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85Top: L. Topor and O.J. Kleppa, "Enthalpies of Formation of First Row Transition Metal Diborides by a New Calorimetric Method," *J. Chem. Thermodyn.*, to be published (1986). (Thermo; Experimental)

*Indicates key reference.
#Indicates presence of a phase diagram.

V-B evaluation contributed by **K.E. Spear** and **P.K. Liao**, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, and **J.F. Smith**, Ames Laboratory-USDOE, Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011. Thermodynamic calculations were made using the computer programs generously made available by H.L. Lukas of the Max-Planck Institute for Metals Research, Stuttgart, Federal Republic of Germany. The work of K.E. Spear and P.K. Liao was supported by the National Bureau of Standards through the Metallurgy Division, while J.F. Smith was supported by the United States Department of Energy. Literature searched through 1984. Professor Spear is the ASM/NBS Category Editor for binary boron alloys, and Professor Smith is the ASM/NBS Category Editor for binary vanadium alloys.

The Au-Cu (Gold-Copper) System

196.9665 63.546

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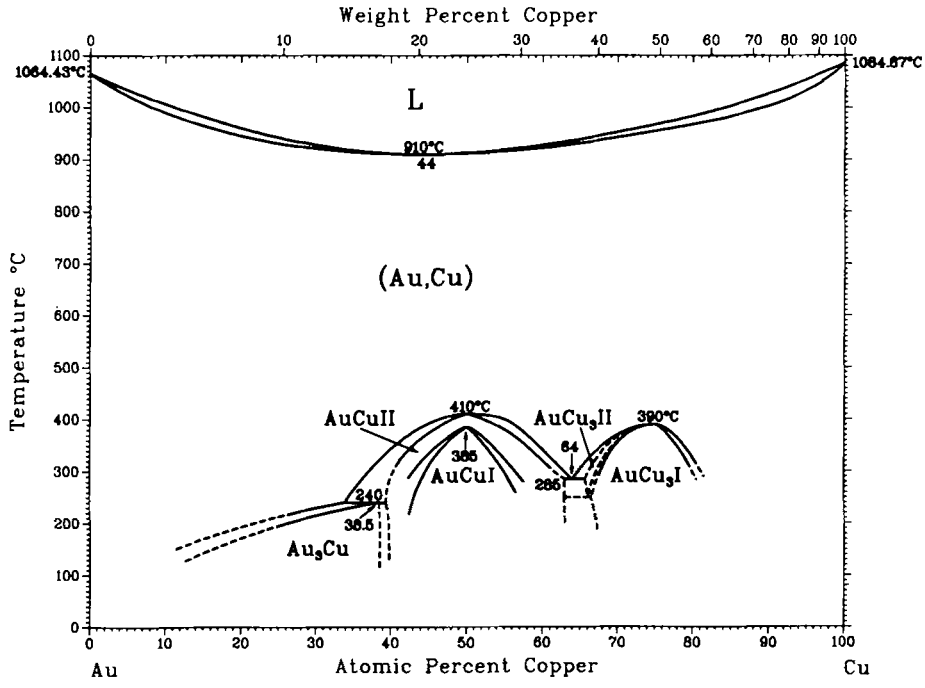
Fig. 1 Assessed Au-Cu Phase Diagram



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The Au-Cu system is one of the earliest systems for which several order-disorder type transformations were established. As a result, a very large volume of work exists on the ordered AuCu and $AuCu_3$ phases. Much of the theory and understanding of the order-disorder phenomena has grown out of extensive studies on these phases. Recent years have seen a surge of publications on this system, as newer features have been discovered. However, only limited phase diagram details have been generated during the past two decades. In this evaluation, only those references that are pertinent to specific information for construction of the phase diagram and the related structural and thermodynamic data are cited.

The structural details of the phases included in the assessed Au-Cu phase diagram (Fig. 1) are summarized in Table 1. Details of the liquidus and solidus, Au_3Cu, AuCu, and $AuCu_3$ regions are shown in Fig. 2 through 5, respectively.

Equilibrium Diagram

Liquidus and solidus boundaries established by [62Ben] (Table 2), who used cooling and heating curves (~2 to 3 °C/min), are accepted in Fig. 1. The assessed liquidus boundaries differ little from the early work of [00Rob]. The decrease in the melting temperature of Cu with additions of Au (up to 3.3 at.%) determined by [1897Hey] is also consistent with the presently accepted liquidus. The liquidus boundary in [Hansen] was based on [34Brol] and [35Bro] (Table 2), whose minimum liquidus temperature is about 20 °C lower than the presently assessed value. Low liquidus temperatures were also reported by [07Kurl] and [64Zai] (Table 2 and Fig. 2). The liquidus and solidus temperatures reported by [34Brol] in the composition ranges near the pure elements were higher than the presently assessed temperatures. As can be seen from Fig. 2, however, the trend proposed by [34Brol] is not supported by other investigators, particularly [62Ben], whose experimental work appears to be the most reliable.

The liquidus in Fig. 1 can also be derived from the present thermodynamic assessment, which is consistent with the reported thermodynamic quantities. The solidus temperatures of [62Ben] are lower than the calculated values (maximum difference ~10 °C) in the composition range ~80 to 90 at.% Cu, where the actual thermodynamic properties may be slightly different from the model properties (see "Thermodynamics").

Table 1 Au-Cu Crystal Structure Data

Phase	Composition, at.% Cu	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Au,Cu)	0 to 100	*cF4*	*Fm3m*	*A1*	Cu
Au_3Cu	10 to 38.5	*cP4*	*Pm3m*	$L1_2$	$AuCu_3$
AuCu(I)	42 to 57	*tP4*	*P4/mmm*	$L1_0$	AuCu
AuCu(II)	38.5 to 63	*oI40*	*Imma*	...	AuCu(II)
$AuCu_3$(I)	67 to 81	*cP4*	*Pm3m*	$L1_2$	$AuCu_3$
$AuCu_3$(II)	66 to ?	*tP28*	*P4mm*	...	Cu_3Pd

