Thermochimica Acta, 48 (1981) 69—82
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THE HEAT CAPACITY AND ENTHALPY OF SOME HUME-ROTHERY PHASES FORMED BY COPPER, SILVER AND GOLD. PART III. Cu + Ga, Ag + Ga, Au + Ga, Cu + In, Ag + In and Au + In SYSTEMS

PETER C. WALLBRECHT *

Technical University of Clausthal, Clausthal (F.R.G.)

ROGER BLACHNIK

Inorganic Chemistry, University of Siegen, 5900-Siegen 21 (F.R.G.)

KENNETH C. MILLS

Division of Chemical Standards, National Physical Laboratory, Teddington, Middlesex (Gt. Britain)

(Received 25 February 1981)

ABSTRACT

Enthalpies and heat capacities have been determined by differential scanning calorimetry for temperatures between 230 and 1000 K for 16 alloys from the Cu + Ga, Ag + Ga, Au + Ga, Cu + In, Ag + In and Au + In systems. In addition, values for the enthalpy of transformation and fusion have been derived for several of these phases. The endotherms monitored in this study provide valuable information concerning the various phase transformations occurring in these systems. Many of these data substantiate the accepted phase diagrams. However, we recommend that the accepted phase diagram for the Cu + In system should be modified to account for the endotherms reported here; phase diagrams for other systems may also have to be altered to account for thermal effects observed in this investigation.

INTRODUCTION

In this paper we describe the determination of the heat capacities and enthalpies of various binary alloy phases formed between gallium or indium with copper, silver or gold. This study constituted a portion of a larger programme of measurements concerned with the thermal properties of Hume—Rothery phases formed by the Group IB metals. From this larger programme it was hoped that the extent to which the heat capacity of a Hume—Rothery phase was affected by the structure of the phase could be ascertained. In previous papers associated with this measurement programme, we have reported heat capacity and enthalpy data for the Group IB alloys with Sb and Bi [1], with Ge, Sn and Pb [2] and the γ phase formed with Cd and Zn [3].

---

* Present address: SABED, 54100 Massa, Italy.

0040-6031/81/0000—0000/$02.50

However, the phase diagrams for Cu, Ag or Au with Ga or In are very complex and contain regions of considerable uncertainty. The thermal effects monitored in these heat capacity measurements provide valuable information concerning the various transformations occurring in these alloys. Thus, it was hoped that this study would also help in the clarification of the uncertain and disputed regions of the various phase diagrams.

EXPERIMENTAL

The alloys used in this study were prepared from high purity materials (99.9995%); the Cu and In were supplied by Preussag AG, the Ag and Au by Degussa and the Ga by IMC Ltd. (U.K.). The alloy components were melted together in sealed silica capsules and the products quenched, ground and annealed at 5 K below the solidus temperature. Discs were prepared from the powder and stored energy effects caused by the cold work were removed by further annealing. Further details of the preparation are given elsewhere [4].

The measurements were carried out in a Perkin-Elmer differential scanning calorimeter (DSC) model 2. Enthalpy and heat capacity values were derived using the methods described previously [5,6]. The performance of the apparatus was checked by measuring the heat capacity of Ag; the scatter of individual C_p points from the $C_p(T)$ curve due to Hultgren et al. [7] had standard deviations of 1% and 2%, respectively, for the temperature ranges 250—600 K and 600—1000 K.

RESULTS AND DISCUSSION

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

Cu + Ga system

The phases, "$CuGa_2$" ζ_2, ζ_1, β and various "γ" phases, whose stability ranges are markedly dependent upon temperature and composition, are reported in the phase diagram due to Hansen and Anderko [8].

The stability ranges of the "ζ" phases have been redefined in the more recent phase diagram due to Kittl and Massalski [9]. These workers have shown that the low temperature phase, denoted ζ', decomposes peritectoidally above 595 K into the close-packed hexagonal ζ phase, which in turn transforms into the β phase above 763 K. Heat capacity and $(H_T - H_{298})$ values for temperatures between 235 and 797 K were measured in the ζ alloy, $Cu_{0.785}Ga_{0.215}$. The results shown in Fig. 1 reveal the presence of an endotherm with the peak in the $C_p(T)$ curve occurring at 600 K. This endotherm is probably due to the $\zeta' \rightarrow \zeta$ transformation. The transformation was found to be readily reversible; this behaviour would thus rule out the possibility that the peritectoid decomposition of the ζ phase, which is known to be diffusion-controlled, could be responsible for the observed endotherm. The ent-

halpy of transformation has a value of ca. 0.7 kJ mole^{-1}; the shoulder on the C_p peak occurring around 550 K is probably caused by the sluggish nature of the $\zeta' \rightarrow \zeta$ transformation and the dynamic nature of the measurement technique.

The two-phase mixture ($\zeta + \gamma_1$) should attain a single (ζ) phase at 690 K [9] but inspection of Fig. 1 shows the absence of any thermal effect around 690 K which could be associated with this event. This behaviour could be a consequence of the combined effects of the sluggishness of this diffusion-controlled process and the relatively high heating rates used in DSC. Heat capacities for temperatures between 250 and 480 K are given by eqn. (1).

$$C_p/\mathrm{J\,K^{-1}\,mole^{-1}} = 25.23 + 27.0 \times 10^{-3}\,(T/\mathrm{K}) - 123\,450\,(T/\mathrm{K})^{-2}. \quad (1)$$

The β phase with a body-centred cubic structure is formed only at high temperature and corresponds to an electron/atom ratio of 21/14. Heat capacities and enthalpies were measured between 235 and 798 K for the composition $Cu_{0.76}Ga_{0.24}$; the results are given in Fig. 2. As very high quenching rates are required to obtain the β phase, this alloy contains only two phases ($\gamma_1 + \zeta'$) below 595 K [9]; at this temperature the $\zeta' \rightarrow \zeta$ transformation occurs and results in an endotherm with the C_p peak at ca. 600 K. The value, $\Delta_{tr}H = 0.45$ kJ mole^{-1} was obtained for this endotherm. Predel and Stein [10] have reported a value for the enthalpy of fusion of the β phase. Heat capacities for the temperature interval 250—480 K are given by eqn. (2)

$$C_p/\mathrm{J\,K^{-1}\,mole^{-1}} = 23.67 + 5.80 \times 10^{-3}\,(T/\mathrm{K}) - 69\,480\,(T/\mathrm{K})^{-2}. \quad (2)$$

