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A Thermodynamic Evaluation of the Ag—Al System**

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Published experimental information on the phase diagram and thermodynamic properties of silver-aluminium alloys have been used in carrying out a critical thermodynamic evaluation of the system. The evaluation provides a set of coefficients which may be used to calculate phase boundary compositions and thermodynamic values in close agreement with experimental measurements.

(Keywords: Phase diagram; Thermodynamic properties; Ag—Al*)*

Eine thermodynamische Auswertung des Ag—Al *Systems*

Veröffentlichte experimentelle Daten zum Phasendiagramm und zu thermodynamischen Eigenschaften von Silber—Aluminium-Legierungen wurden zu einer kritischen thermodynamischen Auswertung des Systems genutzt. Dabei wurde ein Satz von Koeffizienten erhalten, der die Berechnung von Phasen-Grenzzusammensetzungen und thermodynamischen Werten erlaubt, die eng mit experimentellen Messungen übereinstimmen.

1. Introduction

Small additions of Ag to Al—Zn—Mg alloys are found to improve strength and corrosion resistance, while the mechanical properties of Al—Cu alloys are also improved by silver additions [1]. In order that the phase equilibria in these and in other multicomponent alloys containing Ag and Al may be calculated, an evaluation of the available phase diagram and thermodynamic information for the Ag—Al system has been made.

** Dedicated to Prof. Dr. *K. L. Komarek,* Vienna, on the occasion of his 60th birthday.

One particular feature of published phase diagram results for this system is an unusually sharp change in slope of the solvus curve for Al-rich alloys at a composition close to 80 at.% Al [2]. It was hoped that a thermochemical evaluation of the available experimental data might help in establishing the position of this solvus with greater reliability.

2. Experimental Phase Diagram Information

The phase diagram information summarised by *Hansen* and *Anderko* [2] has been used as basis for the present evaluation. More recent experimental results obtained by *Roberts* and *Chadwick* [3] for the solvus curve and for the composition of the eutectic in Al-rich alloys have been given greater weight than those of other authors, however, and are included in the experimental diagram shown in Fig. 1.

An interesting feature of the Ag—Al phase diagram is the direct transformation of the hcp ζ phase into the bcc β phase at a composition close to 25 at.% Al and a temperature of about 875 K. The β/ζ equilibrium phase boundaries have been established by the very careful work of *Hume-Rothery* et al. [4] and result in the observed minimum in the stability range of β. Earlier studies had suggested that β decomposes eutectoidally into