Fig. 2 Detail of Au-Cu Liquidus and Solidus with Experimental Data

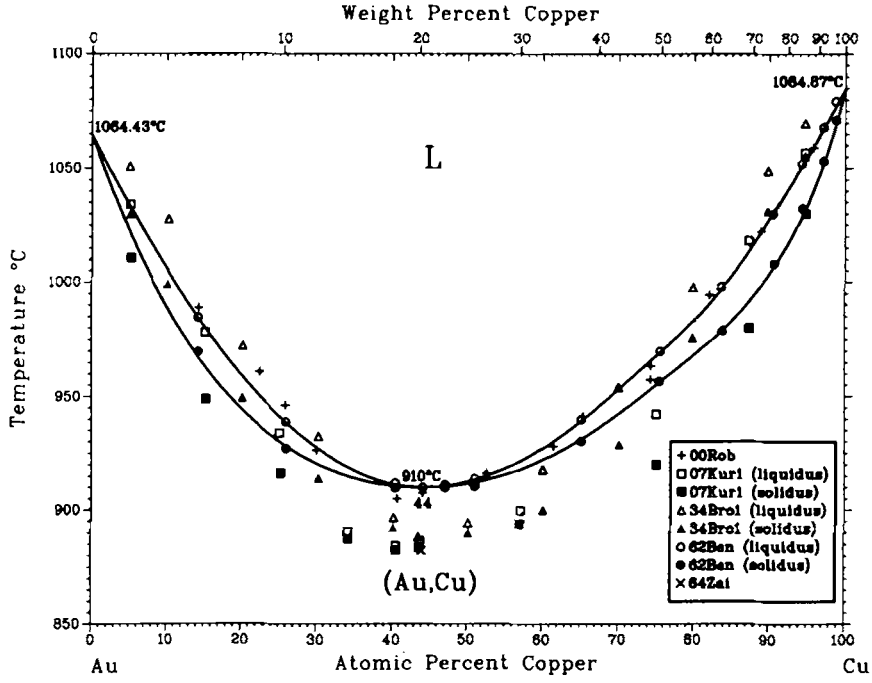

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Table 2 Au-Cu Liquidus and Solidus Temperatures

Reference	Composition, at.% Cu	Liquidus, °C	Solidus, °C
[00Rob]	0	1063	...
	14.00	979	...
	22.20	951	...
	25.55	946	...
	29.68	926	...
	40.51	905	...
	43.81	907	...
	52.46	916	...
	61.30	928	...
	65.42	941	...
	74.16	957	...
	74.28	963	...
	82.12	994	...
	89.04	1022	...
	96.13	1059	...
	100	1083	...
[07Kur1]	0	1063	...
	5	1034	1011
	15	978	949
	25	934	916
	34.07	890	887
	40.50	884	883
	43.66	886	884
	57.06	900	894
	75	942	920
	87.45	1018	980
	95	1056	1030
	100	1084	...
[34Bro1]	0	1063	...
	5	1051	1030
	10	1028	1000
	20	973	950
	30	933	914
	40	897	893
	43.5	889	...
	50	895	890
	60	918	900
	70	954	929
	80	998	976
	90	1049	1031
	95	1073	1055
	100	1083	...
[62Ben]	14.0	983	970
	25.7	939	927
	40.5	912	910
	43.7	910	910
	46.7	911	910
	50.8	914	911
	65.1	940	931
	75.6	970	957
	83.8	998	979
	90.8	1030	1007
	94.5	1052	1032
	97.4	1068	1053
	99.1	1079	1071

The existence of a continuous solid solution phase below the solidus was proposed by many early investigators from various measured physical properties [1860Mat, 01Mae, 06Kur, 07Kur1, 07Kur2, 10Rud, 17Bor, 19Sed, 19Tam, 22Kir, 23Bai1, 24Sed, 25Joh, 25Lan, 27Joh, 28Ark, 28Leb, 28Smi, 28Veg, 31Gru, 31Hau, 31Kur, 32Kur, 32Leb, 34Bro2, 35Leb] (see also [Hansen]).

Au_3Cu. The experimental phase boundary data related to the ordered Au_3Cu phase have been reported as various values by different investigators (Table 3), presumably because of the difficulty in attaining a full equilibrium state at low transformation temperatures (<240 °C). Most of the presently assessed phase boundaries are based on the isothermal change in the electrical resistivity measured by [55Rhi], [59Hir], and [59Kor]. Other portions of Fig. 3 are only tentative. The Cu concentration at the Au-rich limit of the ordered Au_3Cu phase decreases as the temperature is lowered. However, the observed trend is controversial. An X-ray diffraction study of a 22 at.% Cu alloy, heat treated at 160 °C, showed no indication of an ordered Au_3Cu phase [57Bat]. On the other hand, electron diffraction patterns obtained by [59Oku] and [64Tot] indicated the existence of this phase in an alloy containing 9 at.% Cu. Thermal arrest temperatures on heating at a rather high rate (8 °C/min) measured by [71Lut] are not likely to correspond to an equilibrium state, but the occurrence of a reaction involving the Au_3Cu phase is indicated at lower Cu concentration than expected from [57Bat]. From the trend of the [(Au) + Au_3Cu]/Au_3Cu phase boundary and the (Au) + AuCu → Au_3Cu reaction at ~240 °C, the Cu-rich limit of the ordered Au_3Cu phase is about 38.5 at.% Cu, in agreement with the value reported by [64Tot], rather than 35 at.% Cu reported earlier by [31Gru], [32Leb], and [55Rhi]. Neither electrical resistivity [36Joh] nor the superlattice line intensity attain a maximum at 25 at.% Cu. Thus, the Au_3Cu phase is not symmetrical near the stoichiometric composition.

[72Gra] (some data also in [71Gra]), based on electron microscopic evidence, proposed that the Au_3Cu phase consists of two regions: one with the $AuCu_3$-type structure at high temperatures and a high Au concentration range and the other with a one-dimensional antiphase structure at low temperatures and a high Cu concentration range, divided by a ~20 °C two-phase field at 25 at.% Cu. This feature is not included in Fig. 1 (see "Crystal Structures and Lattice Parameters").

AuCu. The occurrence of compound-like phases at the AuCu and $AuCu_3$ stoichiometric compositions was first observed by [15Kur], who employed thermal analysis, hardness, and X-ray measurements. [23Bai1], [23Bai2], and [23Bai3] associated the occurrence of atomic ordering with these compounds on the basis of observed X-ray diffraction lines, in agreement with similar conclusions obtained by [25Joh] and [27Joh]. [36Joh] discovered an additional order-order transformation in AuCu at higher temperatures, in which an orthorhombic AuCu(II) phase forms from the tetragonal AuCu(I) phase. Prior to this, AuCu(I) was thought to transform directly to the disordered fcc phase (AuCu(D)) at higher temperatures.

