtained by Bottema and Jaeger [11,12] are in excellent agreement with those obtained in the present investigation. A value for the enthalpy of fusion, ΔH_{fus} = ca. 20 kJ mole^{-1}, was obtained for $Au_{0.34}Sb_{0.66}$ and this corresponds to an entropy of fusion of ΔS_{fus} = 27 J K^{-1} mole^{-1}.

Au + Bi System

The reported phase diagram [5] shows the presence of only one phase, "Au_2Bi", which undergoes transformations at 514 and 646 K. The C_p and

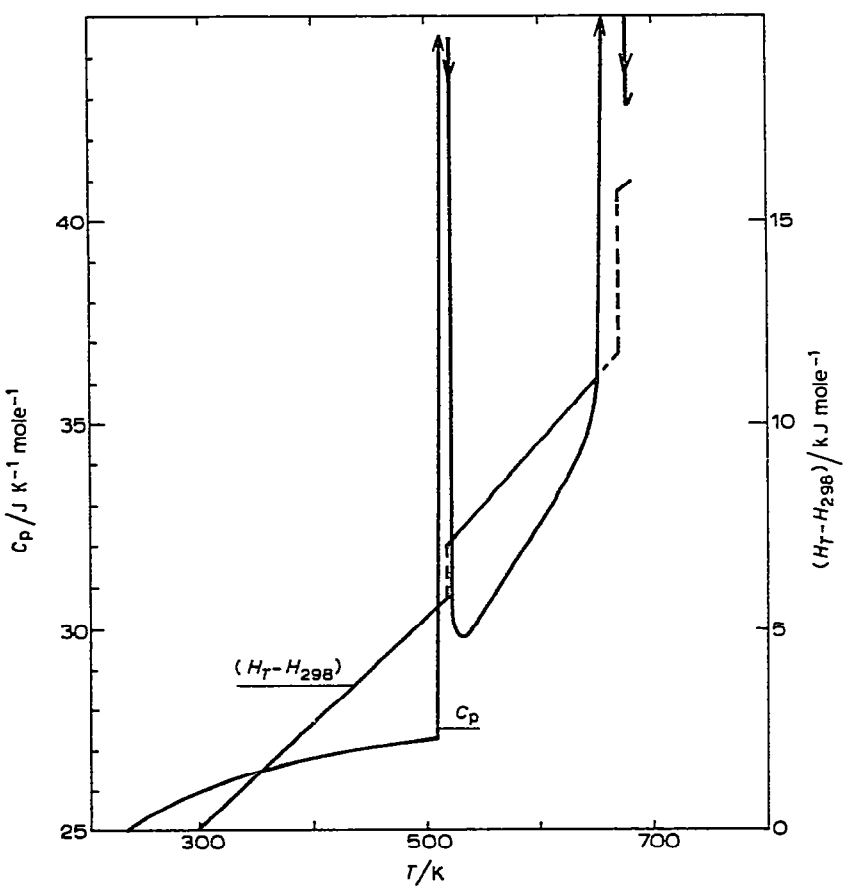

Fig. 9. The heat capacity and enthalpy of the "Au_2Bi" phase, $Au_{0.67}Bi_{0.33}$.

enthalpy values for $Au_{0.67}Bi_{0.33}$ are given in Fig. 9. This figure shows the presence of two transitions which occur at 620 and 668 K; these correspond well with the eutectic and peritectic compositions and indicate that the sample contains some free bismuth, i.e. stoichiometric "Au_2Bi" occurs at a composition with $x_{Au} > 0.67$. The $C_p(T)$ relationship for temperatures between 250 and 510 K is given by eqn. (7)

$$C_p/(\text{J K}^{-1}\ \text{mole}^{-1}) = 24.54 + 6.25 \times 10^{-3}(T/\text{K}) - 30\,105(T/\text{K})^{-2} \quad (7)$$

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