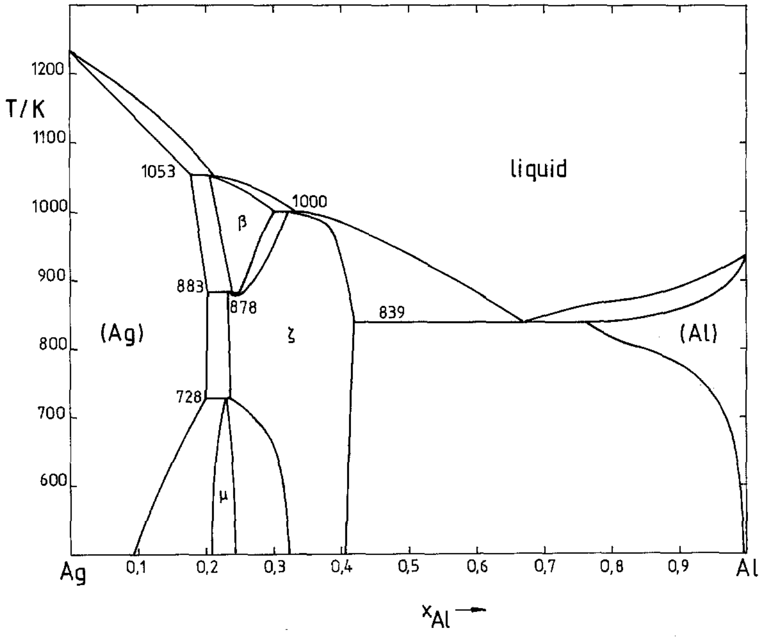

Fig. 1. Experimentally determined Ag—Al phase diagram

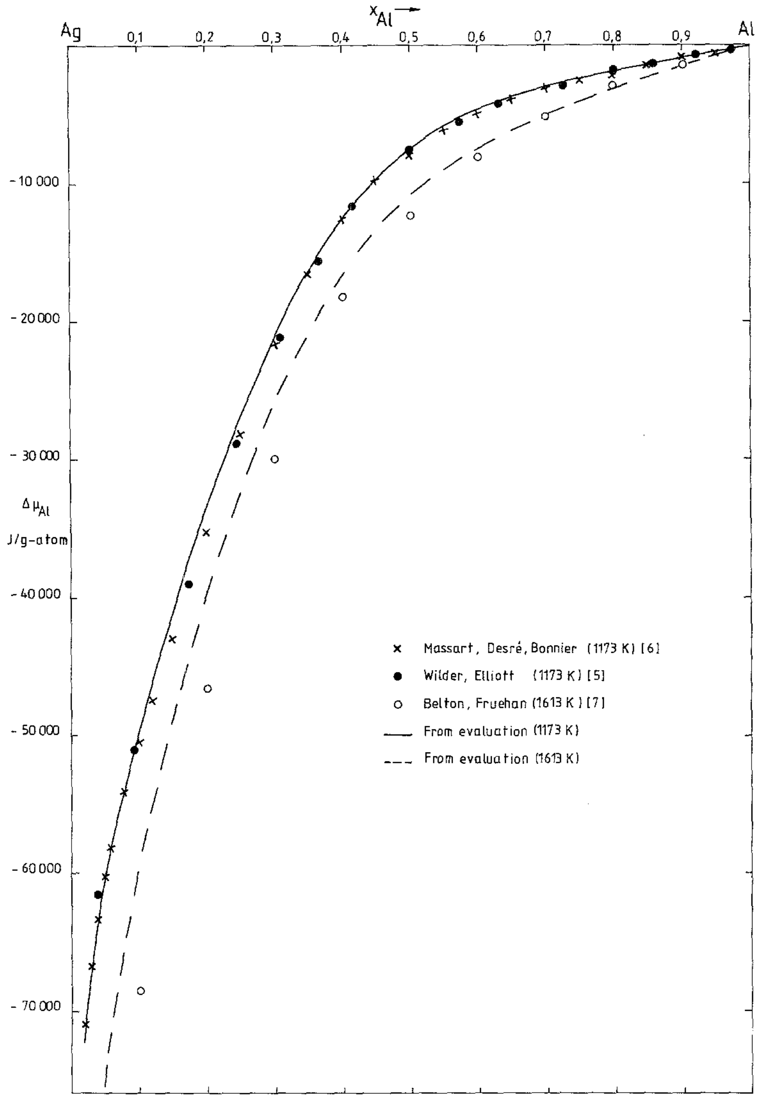

Fig. 2. Relative chemical potential of Al in liquid Ag—Al alloys

(Ag) and ζ at a temperature variously determined to lie between 873 K and 888 K.

The measurements made by [4] also showed that the μ phase has a range of stoichiometry and does not lie at the fixed composition Ag_3Al as reported in earlier work. Its temperature of formation is chosen as 728 K ([2] *Elliott*).