Both the AuCu(II) ⇄ AuCu(I) (order-order) and the AuCu(II) ⇄ AuCu(D) (order-disorder) transformations have been studied extensively by various methods, such as thermal analysis [38Hul, 39Hul, 41Kal, 47Sid, 50Nys, 51Hir2, 54Oga1, 54Rob, 54Hol], electrical resistivity [28Bor, 31Gru, 31Hau, 31Kur, 32Leb, 33Kur, 39Wil, 47Sid, 50Hir, 50Nys, 55Rhi, 62Anq], X-ray [41Kal, 47Bui, 53New, 54New1, 54Rob, 57Pia], dilatometry [31Gru, 31Kur, 33Kur, 50Hir], electromotive force (emf) [39Wei, 54Ori], calorimetry [50Bor, 50Hir, 50Nys, 51Hir1, 57Ray, 58Ori2, 68Mar, 70Mar, 76Mar], thermoelectric power (TEP) [60Blu, 73Bar], differential thermal analysis (DTA) [71Lut, 78Tis], electron diffraction and electron microscopy [54Oga1, 62Sat] (see "Crystal Structures and

Table 3 Au_3Cu Phase Boundary Data

Reference	Composition, at.% Cu	Temperature, °C: (Au)/[(Au) + Au_3Cu]	Temperature, °C: [(Au) + Au_3Cu]/Au_3Cu	Experimental method
[31Gru]	15.04	200	160	Resistivity
	17.25	206	170	
	19.86	218	182	
	22.82	226	204	
	24.77	230	210	
	25.84	233	215	
	27.30	237	223	
	28.93	240	226	
	30.89	250	230	
	33.81	254	232	
	34.84	255	240	
[32Leb]	20	222	200	Resistivity
	30	249	218	
	35	258	240	
	36	278	259	
[55Rhi]	30	231 ± 2	212 ± 2	Resistivity
	34	240 ± 2	227 ± 2	
[57Bat]	22	...	<160	X-ray
	25	...	199 ± 3	
	28	...	209 ± 2	
	30	...	221 ± 2	
	32	...	231 ± 3	
[59Hir]	24.94	...	200 ± 5	Resistivity, X-ray
[59Kor]	25	...	200 ± 3	Resistivity
[59Wri]	25.6	...	190	Resistivity, lattice parameter
[71Lut]	8.5	...	148	Thermal heating, 8 °C/min
	13.3	...	163	
	18.7	...	190	
	21.5	...	195	
	25	...	207	
[80Koz]	27.5	...	208 ± 3	X-ray

Fig. 3 Detail of the (Au, Cu)/Au_3Cu Phase Boundaries with Experimental Data

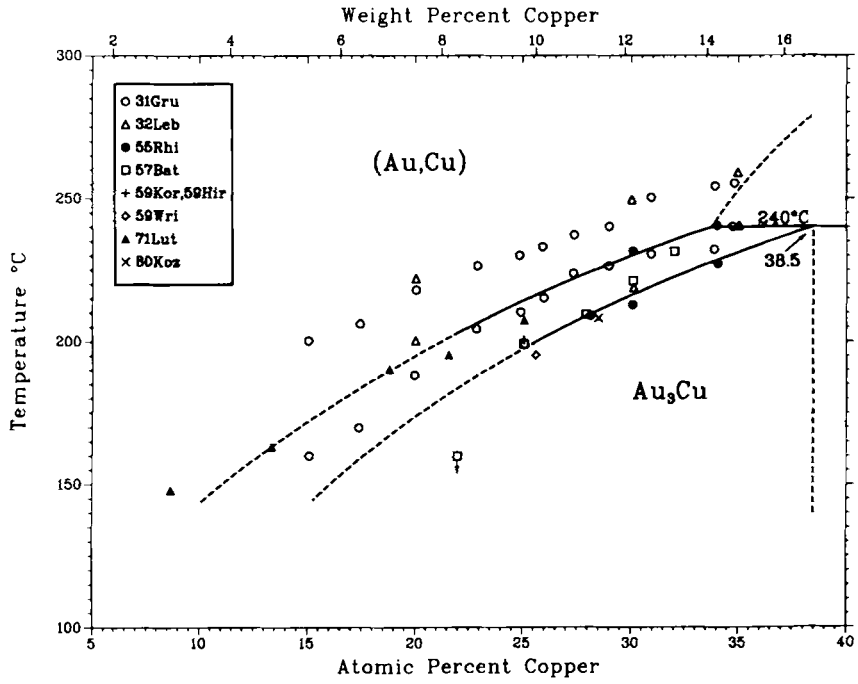

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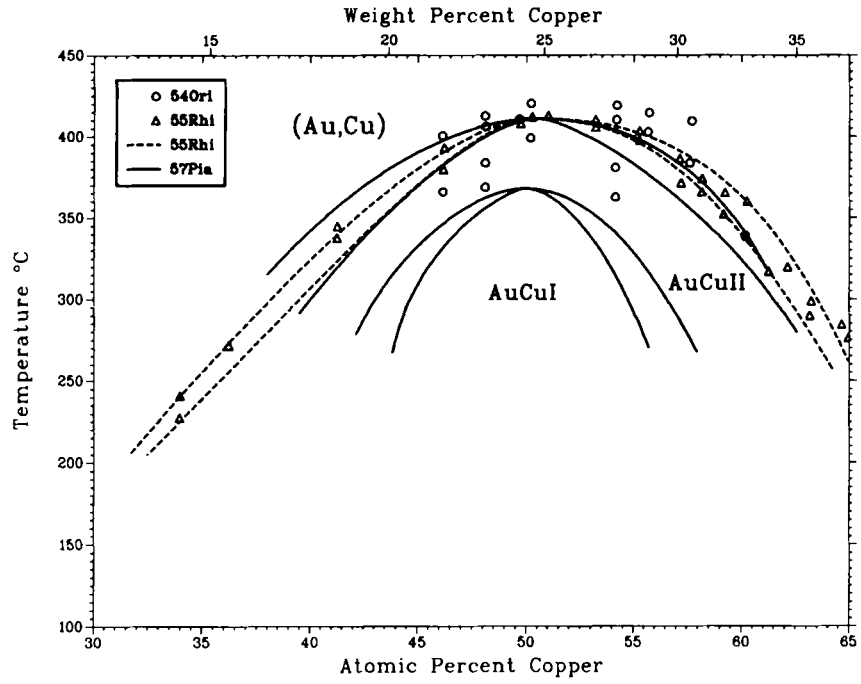
Fig. 4 Detail of the (Au, Cu)/AuCu(II) Phase Boundaries with Experimental Data



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Lattice Parameters" for full reference), and Hall effect [46Sid].

Some of the results on the transformation temperature are presented in Table 4. Detailed phase boundary determinations, including the indications of congruent transformations at $AuCu_3$ and AuCu compositions, were made by [31Hau] and [31Gru] using the resistivity method. They also correctly indicated the existence of two-phase fields between the ordered and disordered phases. An additional phase, Au_2Cu_3, proposed by [31Hau] does not occur, as the work of [31Gru] and subsequent studies confirmed. A third low-temperature phase with an extended phase field that included the stoichiometry Au_3Cu was reported to form peritectoidally by [31Gru]. [53New], [53Rhi], [54New1], and [55Rhi], using electrical resistivity measurements supported by X-ray studies, defined precise boundaries for the different phase fields and confirmed the congruent formation of AuCu and $AuCu_3$ and the peritectoidal formation of Au_3Cu. They also confirmed that all of the order-disorder transformations in this system are of the classical Gibbsian type, with definite two-phase fields, contrary to some conflicting reports in the earlier literature. The galvanic cell studies by [54Ori] showed definite enthalpy changes associated with the transformations AuCu(I) ⇄ AuCu(II) and AuCu(II) ⇄ AuCu(D), thus confirming these to be first-order transformations. [54Ori] also presented detailed boundaries for the two-phase fields near the AuCu composition. [57Pia] and [59Pia1] reported a detailed and precise phase diagram between 40 and 60 at.% Au by the X-ray method. The results of [55Rhi], [54Ori], and [57Pia] are shown in Fig. 4 for comparison. The assessed diagram is primarily based on [55Rhi], [57Pia], and [59Pia1] for the high-temperature boundaries and on [57Pia] for the AuCu(II) ⇄ AuCu(I) boundaries, for