The "γ" phase region corresponds to an electron/atom ratio of 21/13 and it exists as four different modifications, γ, γ_1, γ_2 and γ_3, all of which possess

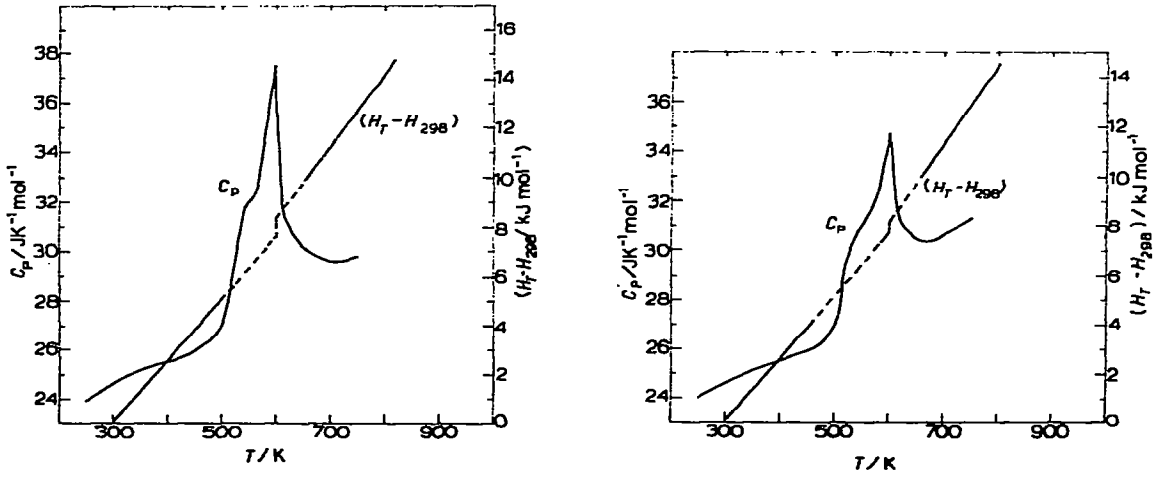


Fig. 1. The heat capacity and enthalpy of the ζ'-phase, $Cu_{0.785}Ga_{0.215}$; — — —, extrapolation of enthalpy data.

Fig. 2. The heat capacity and enthalpy of the ($\gamma + \zeta'$) phase alloy, $Cu_{0.76}Ga_{0.24}$; — — —, extrapolation of enthalpy data.

a γ brass structure with only the copper-rich compositions of the γ phase possessing a full number of atoms per unit cell. The $\gamma_1 \rightarrow \gamma$ transition is of the order—disorder type. Heat capacities and enthalpies were determined for a γ_1 phase alloy with a composition, $Cu_{0.69}Ga_{0.31}$ for the temperature interval 250—798 K. The results, given in Fig. 3, show that no thermal effects were recorded for this temperature range and are thus consistent with extant phase diagrams [8,9]. Predel and Stein [10] have reported an entropy of fusion, $\Delta_{fus}S = 15.4$ J K^{-1} mole^{-1}, from enthalpy of mixing data for an alloy $Cu_{0.679}Ga_{0.321}$. Heat capacities for temperatures between 298 and 700 K are given by eqn. (3).

$$C_p/\text{J K}^{-1}\text{ mole} = 16.46 + 19.8 \times 10^{-3}\,(T/\text{K}) + 147\,700\,(T/\text{K})^{-2}\,. \qquad (3)$$

Ag + Ga system

The phase diagram due to Hansen and Anderko [8] lists the existence of the ζ, ζ' and δ phases. The phase diagram reported by Elliott [11] has modified the stability ranges for the ζ' phase. However, the most recent phase diagram due to Predel and Stein [10] indicates the δ phase does not exist and also shows that the ζ' phase is transformed first to the ζ phase at 698 K and the ζ phase in turn transforms at 790 K to a phase with a different structure. In addition, they report the ζ phase can exist at higher gallium contents than the ζ' phase but on cooling the ζ phase undergoes a tranformation at 573 K to a different, unspecified structure. The ζ and ζ' phases both have closed-packed hexagonal structures.

Heat capacities and enthalpies for the ζ' phase alloy with the composition $Ag_{0.69}Ga_{0.31}$ were measured for the temperature interval 235—798 K. The results shown in Fig. 4 indicate the occurrence of an endotherm which contains four distinct C_p peaks at 585, 620, 675 and 710 K. It is difficult to explain the origin of these peaks on the basis of the extant phase diagrams [8,10,11]. If we adopt the phase diagram due to Predel and Stein [10], the peak at 710 K can be attributed to the completion of the $\zeta' \rightarrow \zeta$ transformation (698 K [10]) and the 620 K peak to the onset of this transformation of the ζ' phase into a two-phase ($\zeta' + \zeta$) mixture. One possible explanation for the peak at 675 K is that it is a non-equilibrium effect caused by the dynamic nature of the measurement technique and sluggishness of the $\zeta' \rightarrow \zeta$ transformation. The C_p peak at 585 K cannot be explained although it may be associated with the thermal effect reported to occur at 573 K on cooling a ζ phase alloy with a higher gallium content [10]. It is obvious that further phase diagram studies are required for an unequivocal interpretation of the data presented in Fig. 4. No attempts have been made to calculate $\Delta_{tr}H$ values from the enthalpy data owing to the difficulties in the interpretation of the various C_p peaks. Predel and Stein [10] have reported a value for the $\Delta_{fus}H$ of the ζ phase. Heat capacities between 250 and 500 K are given by eqn. (4).

$$C_p/\text{J K}^{-1}\text{ mole}^{-1} = 15.38 + 25.9 \times 10^{-3}\,(T/\text{K}) + 189\,500\,(T/\text{K})^{-2} \qquad (4)$$