3. Experimental Thermodynamic Information

3.1. Liquid Alloys

The relative chemical potential of aluminium in liquid Ag—Al alloys has been determined by *Wilder* and *Elliott* [5] (973–1 253 K), and by *Massart, Desré* and *Bonnier* [6] (liquidus—1 323 K) using an emf method, and by *Belton* and *Fruehan* [7] (1 613 K) using *Knudsen*-cell mass-spectrometry. At a common temperature of 1 173 K the results of [5] and [6] are in excellent agreement, while those of [7] are generally more

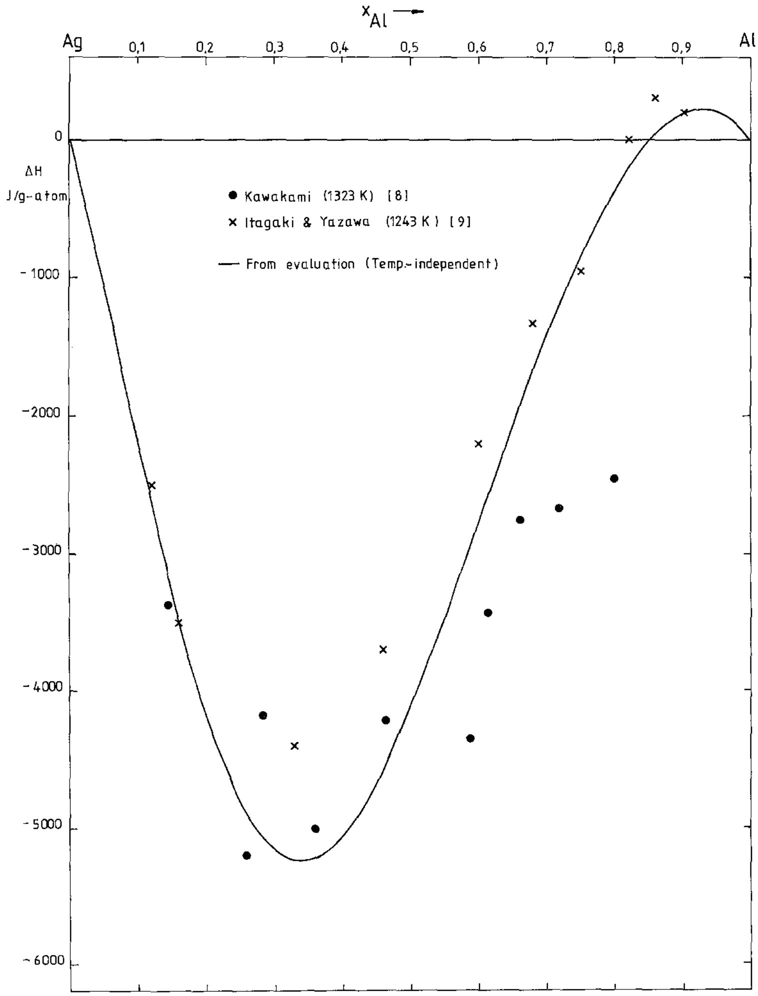

Fig. 3. Enthalpy of mixing of liquid Ag—Al alloys

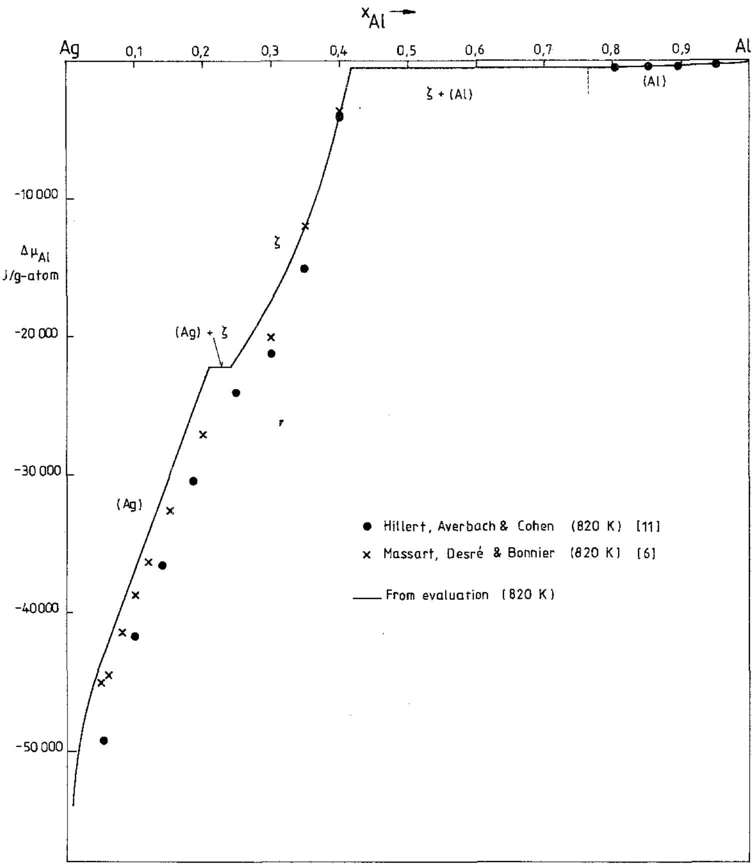

Fig. 4. Relative chemical potential of Al in solid Ag—Al alloys

exothermic, in particular in Ag-rich alloys, than values calculated using the results of the present evaluation (see Fig. 2).

Calorimetric measurements of enthalpies of mixing for liquid Ag—Al alloys have been made by *Kawakami* [8] (1 323 K) and by *Itagaki* and *Yazawa* [9] (1 243 K), while *Mathieu, Jounel, Desré* and *Bonnier* [10] have obtained a value for the relative partial enthalpy of solution at