Table 4 Au-Cu Order-Disorder and Order-Order Transformation Data

(Au, Cu) ⇄ AuCu(II)		AuCu(II) ⇄ AuCu(I)	
Temperature, °C	Reference	Temperature, °C	Reference
411	[73Bar, 77Mar]	388	[77Mar]
412	[71Lut]	380	[73Ton]
408	[62Anq]	385	[73Gol]
410	[55Rhi]	387	[73Bar]
408	[36Joh, 50Bor]	389	[71Lut]
370.8	[15Kur]	364	[62Anq]
410	[Hansen]	380	[50Nys]

which [55Rhi] did not present any data. The AuCu(D) ⇄ AuCu(II) transformation temperature is accepted as 410 ± 2 °C based on [50Bor], [55Rhi], [57Pia], [62Anq], [71Lut], [73Bar], [77Mar], and [Hansen]. The AuCu(II) ⇄ AuCu(I) temperature is accepted as 385 ± 2 °C based on [73Bar] and [73Gol] (see also Table 4). Some conflicting observations by [36Joh] and [39Hul], which indicated the occurrence of the AuCu(II) phase in the AuCu(I) phase fields at lower temperatures, possibly were related to the difficulty in attaining equilibrium at these temperatures.

The existence of a two-phase field between $AuCu_3$ and AuCu(I), from 34 to 37 at.% Au, and the associated eutectoid decomposition of the fcc solid solution was proposed by [31Gru]. [55Rhi] confirmed the eutectoid transformation of (Cu, Au) and precisely determined the eutectoid point to lie at 36 at.% Au and at 284 °C. The accepted phase diagram in this region is based on [31Gru] and [55Rhi], as shown in Fig. 4.

$AuCu_3$. The accepted $AuCu_3$(I) phase boundaries are based primarily on the electrical resistivity and X-ray studies by

Fig. 5 Detail of the (Au, Cu)/$AuCu_3$ Phase Boundaries with Experimental Data

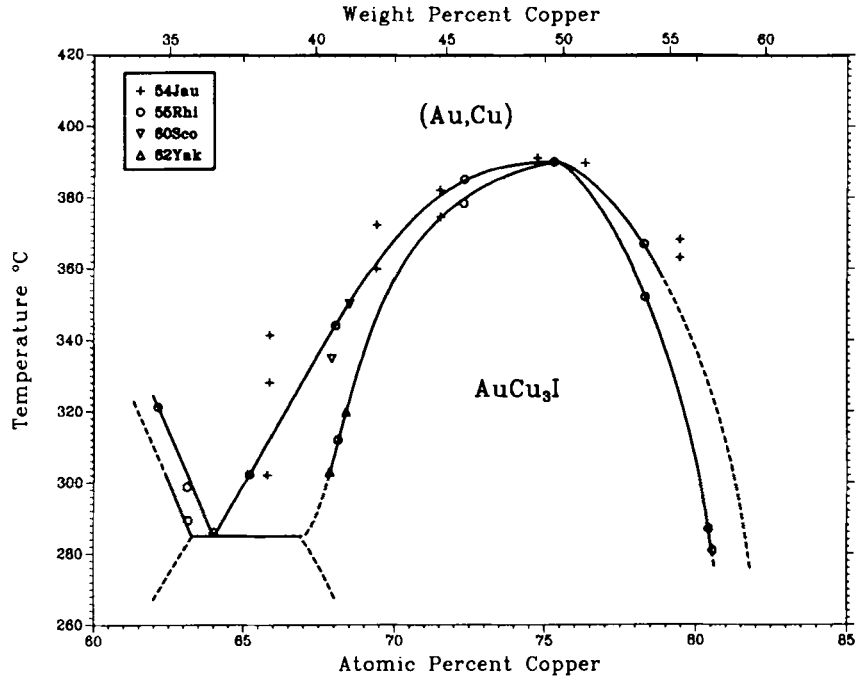

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Table 5 $AuCu_3$ Order-Disorder Transformation Data

(Au, Cu) ⇄ $AuCu_3$	
Temperature, °C	Reference
386.9	[79Che]
394 ± 2	[76Bar1]
389	[75Mor]
392	[71Pre]
390	[55Rhi, 65Her]
394	[41Nix, 54Ori]
394 ± 3	[51Kea]
385	[49Ben]
393	[31Hau]
390 (a)	[28Bor]
382 (b)	[28Bor]
388 ± 3	[Hansen]

(a) Heating. (b) Cooling.

[55Rhi] (see Fig. 1 and 5). The analysis of the X-ray data of [54Jau] by [54New2] near the $AuCu_3$ composition confirmed that a two-phase field occurs not only on the Au-rich side of this composition, but also on the Cu-rich side, contrary to the interpretations of [54Jau]. The $AuCu_3$(I) phase is stable over wide composition limits on both sides of the stoichiometric point. It forms from the disordered phase by a congruent transformation at the stoichiometric composition and at Au-rich limits by a eutectoid transformation. The congruent and eutectoid temperatures at 390 and 284 °C, respectively, and the eutectoid composition at 36 at.% Au are accepted from [55Rhi] as being the most precise. The congruent temperature at 390 °C has also been reported by [64Air] and [65Her]. Some of the reported congruent temperature values are presented in Table 5.

Different parts of the $AuCu_3$ phase boundaries, including the congruent point, were studied by various methods, such as thermal analysis [15Kur, 34Bro1, 35Bro], electrical resistivity [28Bor, 31Gru, 31Hau, 31Kur, 32Kur, 32Leb, 33Kur, 36Syk1, 39Tak, 39Wil, 47Sid, 50Hir, 53Rhi, 55Rhi], X-ray [25Joh, 27Joh, 44Wil, 47Owe, 51Kea, 54Jau, 62Yak], DTA [78Tis], TEP [50Sat, 64Air], emf [39Wei, 54Ori], dilatometry [31Gru, 31Kur, 32Kur, 33Kur, 41Nix, 50Hir], calorimetry [36Syk2, 50Hir, 65Her], modulus of elasticity [40Kos, 40Sie1, 40Sie2, 49Ben, 53Lor], Hall effect [41Kom, 47Sid, 62Elk, 62Nei], and electron diffraction and electron microscopy [51Rae, 62Yam, 63Mar, 70Bea]. The observation of a supposed two-phase region at the congruent point of $AuCu_3$ from X-ray determinations by [68Gan] is not correct, because it violates the Gibbs phase rule.