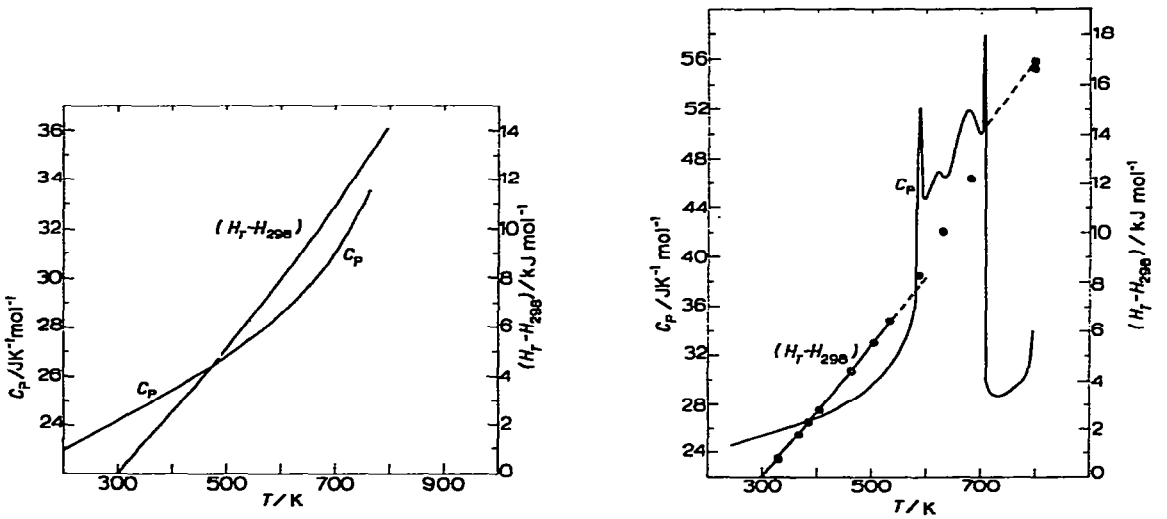


Fig. 3. The heat capacity and enthalpy of the γ_1 phase, $Cu_{0.69}Ga_{0.31}$.

Fig. 4. The heat capacity and enthalpy of the ζ' phase, $Ag_{0.69}Ga_{0.31}$; ●, experimental values of $(H_T - H_{298})$; — — —, extrapolation of enthalpy values, no attempt has been made to extrapolate values in the region of the transformations.

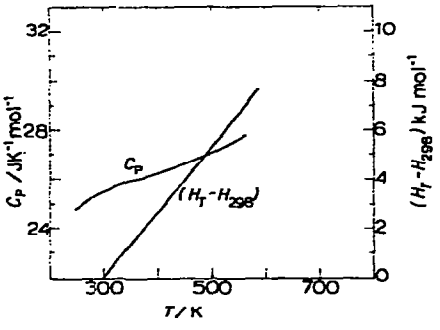
Au + Ga system

The phase diagram due to Cooke and Hume-Rothery [12] contains the β, γ, "AuGa" and "$AuGa_2$" phases.

The γ phase has an electron/atom ratio of 21/13 but does not possess the characteristic, cubic, γ brass structure. The γ phase alloy studied here had a composition $Au_{0.692}Ga_{0.308}$ and heat capacities and enthalpies were determined between 235 and 585 K. The results shown in Fig. 5 indicate that no transformations occur in this temperature range. Heat capacities for this temperature interval are given by eqn. (5).

$$C_p/\mathrm{J\,K^{-1}\ mole^{-1}} = 23.37 + 7.68 \times 10^{-3}\,(T/\mathrm{K}) - 26\,126\,(T/\mathrm{K})^{-2}. \qquad (5)$$

The "AuGa" phase has a MnP type structure. Heat capacities and values of $(H_T - H_{298})$ were determined for $Au_{0.5}Ga_{0.5}$ for temperatures between 235 and 768 K. The results, given in Fig. 6, indicate the presence of an endotherm due to the fusion of the sample, which occurs at 735 K according to Cooke and Hume-Rothery [12]. The values, of $\Delta_{fus}H = 13.6$ kJ mole^{-1} and $\Delta_{fus}S = 18.1$ J K^{-1} mole^{-1} were obtained from these data; the latter value is in reasonable agreement with the value $\Delta_{fus}S = 16.2$ J K^{-1} mole^{-1} obtained from calorimetric studies by Bergman et al. [13], but is much smaller than the value $\Delta_{fus}S = 26.5$ J K^{-1} mole^{-1}, obtained by Predel and Stein [10] from enthalpy of mixing data. These values can be compared with estimated $\Delta_{fus}S$ values; the value $\Delta_{fus}S = 13.9$ J K^{-1} mole^{-1} was obtained using the additive



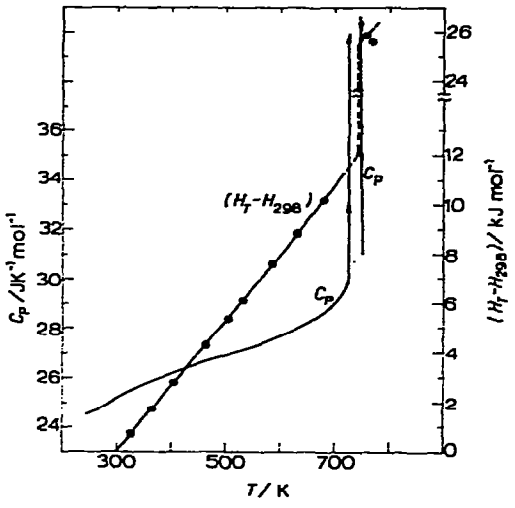


Fig. 5. The heat capacity and enthalpy of the γ phase, $Au_{0.692}Ga_{0.308}$.

Fig. 6. The heat capacity and enthalpy of $Au_{0.5}Ga_{0.5}$; ●, experimental values for $(H_T - H_{298})$; — — —, extrapolation of enthalpy values.

method * and a value $\Delta_{fus}S = 19.7$ J K^{-1} mole^{-1} was obtained when the additional term for ordering was introduced. As this compound exhibits a narrow range of homogeneity, the $\Delta_{fus}S$ term would be expected to be closer to the latter value. Thus the estimated value would appear to support the experimental value $\Delta_{fus}S = 18.9$ J K^{-1} mole^{-1} obtained in this investigation.