infinite dilution of Ag in liquid Al at 960 K using liquid aluminium solution calorimetry. There is a rather large scatter in the values determined by [8], which differ by up to ~ 2 kJ/g-atom from those of [9], in particular in Al-rich alloys (Fig. 3).

3.2. Solid Alloys

The relative chemical potential of aluminium in solid Ag—Al alloys has been determined by *Hillert, Averbach* and *Cohen* [11] (642–820 K) for

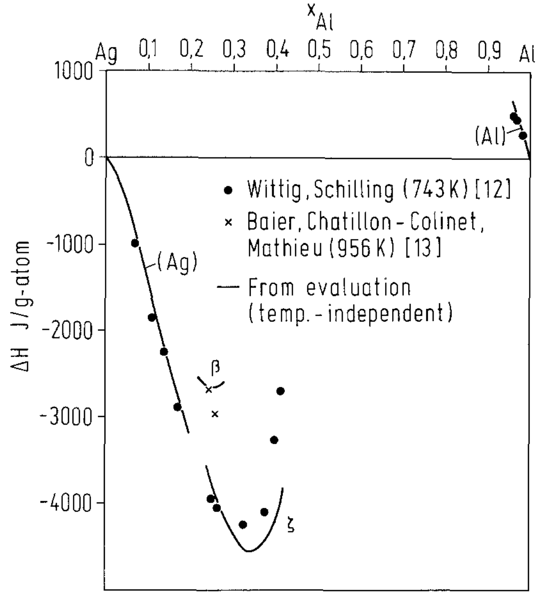

Fig. 5. Enthalpy of formation of solid Ag—Al alloys

the (Ag), ζ and (Al) phases and by *Massart, Desré* and *Bonnier* [6] (623 K—solidus) for the (Ag) and ζ phases. An emf method was used in both investigations. The results obtained by [6] are presented as values of $\Delta\overline{H}_{Al}$ and $\Delta\overline{S}_{Al}$ for each alloy composition. When these are used to calculate $\Delta\mu_{Al}$ at a temperature of 820 K for comparison with the results of [11], there is generally satisfactory agreement between the two sets of experiments, the values from [11] being somewhat more exothermic (~ 2 kJ/g-atom) than those of [6] (Fig. 4).