As predicted theoretically by [76Coo], the occurrence of incoherent, coherent, and spinodal ordering regions in the phase diagram were subsequently drawn by [77Che] and [79Che], based on X-ray diffuse scattering and inelastic neutron scattering. The coherent phase boundary was shown to be 3 to 13 °C below T_c, the incoherent phase boundary, and the continuous ordering temperature was found at 358.2 °C. Theoretical calculation of the ordered phase boundaries was reported by [86Kik].

$AuCu_3$(II). Much experimental work exists in which the occurrence of the long-period superlattice (LPS) structure is reported. Appearances of splitting of superstructure reflections during early stages of ordering in $AuCu_3$ alloys were observed in both X-ray [52Rae] and electron diffraction patterns [61Yam, 71Sak]. In addition, side bands or satellites around fundamental reflections were also observed [48Gui, 52Rae, 72Mat]. High-resolution lattice

imaging by electron microscopy showed what appeared to be discrete ordered domains in a periodic antiphase arrangement [69Poq, 75Sin, 71Sak].

By analogy with the occurrence of the AuCu(II) structure and based on his X-ray studies and observations by others, [60Sco] proposed that a one-dimensional LPS structure, designated $AuCu_3$(II), occurs at Au-rich off-stoichiometric compositions. The narrow single-phase field was shown to lie inside the (Cu, Au) and $AuCu_3$(I) two-phase field, and the likely boundaries were also proposed [60Sco, 74Per]. Numerous structural studies claiming the occurrence of the LPS structure were reported by [59Pia1, 59Pia2] (X-ray) and by [61Yak, 62Yak, 62Tot, 62Yam, 63Mar, 72Sou, 73Bel, 74Goe, 75Ras] (electron diffraction). Two-phase fields were drawn between the disordered and $AuCu_3$ phase, whereas those between $AuCu_3$(II) and $AuCu_3$(I) were considered too narrow for resolution [62Yak].

According to [80Wil], the $AuCu_3$(II) phase does not exist. The existence of a two-phase mixture of $AuCu_3$(I) and a disordered Au-Cu solid solution is sufficient to explain the scattering phenomenon usually associated with the $AuCu_3$(II) LPS [80Wil]. This is an interesting suggestion, but experimental observation of the disordered regions must be presented before the LPS structure is rejected.

Crystal Structures and Lattice Parameters

The crystal structures occurring in the Au-Cu system are summarized in Table 1.

Continuous Solid Solution, fcc Phase. The lattice parameters of the continuous solid solution phase show a positive deviation from an assumed Vegard's law [22Kir, 25Joh, 25Lan, 28Ark, 28Smi, 28Veg, 32Leb, 34Veg, 36Joh, 47Owe, 53New, 61Dav, 66Lu1, 66Lu2, 72Ber] (Fig. 6). Only the more recent results are given in Table 6 for alloys quenched from 600 °C [66Lu1] and from 800 °C [72Ber]. The lattice parameters show no discernible dependence on the homogenization temperature, at least in this temperature range. Least-squares fitting of the data in Table 6 yields:

$$a = 0.40784(1 - X) + 0.36149\,X + 0.01198\,X(1 - X)\ \text{nm}$$

where X is the atomic fraction of Cu in the alloys, and the lattice parameters of the pure elements are from [King1]. The standard deviation in this expression is 0.00031 nm. The relation between the lattice parameter and the short-range order parameter in the fcc phase was discussed by [58Die]. The accuracy of the data used in the discussion [25Joh, 28Ark] may be insufficient.

Au_3Cu. The crystal structure of Au_3Cu is the $AuCu_3$-type, according to X-ray measurements by [51Hir2] and [52Hir] or electron diffraction measurements by [51Oga] and [52Oga]. The existence of larger unit cells was first observed by [36Joh]. Subsequently, various features were reported on the structure of the alloys with ~25 at.% Cu: (1) domain structures with average size of ~5 nm as a consequence of nucleation and growth [57Bat, 64Tot, 65Sat]; (2) a two-dimensional antiphase structure [59Hir] with the Cu_3Pd-type structure [65Wat]; (3) density modulation in each domain [59Oku]; and (4) domains of dodecahedron structure [64Iwa]. [72Gra] considered that these complexities arise from the two phases with ordinary $AuCu_3$-type and one-dimensional antiphase structures (see "Equilibrium Diagram"). According to [64Tot] and [66Sat], however, these LPS are nonequilibrium structures. This is supported by the fact that the size of ordered Au_3Cu domains

Fig. 6 Relationship of Lattice Parameters and Composition in the Disordered fcc Phase in the Au-Cu System

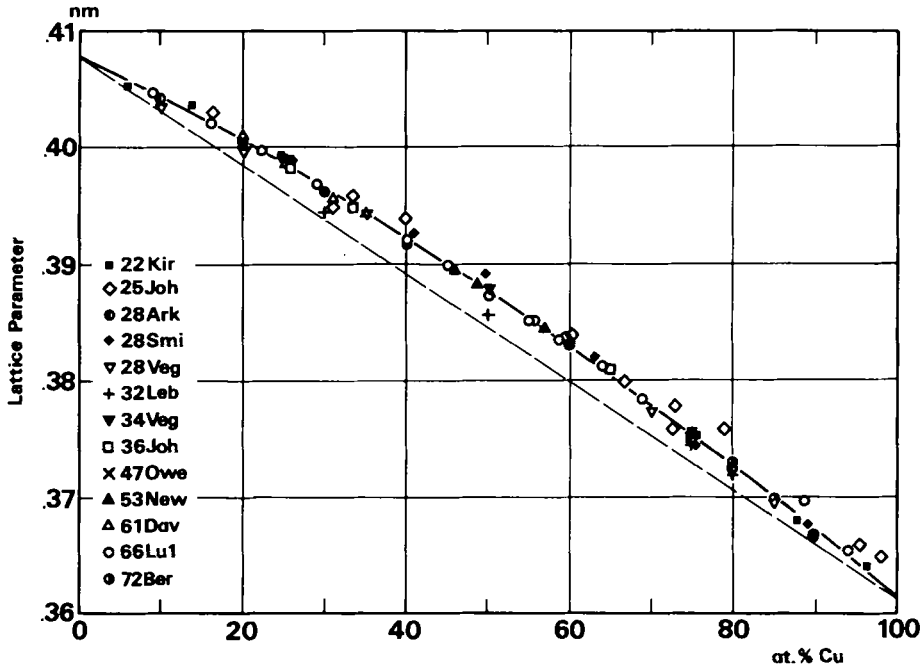

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Table 6 Lattice Parameter of the Disordered Au-Cu fcc Phase