Heat capacities for temperatures between 235 and 700 K are given by eqn. (6).

$$C_p/\text{J K}^{-1}\text{ mole}^{-1} = 23.73 + 6.86 \times 10^{-3}\,(T/\text{K}) - 33\,480\,(T/\text{K})^{-2} \qquad (6)$$

The "$AuGa_2$" phase has a cubic (CaF_2-type) structure. Heat capacities and $(H_T - H_{298})$ values were determined between 235 and 782 K for the alloy $Au_{0.34}Ga_{0.66}$. The results given in Fig. 7 show that an endotherm occurs between 715 and 775 K and that two peaks in C_p were observed at 725 and 773 K; these correspond to the solidus and liquidus temperatures, respectively. The values $\Delta_{fus}H = 16.8$ kJ mole^{-1} and $\Delta_{fus}S = 21.7$ J K^{-1} mole^{-1} were obtained for $Au_{0.34}Ga_{0.66}$; the latter value is in reasonable agreement

* In the additive method [14,15], $\Delta_{fus}S$ for an alloy A_yB_{1-y} is estimated by addition of the contributions for each element, viz.

$$\Delta_{fus}S[A_yB_{1-y}] = y\,\Delta_{fus}S[A] + (1-y)\,\Delta_{fus}S[B]$$

However, a highly-ordered alloy has an additional entropy term available to it which is not available to an element on disordering at the melting point; this additional ordering term would have a value of $-R(x_A \ln x_A + x_B \ln x_B)$, where R is the gas constant. It has been pointed out [15] that highly-ordered solids for which this term would be applicable would usually possess a very narrow range of homogeneity.

with the value $\Delta_{fus}S = 19.4$ J K^{-1} mole^{-1} obtained from calorimetric studies [13]. Predel and Stein [10] have reported a much larger value, $\Delta_{fus}S = 28.6$ J K^{-1} mole^{-1}, from enthalpy of mixing data; however, an estimated value, $\Delta_{fus}S = 15.4$ J K^{-1} mole^{-1}, was obtained by the additive method and a value of 20.7 J K^{-1} mole^{-1} was obtained when the additional contribution for the ordering in alloys was included. As this phase possesses a very narrow range of homogeneity, it would be expected to contain a high degree of ordering and thus $\Delta_{fus}S$ would be expected to be close to the higher estimated value. Thus, the estimated value would appear to support the $\Delta_{fus}S$ obtained in the present investigation.

Values for the heat capacity for temperatures between 235 and 700 K are given by eqn. (7).

$$C_p/\text{J K}^{-1}\text{ mole}^{-1} = 24.12 + 6.29 \times 10^{-3}\,(T/\text{K}) - 63\,600\,(T/\text{K})^{-2} \quad (7)$$

Cu + In system

The phase diagram due to Hansen and Anderko [8] shows the existence of the η, β, δ and φ phases. The β phase with a body-centred cubic structure exists only at temperatures above 847 K; it decomposes into the $(\alpha + \delta)$ phases below this temperature. The β phase does not occur at the usual electron/atom ratio of 21/14, owing to size factor effects. Heat capacities and enthalpies were determined for temperatures between 239 and 798 K for the composition $Cu_{0.8}In_{0.2}$. The results given in Fig. 8 show a sharp increase in C_p above 700 K, this is possibly associated with the incipient formation of the β phase from a mixture of $(\alpha + \delta)$ phases. Alternatively, the endotherm may be due to a hitherto unreported transformation. Heat capacities for

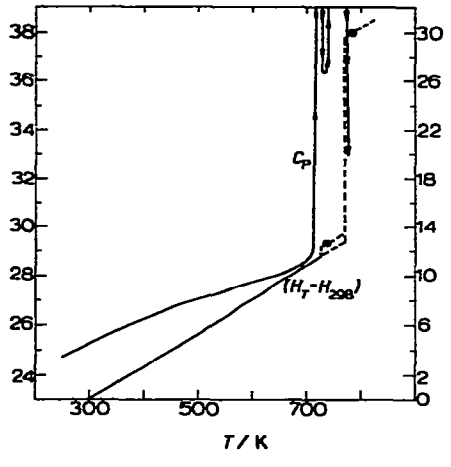


Fig. 7. The heat capacity and enthalpy of $Au_{0.34}Ga_{0.66}$; ●, experimental values for $(H_T - H_{298})$; — — —, extrapolation of enthalpy values.

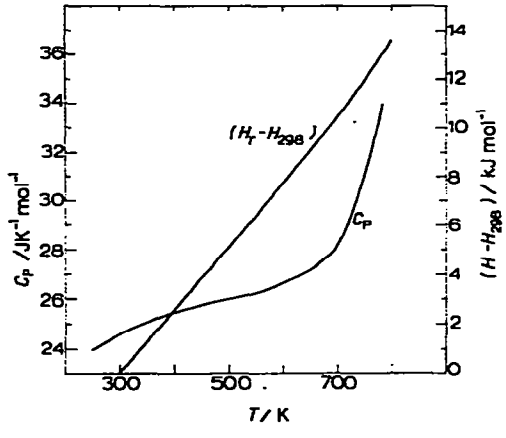


Fig. 8. The heat capacity and enthalpy of the $(\alpha + \delta)$ phase alloy, $Cu_{0.8}In_{0.2}$.

temperatures between 250 and 650 K are given by eqn. (8).

$$C_p/\text{J K}^{-1}\ \text{mole}^{-1} = 24.47 + 3.88 \times 10^{-3}\ (T/\text{K}) - 92\,720\ (T/\text{K})^{-2} \quad (8)$$

The δ phase decomposes above 900 K into the γ phase; the structure of the latter has been variously reported as tetragonal and as a superlattice structure of the NiAs type. The δ phase has an electron/atom ratio of slightly less than the normal 21/13 ratio owing to size factor effects. Heat capacities and enthalpies for the alloy $Cu_{0.7}In_{0.3}$ were determined for the temperature interval 230—984 K. The results shown in Fig. 9 indicate the occurrence of two endotherms with the peaks in the C_p occurring at 910 and 960 K, respectively; these are associated with the transformations ($\delta \rightarrow \gamma$) and ($\gamma \rightarrow$ liquid), reported [8] to occur at 903 and 995 K, respectively. Enthalpy and entropy values for the ($\delta \rightarrow \gamma$) transformation and the ($\gamma \rightarrow$ liquid) fusion were derived from the enthalpy values plotted in Fig. 9; these were $\Delta_{tr}H = 2.45$ kJ mole^{-1}, $\Delta_{tr}S = 2.7$ J K^{-1} mole^{-1}, $\Delta_{fus}H \simeq 9.3$ * kJ mole^{-1} and $\Delta_{fus}S \simeq 9.7$ * J K^{-1} mole^{-1}, respectively. The value, $\Delta_{fus}S \simeq 9.0$ J K^{-1} mole^{-1} was estimated by the additive method; this implies that the γ phase does not possess a high degree of ordering; this view is supported by the wide range of homogeneity exhibited by the γ phase. Heat capacities for temperatures between 250 and 750 K are given by eqn. 9;

$$C_p/\text{J K}^{-1}\ \text{mole}^{-1} = 23.81 + 5.68 \times 10^{-3}\ (T/\text{K}) - 64\,200\ (T/\text{K})^{-2} \quad (9)$$