Enthalpies of formation for the (Ag), ζ and (Al) phases have been measured by *Wittig* and *Schilling* [12] (743 K) and for the β phase by *Baier, Chatillon-Colinet* and *Mathieu* [13] (955 K) using liquid metal solution calorimetry. Since no measurement has been made of the enthalpy of transformation ζ → β, it is difficult to compare the consistency of the two sets of results. If the difference in the measurement temperatures for ΔH of ζ and β alloys is ignored, the two sets of experiments provide a value of approx. 1200 J/g-atom for the ζ → β transformation enthalpy.

The experimental enthalpies of formation are illustrated in Fig. 5, which shows that the asymmetric form of the ΔH curve found for liquid alloys (Fig. 3) is reproduced in the solid.

4. Method of Evaluation

The individual experimental values reported in references [1] to [13], together with an estimated error for each value and with corresponding individual errors for the temperature and composition of each measurement, were used as input data for the optimization program written by *Lukas* et al. [14]. Using this program, a set of G^E coefficients for the liquid, fcc (treated as one phase existing both at the Ag-rich and Al-rich ends of the system), β, ζ and μ phases of the system were obtained, where G^E is represented by a *Redlich-Kister* polynomial equation of the form:

$$G^E = x_i x_j \sum_{v=0}^{n} (x_i - x_j)^v L_{ij}^{(v)}(T) \tag{1}$$

with $L_{ij}^{(v)}(T) = A_{ij}^{(v)} + B_{ij}^{(v)} \cdot T$ $(i = \mathrm{Ag}, j = \mathrm{Al})$.

The coefficients $L_{ij}^{(v)}(T)$ are linear functions of temperature, i.e. $A_{ij}^{(v)}$ and $B_{ij}^{(v)}$ correspond to the temperature-independent values of the enthalpy and excess entropy of mixing.

For the pure components Ag and Al, a conventional *Gibbs* Energy function of the form

$$G = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} \tag{2}$$

was used to represent the data of the stable and metastable phases. Data for the stable phases of Ag (fcc, liquid) and Al (fcc, liquid) were taken from the *Barin, Knacke, Kubaschewski* Tables [15]. For the metastable phases of the pure metals (required to express the excess properties of mixing of the different solution phases in the system), *Gibbs* energies were calculated by combining data for the stable phases of Ag and Al with *Kaufman*'s values for the transformation energies Ag (fcc → bcc) [16] and Al (fcc → bcc; fcc → hcp) [17]. Since no value is available for the Ag (fcc → hcp) transformation, the transformation energy of Cu (fcc → hcp) [18] was used. To describe the *Gibbs* energies of Ag and Al in the μ (cubic, A13) structure, bcc phase stability values were used.

5. Results and Discussion

The *Gibbs* energy values (phase stabilities) for Ag and Al and the G^E coefficients for the solution phases of the Ag—Al system are summarised in Tables 1 and 2 respectively. The complete, evaluated set of coefficients has been used to calculate the thermodynamic properties of the solid and liquid phases as well as the Ag—Al phase diagram.

In Fig. 2 a comparison is made between the different experimental results for the relative chemical potential of Al in liquid Ag—Al alloys and the corresponding values obtained from the evaluation. There is excellent

Table 1. *Phase stabilities of* Ag *and* Al: $G = a + bT + cT\ln T + dT^2 + eT^3 + f/T$ (J mol^{-1})

	a	b	c	d	e	f
Liquid Phase						
Ag (liq)	− 3 577.5	180.813	− 33.472	0	0	0
Al (liq)	− 785.1	177.381	− 31.74819	0	0	0
(Ag) *and* (Al) *Phase*						
Ag (fcc)	− 4 794.8	90.0937	− 19.7317	-4.79905×10^{-3}	0	− 266 521
Al (fcc)	− 10 019.1	179.8848	− 31.3758	8.19645×10^{-3}	-3.45883×10^{-6}	180 330.5
β *and* μ *Phase*						
Ag (bcc)	− 1 029.2	88.2109	− 19.7317	-4.79905×10^{-3}	0	− 266 521
Al (bcc)	64.3	175.0722	− 31.3758	8.19645×10^{-3}	-3.45883×10^{-6}	180 330.5
ζ *Phase*						
Ag (hcp)	− 4 166.8	91.3487	− 19.7317	-4.79905×10^{-3}	0	− 266 521
Al (hcp)	− 4 459.5	178.0302	− 31.3758	8.19645×10^{-3}	-3.45883×10^{-6}	180 330.5