Reference	Composition, at.% Cu	Lattice parameter, nm
[66Lu1]	0	0.40778
	9.0	0.40469
	16.0	0.40205
	22.0	0.39968
	29.0	0.39682
	35.0	0.39431
	40.0	0.39213
	45.0	0.38981
	50.0	0.38740
	55.0	0.38503
	55.5	0.38337
	58.5	0.38337
	69.5	0.38369
	64.0	0.38107
	69.0	0.37841
	75.0	0.37538
	88.5	0.36950
	94.0	0.36539
	100	0.36146
[72Ber]	0	0.4078
	20	0.4003
	30	0.3965
	40	0.3921
	45	0.3898
	50	0.3875
	60	0.3828
	65	0.3804
	75	0.3755
	80	0.3728
	85	0.3700
	90	0.3672
	95	0.3643
	100	0.3615
[King1](a)	0	0.40784
	100	0.36149

(a) Compilation.

formed in alloys quenched from high temperatures such as 800 °C (excess vacancies facilitate the ordering process) increases when annealed at 150 °C, as observed by resistivity and thermoelectric power measurements [71Lee] or electron microscopy measurements [75Bro].

The lattice parameter of the ordered Au_3Cu (Table 7) is slightly smaller than that of the disordered state at the same composition (Fig. 7).

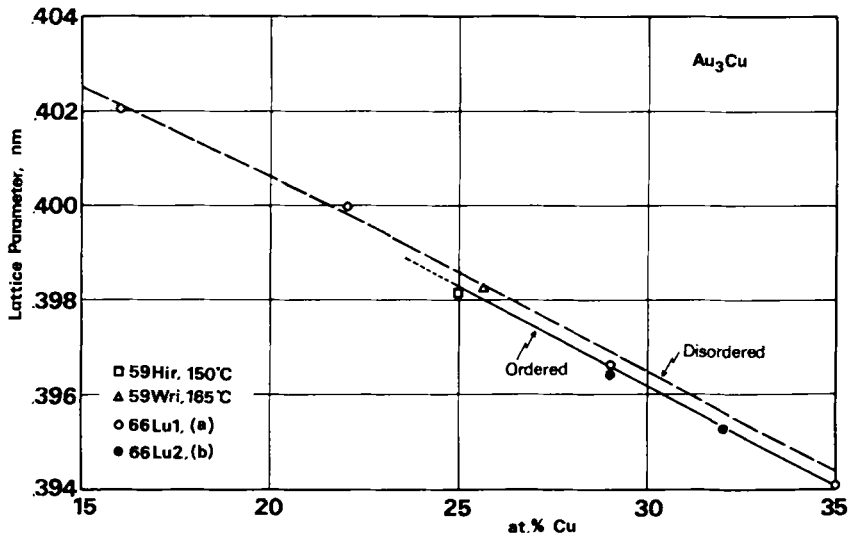
AuCu(I). The crystal structure of AuCu(I) has the $L1_0$ prototype structure (see Table 1) and consists of alternate planes of Cu and Au atoms perpendicular to the c-axis of the original fcc lattice. The resultant structure has a tetragonal distortion, with the $c:a$ ratio reported between 0.931 to 0.938 [28Leb, 39Hul, 77Nov]. X-ray diffraction (XRD) studies of the structure have been reported by [25Joh], [27Joh], [28Gor], [28Leb], [30Deh], [30Osh], [31Pre], [32Deh], [36Joh], [53New], [67Bje], and [77Nov]. The conditions for the stability of the structure in terms of size ratio and electron concentration were analyzed by

Table 7 Ordered Au_3Cu Lattice Parameter Data

Reference	Composition, at.% Cu	Lattice parameter, nm	Heat treatments
[59Hir]	24.94	0.39810	150 °C, 4 months
[59Wri]	25.60	0.39820	165 °C, ~100 days
[66Lu1]	16	0.40205 (a)	600 °C, 2 days
	22	0.39965 (a)	→ 200 °C, 72 days
	29	0.39661	→ Room temperature
	35	0.39404	
[66Lu2]	29	0.39642	170 °C, 45 days
	32	0.39525	→ 150 °C, 120 days
			→ 130 °C, 15 days
			→ Room temperature

Note: → = Slow cool to the next annealing temperature.
(a) Mainly disordered phase, according to Fig. 3.

Fig. 7 Comparison of the Lattice Parameters of Ordered and Disordered Au_3Cu



(a) Slow cooled from 600 °C. (b) Slow cooled from 170 °C. Details in Table 7.
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Table 8 Lattice Parameter Data of AuCu and $AuCu_3$ Ordered Phases

Phase	Composition, at.% Cu	Lattice parameters, nm a	b	c	Comment	Reference
AuCu(I)	46	0.2810	...	0.3712	(a)	[67Bje]
	48	0.2808	...	0.3688		
	50	0.2845	...	0.3671		
	52	0.2795	...	0.3673		
	54	0.2785	...	0.3675		
AuCu(II)	50	0.3956 ± 3	0.3972 ± 2	0.3676 ± 2	(b)	[68Oka]
$AuCu_3$(I)	75	0.37426 ± 3			(c)	[60Fli]

(a) Powder pattern. (b) Single crystal. (c) Single crystal at 25 °C.

[78Pea]. The lattice parameter values have been accepted from [67Bje], and they compare well with other reported results (see Table 8).

AuCu(II). The AuCu(II) phase was discovered by [36Joh], and its crystal structure was identified as orthorhombic from X-ray powder diffraction studies. Electron diffraction studies on single-crystal thin films by [54Oga2] further revealed that the structure consisted of a one-dimensional LPS, based on the AuCu(I) unit cell. Thus, the (002) planes are alternately occupied by Cu or Au atoms; however, halfway along the b-axis of the unit cell, the Cu planes are replaced by Au planes, and vice versa. This gives rise to what is known as the antiphase boundary (APB). The spacing between the boundaries, M, which is equivalent to half of the long period of the ordered structure, was found to be approximately five unit cells of the AuCu(I) structure. The accepted lattice parameter values are taken from the XRD studies on single crystals of a 50:50 alloy by [68Oka] (see Table 8). Both the lattice parameters and the deviation from cubic symmetry values (b/a = 1.004, c/a = 0.929) given by these authors compare well with other works. The value of M in units of b was 5.0 ± 0.05, as compared to 5.1 given by [64Jeh]. According to [58Oga], M has two values, 5 and 6. Depending on the temperature and composition, the average value of M varies and can appear to be fractional, such as 5.4 due to a mixture of the above two domain sizes.

X-ray powder diffraction studies of AuCu(II) were reported by [38Hul], [39Hul], [41Kal], [57Pia], and [59Pia2], and single-crystal studies were reported by [62Jeh], and [64Jeh]. The LPS structure attracted considerable electron diffraction and electron microscopic studies involving thin films and single crystals, and more details of the structure are still being revealed. [58Pas], [59Glo], and [58Oga] succeeded in observing the antiphase domain boundaries by high-resolution electron microscopy and measured distances of 2 nm. This is consistent with the diffraction results.