The η phase which possesses a NiAs type structure, corresponds to an electron/atom ratio of 21/12 and exhibits an appreciable and complex range of homogeneity [16]. Heat capacities and enthalpies were determined between 230 and 888 K for two compositions of the η phase, $Cu_{0.65}In_{0.35}$ and $Cu_{0.625}In_{0.375}$; the results are given in Figs. 10 and 11, respectively.

The $C_p(T)$ curve for $Cu_{0.65}In_{0.35}$ reveals the occurrence of two endotherms, the peaks in C_p occurring at 675 and 740 K. Weibke and Eggers [17] have reported that a transformation occurs at 662 K but this transition was undetected in a subsequent study [18]; however, the most thorough investigation due to Jain et al. [16] indicates that transformations occur at 615, 660, 723 and 750 K. No thermal effect of 615 K was detected in this study, corresponding to the transition [16], $Cu_{2-x}In(C)$ ** $\rightarrow$ $Cu_{2-x}In(B)$ **. However, the transition at 675 K, $\Delta_{tr}H \simeq 0.17$ kJ mole^{-1}, observed in this study corresponds to the transformation [16] of the latter into $Cu_{2-x}In(A')$. According to Jain et al. [16] the A′ phase should undergo the following transitions

$$Cu_{2-x}In(A') \xrightarrow{723\ K} Cu_{2-x}In(A) \xrightarrow{750\ K} Cu_{2-x}In(h)$$

The endotherm recorded at 740 K, $\Delta_{tr}H \simeq 0.22$ kJ mole^{-1} probably corre-

* The proximity of the various C_p peaks to each other makes the selection of temperature ranges for the determination of $\Delta_{tr}H$ or $\Delta_{fus}H$ extremely difficult. Attempts have been made to determine these values but the values obtained may be slightly low owing to the nature of these experiments.

** Nomenclature adopted by Jain et al. [16].

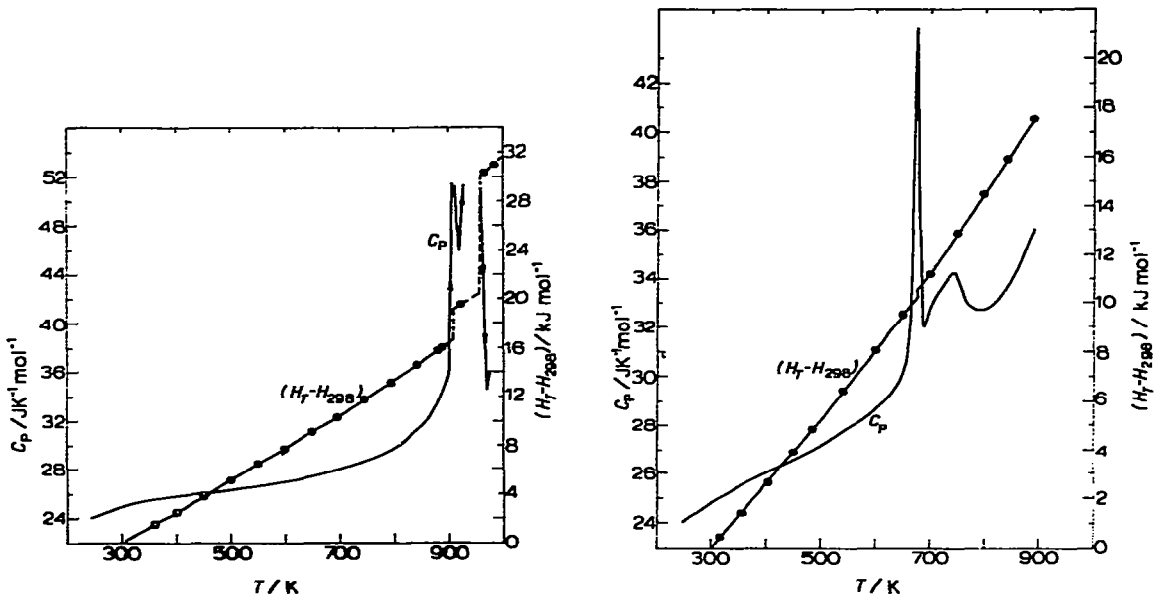


Fig. 9. The heat capacity and enthalpy of the δ phase, $Cu_{0.7}In_{0.3}$; ●, experimental values for $(H_T - H_{298})$; — — —, extrapolation of enthalpy values.

Fig. 10. The heat capacity and enthalpy of the η phase, $Cu_{0.65}In_{0.35}$; ●, experimental values for $(H_T - H_{298})$.

sponds to the combined thermal effects for both these transitions.

Heat capacities for temperatures between 250 and 600 K are given by eqn. (10)

$$C_p/\text{J K}^{-1}\text{ mole}^{-1} = 20.63 + 13.2 \times 10^{-3}\,(T/\text{K}) + 11\,960\,(T/\text{K})^{-2} \qquad (10)$$