Table 2. *Excess Gibbs energy, G^E, coefficients for the liquid,* (Ag), (Al), *β, ζ and μ phases of the* Ag—Al *system:*

$$G^E = x_{Ag} x_{Al} \sum_{v=0}^{n} (x_{Ag} - x_{Al})^v L^{(v)}_{AgAl}(T)$$

$$L^{(v)}_{AgAl} = A^{(v)}_{AgAl} + B^{(v)}_{AgAl} \cdot T \quad (v = 0, 1, 2, 3, 4)$$

Phase	v	$A^{(v)}_{AgAl}$	$B^{(v)}_{AgAl}$
Liquid	0	− 16 530.9	− 4.52985
	1	− 24 126.7	4.03342
	2	4 153.2	− 6.29185
	3	11 892.6	− 4.23046
	4	6 907.2	− 2.44432
(Ag), (Al) (fcc)	0	− 3 444.2	− 9.49631
	1	− 39 811.3	20.95965
	2	− 517.9	− 8.01109
	3	30 653.3	− 27.72050
	4	10 065.3	2.27910
β (bcc)	0	− 22 367.0	− 3.53992
	1	− 43 001.5	9.06848
	2	4 880.5	9.57410
ζ (hcp)	0	− 16 640.0	− 1.46286
	1	− 93 430.8	− 13.27040
	2	215 739.9	64.42568
	3	− 228 243.2	− 116.43643
	4	129 700.0	− 0.30558
μ (cubic, A13)	0	− 10 231.8	14.55079
	1	− 139 026.4	4.65487
	2	87 093.0	26.00678

agreement with the results of the emf experiments [5, 6] at 1 173 K and moderate to good agreement with the mass-spectrometric values [7] at 1 613 K.

The comparison between experimental and evaluated enthalpies of mixing for liquid alloys shown in Fig. 3 reveals the greater self-consistency of the measurements made by *Itagaki* and *Yazawa* [9] than those made by *Kawakami* [8]. The evaluated curve is in good agreement with the data of [9] except at compositions between about 30 to 50 at.% Al, where the deviation is approx. 800 J/g-atom.

In Fig. 4, the evaluated relative chemical potential of Al in the fcc [(Ag) and (Al)] and hcp (ζ) phases is compared with the results of emf experiments [6, 11] at 820 K. The agreement is generally satisfactory, although at lower Al concentrations the evaluated $\Delta\mu_{Al}$ values are somewhat less exothermic than the measured data.

Fig. 5 compares the evaluated and measured [12, 13] enthalpies of formation of (Ag), β, ζ and (Al) alloys. There is excellent agreement between the experimental and evaluated results except for compositions on the Al-richer side of the ζ phase, where the evaluated data are ~ 1 to 1.2 kJ/g-atom more exothermic than the measured [12] values. The transformation enthalpy $\zeta \rightarrow \beta$ (875 K) obtained from the evaluation for an alloy of composition $x_{Al} = 0.245$ is 1 008 J/g-atom. This may be compared with the approximate experimental value of 1 200 J/g-atom.