As a consequence of the orthorhombic distortion of the lattice due to ordering, a splitting in the superlattice reflections is expected. This was first observed by [48Gui] in X-ray single-crystal work and by [52Rae]. In electron diffraction, characteristic cross patterns were observed at superlattice reflection positions, resulting from the occurrence of two sets of antiphase boundaries whose c-axes were parallel to the beam direction, but whose b-axes were perpendicular. "Crosses" at superlattice reflection positions and satellites around the normal reflections were observed by [54Oga1] and [54Oga2]. Side bands around fundamental reflections in X-ray were, likewise, observed by [72Mat] on 20 and 21 at.% Au alloys. [58Oga] and [59Oga] observed that the satellite reflections always accompanied the LPS structure, and could not have been entirely due to multiple reflections caused by split superlattice reflection, as postulated by [59Glo]. [64Fuj], [72Mat], and [79Iwa] also arrived at the same conclusion. A detailed structural study by [62Jeh], [64Jeh], and [68Oka] based on XRD, and by [59Per1] and [59Per2] using electron diffraction, led them to postulate the existence of lattice modulation, in that the atoms were displaced from lattice sites at the antiphase boundaries along the long-period direction, the period of which was commensurate with the out-of-step shift. Theoretical treatments of the phenomenon were attempted by [61Sat], [66Tac1], [66Tac2], and [81Kat]. The occurrence of regular steps in the antiphase boundaries for alloys of 59 and 63 at.% Au was suggested by [75Wat], based on observations of deviations in the splitting directions in electron diffraction patterns of single-crystal thin films. Such steps were observed by [75Wat] in high-resolution electron microscopy and by [71Mih] with dark field imaging and lattice imaging.

Theoretical treatments of the LPS structure in terms of the Brillouin zone interactions with conduction electrons at the Fermi surface was given by [51Sla]. [61Sat] made a detailed study of the effect of different elements on this proposed interaction. A definite relation was found to exist between the electron:atom ratio and the domain size. Theories based on the minimization of energy of conduction electrons by the formation of a LPS structure have been developed by [62Sat], [66Tac1], and [66Tac2]. The model of [62Sat] envisages an intimate contact of the Fermi surface of the alloy with certain Brillouin zone boundaries.

$AuCu_3$(I). The crystal structure of the $AuCu_3$(I) phase forms the prototype of the $L1_2$ type of ordered cubic structure, in which the corners of the unit cell are occupied by Au and the face centers by Cu atoms (see Table 1). Structural studies using X-ray and electron diffraction were reported by [25Joh], [26Phr], [27Joh], [28Leb], [31Sac], [48Bet], [51Kea], and [60Fli]. The lattice parameters for a 24.09 at.% Au alloy, when corrected for $AuCu_3$ composition, gave the values 0.37485 and 0.37604 nm (converted from kx units) for the ordered and disordered conditions, respectively, according to [48Bet]. The accepted lattice parameter for ordered $AuCu_3$(I) is taken from a more recent study by [60Fli] that compares well with other reported results (see Table 8).

$AuCu_3$(II) was described as tetragonal by [62Tot] and [62Yak]. The unit cell was described as made up of 18 $AuCu_3$(I) unit cells, with the antiphase domain boundary located after 9 unit cells. [60Sco] also observed the period to consist of 18 subcells for 68.4 at.% Cu. [59Pia2], on the other hand, found an orthorhombic structure. The number of subcells, as with the AuCu(II) structure, was found to vary with both composition and temperature [59Pia2, 62Tot, 62Yak].

Nature of Ordering Transformation in AuCu. Ordering reactions may occur either homogeneously or heterogeneously. In the former, the ordering reaction proceeds more or less uniformly within a single-phase grain. In the latter, regions of localized order coexist with regions of disorder within grains of the alloy. Homogeneous reactions are also called continuous. If the transformation occurs continuously at equilibrium, it is a higher order transformation. If finite undercooling is needed for the process to occur continuously, the transformation is a first-order (Gibbsian) transformation. The AuCu transformation is first order. The experimental evidence is summarized below.

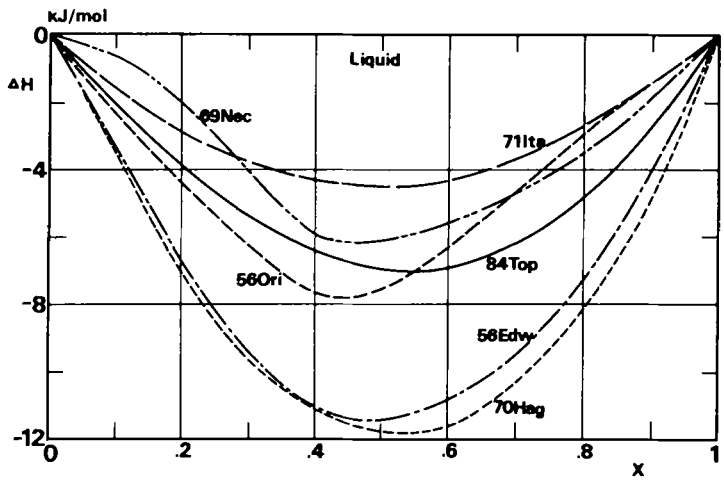
Early X-ray studies by [48Bor] (below 350 °C) and by [41Kal] suggested a uniform ordering (*i.e.*, continuous) mode throughout the entire crystal. However, electrical resistivity studies by [55Kuc] on samples ordered for varying lengths of time at 300 °C suggested a classical nucleation and growth type of transformation. The latter conclusion was supported by [59Obr] from kinetic studies of disorder to order by XRD. [69Man] studied ordering at 100 and 150 °C on samples quenched from 450 °C by the X-ray method and found a homogeneous ordering trend. Homogeneous ordering is characterized by a gradual shift of the X-ray lines from disordered to the superlattice positions. First-order (nucleation) transformations, on the other hand, would show a gradual build-up of intensities of the already existing superlattice lines and waning of intensities of lines due to disordered phases, occurring simultaneously.

The observations of [69Man] are consistent with the theoretical treatments of [75Def] and [76Coo], who observed that continuous ordering is possible in samples quenched well below the phase boundaries for the first-order transformations. Such ordering instability temperatures were determined experimentally from absolute intensities of X-ray diffuse scattering by [77Che], [79Che], and [81Che] for two compositions of Au-Cu. The same were calculated theoretically by [78Def] using the cluster variation method, to give a locus of ordering instability temperature from about 20 to 80 at.% Au.

The position of the instability temperature is dependent on the degree of prior short-range order (SRO), quenching rate, and other path-dependent parameters. Thus, it is impossible to correlate all of the above experiments exactly. However, the reaction has been observed to be both continuous and discontinuous, which verifies that it must be first order.