Three endotherms were detected in the $C_p(T)$ curve for $Cu_{0.625}In_{0.375}$ shown in Fig. 11; the peaks in C_p occurred at 430, 590 and 635 K. The endotherm at 430 K, with $\Delta_{tr}H = 0.043$ kJ mole^{-1}, is obviously associated with the presence of free indium (m.p. 430 K). This provides clear evidence that the φ phase does not exist. Calculations based on the recorded $\Delta_{tr}H$ value permit the amount of free indium to be calculated and from this we deduce that the B phase must occur at ca. $Cu_{0.633}In_{0.367}$, in excellent agreement with the findings of Jain et al. [16]. The phase diagram reported by Jain et al. [16] indicates that transformations should occur at 580, 640 and 720 K. The endotherm at 590 K ($\Delta_{tr}H \simeq 0.70$ kJ mole^{-1}) corresponds to the transition [16]

$$Cu_{2-x}(B) \xrightarrow{580\,K} Cu_{2-x}\,In(A')$$

and that at 635 K to

$$Cu_{2-x}\,In(A') \xrightarrow{640\,K} Cu_{2-x}\,In(A)$$

No thermal effect was detected at ca. 720 K in this investigation which

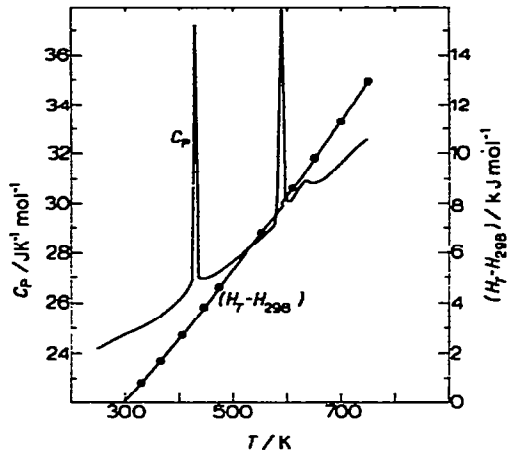


Fig. 11. The heat capacity and enthalpy of the η phase, $Cu_{0.625}In_{0.375}$; ●, experimental values for $(H_T - H_{298})$.

corresponds to the transformation

$$Cu_{2-x}In(A) \xrightarrow{720\,K} Cu_{2-x}In(h)$$

Ag + In system

The phase diagram due to Hansen and Anderko [8] shows the presence of the ζ', γ' and φ phases at room temperature; the β, ζ and γ phases are stable at higher temperatures. However, there are considerable uncertainties in the phase diagram, particularly in the compositional range $x_{In} = 0.2$—0.4.

The cubic (bcc) β phase exists only at high temperatures and decomposes on cooling first to the ζ phase and then to the ζ' phase. The β phase corresponds to an electron/atom ratio of 21/14. Heat capacities and enthalpies were measured for temperatures between 229 and 888 K for an alloy $Ag_{0.745}In_{0.255}$; the results are given in Fig. 12. One endotherm, with the peak in C_p at 493 K, was observed. This endotherm can be attributed to the $\zeta' \rightarrow \zeta$ transformation reported to occur at 460 K [8]. This transformation is reported to belong to the order—disorder type; the values $\Delta_{tr}H \simeq 1.0$ kJ mole^{-1} and $\Delta_{tr}S \simeq 2.1$ J K^{-1} mole^{-1} were derived for this transition.

Heat capacities and enthalpies were determined over the temperature range 108—936 K for the γ' phase alloy $Ag_{0.67}In_{0.33}$. The results given in Fig. 13 reveal the presence of three endotherms, with C_p peaks at 445, 567 and 918 K. The endotherm at 445 K is probably associated with the $\gamma' \rightarrow \gamma$ transition, which is reported to be an order—disorder transformation. However, the recorded $\gamma' \rightarrow \gamma$ transition temperature (445 K) is considerably lower than the temperature cited in the phase diagram [8] (477 K). An alternative but less likely explanation is that the sample contained some φ phase and this underwent peritectic decomposition at 439 K [8]. The value $\Delta_{tr}H =$

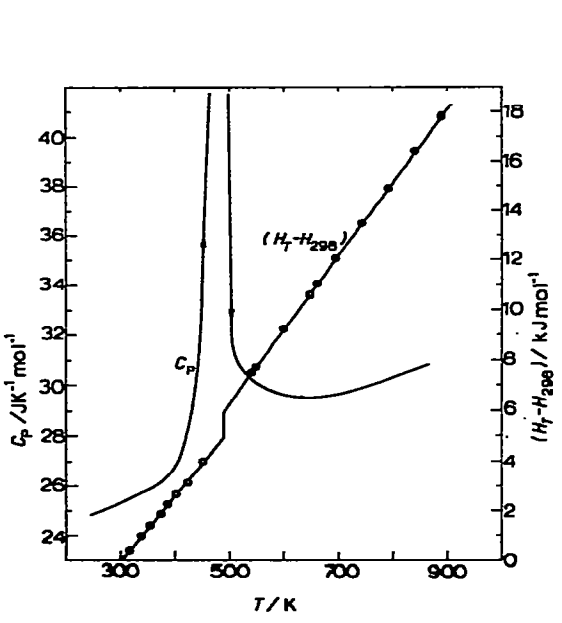


Fig. 12. The heat capacity and enthalpy of the ζ' phase, $Ag_{0.745}In_{0.255}$; ●, experimental values for $(H_T - H_{298})$.

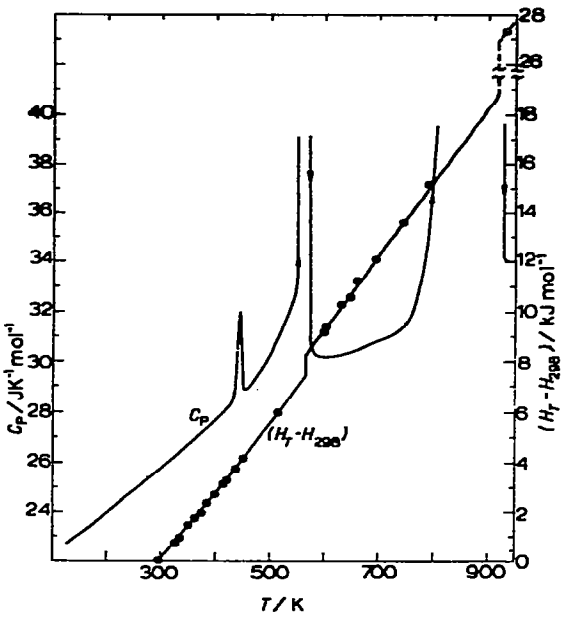


Fig. 13. The heat capacity and enthalpy of the γ' phase, $Ag_{0.67}In_{0.35}$; ●, experimental values for $(H_T - H_{298})$; — — —, extrapolation of enthalpy data.

0.015 kJ mole^{-1} was obtained for this endotherm, although this may not represent an equilibrium value for an assumed $\gamma' \rightarrow \gamma$ transformation, as annealing times of considerable duration would be required for the conversion of any γ phase left on quenching the sample.