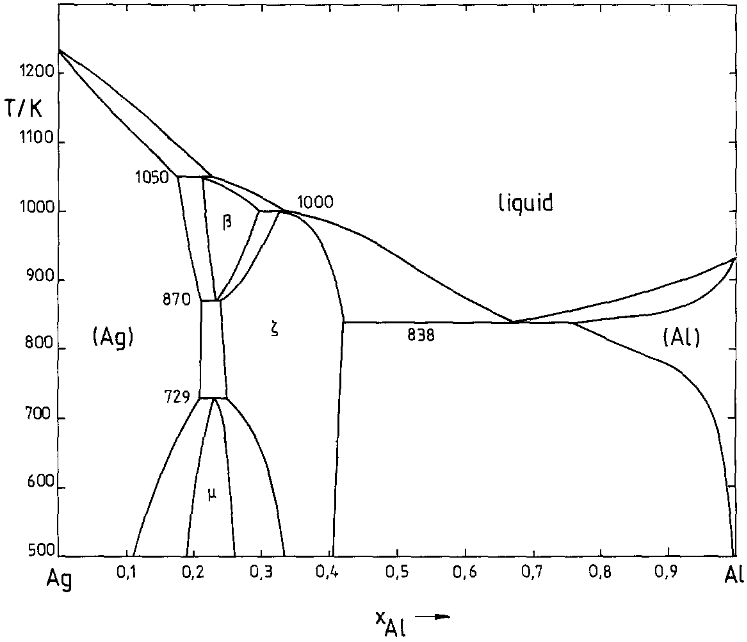

Fig. 6. Ag—Al phase diagram calculated using the evaluated data

The phase diagram calculated with the evaluated set of coefficients given in Tables 1 and 2 is shown in Fig. 6. The agreement with the experimentally-determined phase diagram is generally very good, as can be seen from Fig. 1 and 6 and from the comparison of calculated and measured 3-phase equilibria given in Table 3. However, the observed minimum in the β-phase [4] was found impossible to reproduce without producing a small range of stability of ζ in the (Ag) phase at compositions between approx. $x_{Al} = 0.1$ and 0.2 and temperatures of about 1 075–

Table 3. *Experimental and calculated 3-phase equilibria in the* Ag—Al *system*

Equilibrium	Experimental results [2]		Calculated results	
Peritectic (Ag) + liq ↔ β	$T = 1\,053\,\mathrm{K}$	$x_{\mathrm{Al}}^{(\mathrm{Ag})} = 0.178$ $x_{\mathrm{Al}}^{\beta} = 0.207$ $x_{\mathrm{Al}}^{\mathrm{liq}} = 0.212$	$T = 1\,050\,\mathrm{K}$	$x_{\mathrm{Al}}^{(\mathrm{Ag})} = 0.177$ $x_{\mathrm{Al}}^{\beta} = 0.212$ $x_{\mathrm{Al}}^{\mathrm{liq}} = 0.225$
Peritectic β + liq ↔ ζ	$T = 1\,000\,\mathrm{K}$	$x_{\mathrm{Al}}^{\beta} = 0.300$ $x_{\mathrm{Al}}^{\zeta} = 0.320$ $x_{\mathrm{Al}}^{\mathrm{liq}} = 0.330$	$T = 1\,000\,\mathrm{K}$	$x_{\mathrm{Al}}^{\beta} = 0.297$ $x_{\mathrm{Al}}^{\zeta} = 0.326$ $x_{\mathrm{Al}}^{\mathrm{liq}} = 0.333$
Eutectic liq ↔ ζ + (Al)	$T = 839\,\mathrm{K}$	$x_{\mathrm{Al}}^{\zeta} = 0.420$ $x_{\mathrm{Al}}^{\mathrm{liq}} = 0.670$ $x_{\mathrm{Al}}^{(\mathrm{Al})} = 0.762$	$T = 838\,\mathrm{K}$	$x_{\mathrm{Al}}^{\zeta} = 0.419$ $x_{\mathrm{Al}}^{\mathrm{liq}} = 0.673$ $x_{\mathrm{Al}}^{(\mathrm{Al})} = 0.764$
(Ag)/β/ζ equilibrium*	Peritectoid (Ag) + β ↔ ζ $T = 883\,\mathrm{K}$	$x_{\mathrm{Al}}^{(\mathrm{Ag})} = 0.203$ $x_{\mathrm{Al}}^{\zeta} = 0.235$ $x_{\mathrm{Al}}^{\beta} = 0.238$	Eutectoid β ↔ (Ag) + ζ $T = 870\,\mathrm{K}$	$x_{\mathrm{Al}}^{(\mathrm{Ag})} = 0.210$ $x_{\mathrm{Al}}^{\beta} = 0.234$ $x_{\mathrm{Al}}^{\zeta} = 0.239$
Peritectoid (Ag) + ζ ↔ μ	$T = 728\,\mathrm{K}$	$x_{\mathrm{Al}}^{(\mathrm{Ag})} = 0.199$ $x_{\mathrm{Al}}^{\mu} = 0.232$ $x_{\mathrm{Al}}^{\zeta} = 0.238$	$T = 729\,\mathrm{K}$	$x_{\mathrm{Al}}^{(\mathrm{Ag})} = 0.209$ $x_{\mathrm{Al}}^{\mu} = 0.231$ $x_{\mathrm{Al}}^{\zeta} = 0.249$