The endotherm of 567 K can be attributed to the peritectic decomposition of the γ phase and the formation of the ζ phase, reported to occur at ca. 560 K [8]. The values $\Delta_{tr}H = 0.90$ kJ mole^{-1} and $\Delta_{tr}S = 1.6$ J K^{-1} mole^{-1} were obtained for this transformation.

The third endotherm commences around 760 K and culminates in a C_p peak at 919 K; this endotherm is clearly attributable to the ($\zeta \rightarrow \zeta$ + liquid) transformation, as the temperatures are in agreement with those cited in the phase diagram [8] (770 and 910 K). It is possible to derive ΔH and ΔS for the fusion of the ζ phase by extrapolation of the $(H_T - H_{298})$—temperature relationship for the range (600—750 K) to 918 K; the values obtained, $\Delta_{fus}H \simeq 8$ * kJ mole^{-1} and $\Delta_{fus}S \simeq 8.7$ * J mole^{-1} K^{-1}, are identical with values obtained by the additive method.

Au + In system

According to the phase diagram reported by Shunk [19], the following phases exist at room temperature, "$AuIn_2$", "AuIn", γ', ϵ', ζ_1 and ζ and the γ, and ϵ phases exist at higher temperatures. In this study we have measured heat capacities of the $AuIn_2$, AuIn and γ' phases.

---

* See footnote p. 76.

The γ and γ' phases correspond to an electron/atom ratio of 21/13; the γ' phase has a γ brass structure and the γ phase has a close-packed hexagonal structure. Heat capacities and enthalpies were determined for temperatures between 235 and 798 K for the γ' phase alloy, $Au_{0.7}In_{0.3}$; the results are given in Fig. 14. Two endotherms were observed.

The first endotherm, which exhibited a peak in C_p at 665 K, is due to the $\gamma' \rightarrow \gamma$ transformation which has been reported [8] to occur at 638 K and 646 K for In-rich and Au-rich boundaries of the γ' phase, respectively; values of $\Delta_{tr}H = 0.82$ kJ mole^{-1} and $\Delta_{tr}S = 1.25$ J K^{-1} mole^{-1} were calculated for this transformation.

The second endotherm contains two C_p peaks at 740 and 760 K and these represent the solidus and liquidus temperatures, respectively, for the fusion of the γ phase. These temperatures are in agreement with the solidus and liquidus temperatures 738 and 758 K, respectively, cited in the phase diagram due to Shunk [19]. Values of $\Delta_{fus}H = 7.0$ * kJ mole^{-1} and $\Delta_{fus}S = 9.2$ * J K^{-1} mole^{-1} were derived from these measurements. The latter value can be compared with the estimated value, $\Delta_{fus}S = 8.9$ J K^{-1} mole^{-1} calculated using the additive method. This suggests that this phase does not possess a high degree of ordering, a view supported by the wide range of homogeneity of the γ phase. Heat capacities for temperatures between 250 and 550 K are given by eqn. (11).

$$C_p/\text{J K}^{-1}\text{ mole}^{-1} = 21.39 + 11.6 \times 10^{-3}\,(T/\text{K}) - 488\,80\,(T/\text{K})^{-2} \qquad (11)$$

The "AuIn" phase has a triclinic structure. Heat capacities and enthalpies were determined for the alloy $Au_{0.5}In_{0.5}$ for temperatures between 229 and 749 K. The results given in Fig. 15 show the occurrence of three endotherms with C_p peaks at 636, 730 and 790 K. The 790 K endotherm obviously refers to the liquidus temperature and the 730 K endotherm refers to the solidus temperature for compositions lying outside the Au-rich boundary of the "AuIn" stability range. Thus, the Au-rich boundary of this phase must occur at a composition $Au_{0.5+y}In_{0.5-y}$, where y is positive. The small value derived for $\Delta_{tr}H = 0.015$ kJ mole^{-1} obtained for the 730 K endotherm, indicates the rather small quantity of γ phase present. The values $\Delta_{fus}H = 11.34$ kJ mole^{-1} and $\Delta_{fus}S = 14.4$ J K^{-1} mole^{-1} were obtained from experimental data. The latter value can be compared with estimated $\Delta_{fus}S$ values of 8.5 J K^{-1} mole^{-1} obtained by the additive method and 14.3 J K^{-1} mole^{-1} when the additional contribution for ordering in alloys is included. Thus "AuIn" would appear to have a fully-ordered structure, in keeping with the narrow homogeneity range exhibited by this phase.

The cause of the endotherm at 636 K cannot be readily explained on the basis of the phase diagram due to Shunk [19]. At first glance it would appear that an earlier phase diagram [8] affords a possible explanation for the occurrence of this endotherm at 636 K; we have seen above that the sample contains a small amount of the γ' phase and that this transforms to the γ phase at 637 K [8]. However, this explanation would appear to be unlikely because by use of the value $\Delta_{tr}H = 0.120$ kJ mole^{-1} for this transition we can calculate that the sample contained 15 mole % of the γ phase ** and this

* See footnote p. 76.

** Based on the value $\Delta_{tr}H = 0.82$ kJ mole^{-1} for $Au_{0.7}In_{0.3}$.

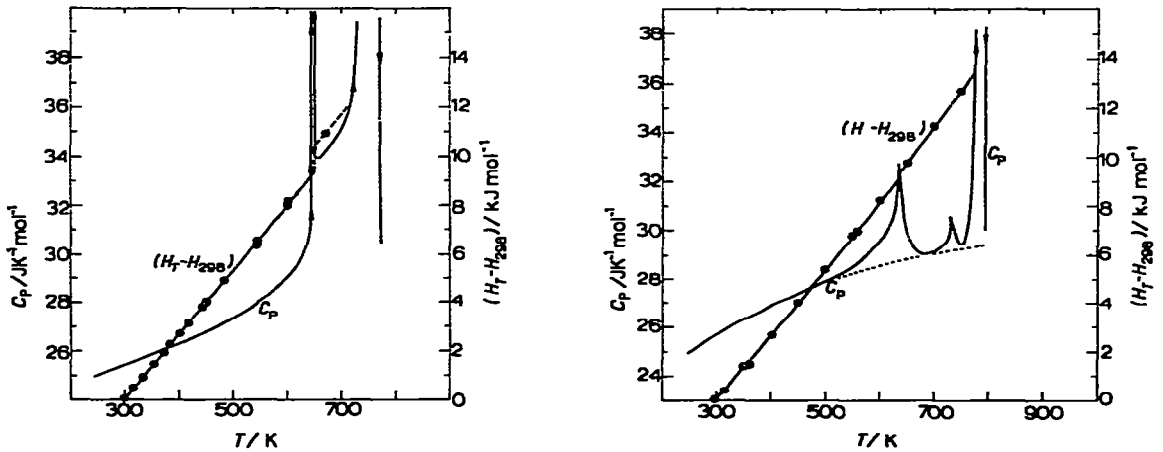


Fig. 14. The heat capacity and enthalpy of the γ phase, $Au_{0.7}In_{0.3}$; ⊕, experimental values for $(H_T - H_{298})$.