* See text

1 125 K. This is because the ΔG curves for the fcc and ζ phases are almost superimposed in the composition range between $x_{\mathrm{Ag}} = 0.1$ and 0.25, as is required to reproduce the narrow fcc + ζ two-phase region between approx. 730 K and 880 K. Attempts to make ζ only very slightly more stable at compositions to the Ag-richer side of the β-minimum enabled the minimum in β to be described but also resulted in the effect described above. The calculated eutectoid behaviour has therefore been retained. Since such an eutectoid was in fact found in earlier investigations of the Ag—Al phase diagram, it is evident that the differences in stability between the two types of equilibria in this composition and temperature range are very small.

Fig. 7 illustrates the experimental and calculated silver solubilities in Al. The solubility curve obtained from the present evaluation lies very close to the experimental data of *Roberts* and *Chadwick* [3] and does not show the very sharp change in slope observed by *Raynor* and *Wakeman* [19] and by *Köster* and *Knödler* [20] at a composition close to 80 at.% Al.

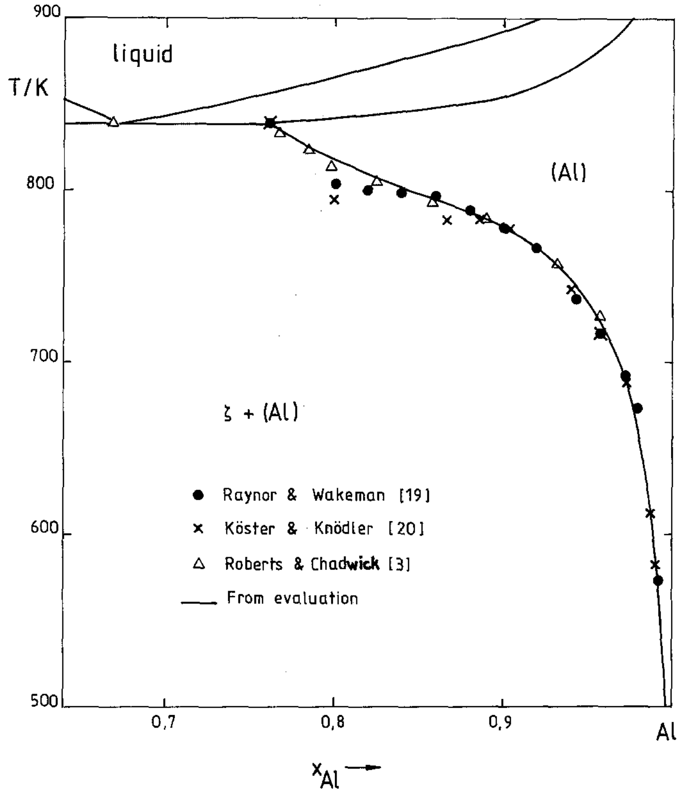

Fig. 7. Experimental and calculated solubility of Ag in solid Al

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