Fig. 15. The heat capacity and enthalpy of the phase, $Au_{0.5}In_{0.5}$; ●, experimental values for $(H_T - H_{298})$; · · · · · ·, extrapolation of C_p data.

is obviously not the case. Thus, we must conclude that further phase studies are required to account for the endotherm at 636 K. Heat capacities for the range 250—500 K are given by eqn. (12).

$$C_p\,/\mathrm{J\,K^{-1}\ mole^{-1}} = 23.77 + 8.65 \times 10^{-3}\,(T/\mathrm{K}) - 57\,860\,(T/\mathrm{K})^{-2} \qquad (12)$$

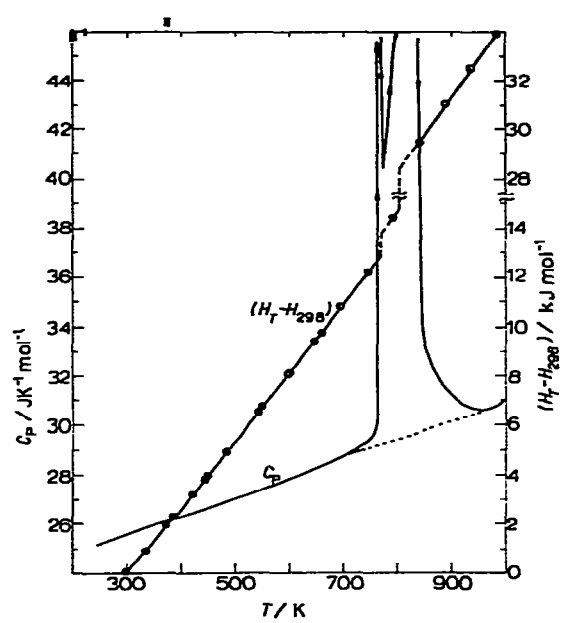


Fig. 16. The heat capacity and enthalpy of the phase, $Au_{0.34}In_{0.66}$; ●, experimental values for $(H_T - H_{298})$; · · · · · ·, extrapolation of C_p data; — — —, extrapolation of enthalpy data.

The $AuIn_2'$ phase has a cubic (CaF_2-type) structure. Heat capacities and enthalpies for the composition $Au_{0.34}In_{0.66}$ were determined for the temperature range 235—984 K. The results given in Fig. 16 show the occurrence of two endotherms with C_p peaks at 771 and 827 K. These represent the solidus and liquidus temperatures for compositions lying outside the Au-rich boundary of the "$AuIn_2$" phase; the phase diagram [19] cites temperatures at 769 and 813 K, respectively. The values $\Delta_{fus}H = 14.5(b)$ kJ mole^{-1} and $\Delta_{fus}S = 17.5(b)$ J K^{-1} mole^{-1} were calculated from the experimental data. The latter value can be compared with estimated $\Delta_{fus}S$ values of 8.2 J K^{-1} mole^{-1} using the additive method and 13.5 J K^{-1} mole^{-1} when the additional term for ordering in an alloy is included. Thus, we conclude that the "$AuIn_2$" phase contains a high degree of ordering. Heat capacities for temperatures between 250 and 700 K are given by eqn. (13).

$$C_p/\text{J K}^{-1}\text{ mole}^{-1} = 22.91 + 8.15 \times 10^{-3}\,(T/\text{K}) + 17\,820\,(T/\text{K})^{-2} \qquad (13)$$

ACKNOWLEDGEMENT

We wish to thank Dr. M.J. Richardson for his help and for the discussions concerning the work described in this paper.

REFERENCES

1 P.C. Wallbrecht, R. Blachnik and K.C. Mills, Thermochim. Acta, 45 (1981) 189.
2 P.C. Wallbrecht, R. Blachnik and K.C. Mills, Thermochim. Acta, 46 (1981) 167.
3 P.C. Wallbrecht, F. Black, R. Blachnik and K.C. Mills, Scr. Metall., 10 (1976) 579.
4 P.C. Wallbrecht, PhD Thesis, Technical University of Clausthal, F.R.G., 1976.
5 K.C. Mills and M.J. Richardson, Thermochim. Acta, 6 (1973) 427.
6 M.J. Richardson and P. Burrington, J. Therm. Anal., 6 (1974) 345.
7 R. Hultgren, J.D. Desai, D.J. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of Thermodynamic Properties of the Elements, Am. Soc. Met., Metals Park, Ohio, 1973.
8 M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.
9 J.E. Kittl and T.B. Massalski, J. Inst. Met., 93 (1964/1965) 182.
10 B. Predel and D.W. Stein, Acta Metall., 20 (1972) 681.
11 R.P. Elliott, Constitution of Binary Alloys, McGraw-Hill, New York, 1965.
12 C.J. Cooke and W. Hume-Rothery, J. Less-Common Met., 10 (1966) 42.
13 C. Bergman, J.P. Bros, M. Carbonel, M. Gambino and M. Laffitte, Rev. Int. Hautes Temp. Refract., 8 (1971) 205.
14 C. Wagner, Z. Metallkd., 31 (1939) 18.
15 O. Kubaschewski, E.L. Evans and C.B. Alcock, Metallurgical Thermochemistry, Pergamon Press, London, 1967, pp. 212—213.
16 K.C. Jain, M. Ellner and K. Schubert, Z. Metallkd., 63 (1972) 456.
17 J. Weibke and H. Eggers, Z. Metallkd., 31 (1939) 209.
18 J. Reynolds, W.A. Wiemann and W. Hume-Rothery, J. Inst. Met., 80 (1951/1952) 637.
19 F.A. Shunk, Constitution of Binary Alloys, McGraw-Hill, New York, 1969.