Short-Range Order (SRO). Past studies have shown that above the critical temperature of order-disorder (T_c) the structure is far from completely disordered and that small regions of ordered domains persist at temperatures substantially above T_c. From Fourier analysis of the diffuse scattering intensity in $AuCu_3$ single crystals heated to above T_c, [50Cow1] determined SRO parameters. The SRO parameters in different coordination spheres were found to vary with varying Au and Cu compositions [77Kat]. Splitting of diffuse peaks at superlattice positions (in single crystals of $AuCu_3$ heated to above T_c) was observed in electron diffraction patterns [52Rae, 63Mar, 65Wat], and was subsequently confirmed by X-ray studies [65Mos]. Likewise, [62Sat] observed the presence of short chains of antiphase domains with the degenerate AuCu(II)-type structure, by high-temperature electron diffraction studies on (evaporated) thin films of AuCu. These observations suggest, as proposed by [66Cow], that in systems with the LPS structure the atomic correlations can extend from 2 to 3 nm in distance, and considerable degrees of order can exist in these regions. Thus, in disordered alloys, when only SRO is present, nuclei of ordered domains are present

Fig. 8 Enthalpy of Mixing for Liquid Au-Cu as a Function of Mole Fraction of Cu



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in equilibrium [66Cow, 61Dam]. Short-range order studies have also been reported by [38Nix], [50Cow2], [53Sut], [55Fed], [56Bor], [56Gib], [63Mar], [64Mos], [65Gua], [65War], [66Tor], [76Bar1], and [76Bar2] for $AuCu_3$ and by [54Rob] and [61Bor] for AuCu compositions.

Short-Range Order and Anomalous Behaviors in $AuCu_3$ at High Temperatures. Anomalies in specific heat and thermal expansion results were noted by [56Kuc] at 600 and 850 °C. [57Hir] failed to reproduce the above anomalies in high-temperature calorimetric studies and concluded that the difference was due to the use of quenched samples by [56Kuc]. According to [57Hir], it is difficult to suppress partial ordering in samples quenched from 600 °C and above, due to the presence of a large amount of quenched-in vacancies. However, indications of an anomaly around 600 °C were also observed by [55Fed] in the lattice parameter and by [56Bor] in SRO studies. [76Bar1] correlated the anomalies observed by [56Kuc] with changes in local atomic arrangements. According to [76Bar1], at 600 °C the anomaly corresponds to the $D0_{22}$-type fluctuations in SRO structure, whereas at 850 °C, it is due to the development of CuPt-like ordered regions. Additional physical property effects were also reported just above T_c in high-temperature $AuCu_3$ alloys by [76Bar1].

Fig. 9 $\Delta G^{ex}/X(1 - X)$ for Liquid Au-Cu as a Function of Mole Fraction of Cu

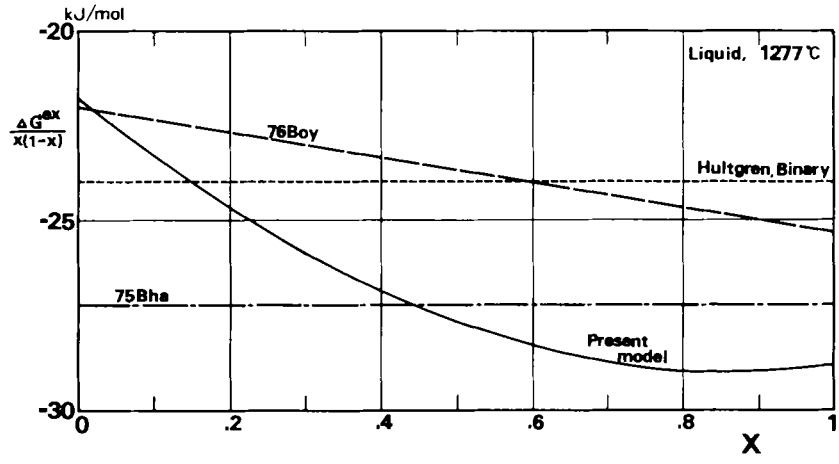

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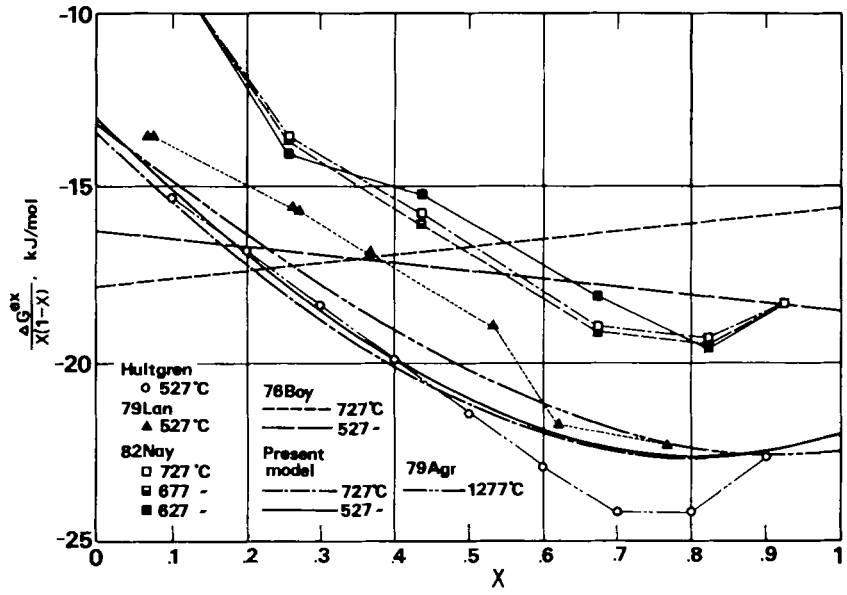
Fig. 10 $\Delta G^{ex}/X(1 - X)$ for the fcc Solid Solution as a Function of Mole Fraction of Cu



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Kinetics of ordering studies were reported by [38Jon], [55Bur], [61Dam], [62Nag1], [62Nag2], [63Dav], [71Sak], and [74Mor], and of disordering by [74Mor] and [75Mor].

Pressure

The LPS structure, according to [62Sat], [66Tac1], and [66Tac2], is associated with a particular energy band structure of conduction electrons that can be altered by pressure. The AuCu(II) → AuCu(I) transition temperature was found to increase with the measured pressure, up to 70 kbar, at the rate of 1.5 ± 0.2 °C/kbar by [72Iwa] and [74Iwa]. Above 50 kbar, the AuCu(II) structure disappeared and only the ordered structure AuCu(I) was present. Similarly, the structure retained following annealing under pressure between 350 and 500 °C was studied at room temperature using X-rays. [75Asa] observed the transition temperature to increase with pressure at the rate of 2.0 °C/kbar, which compares well with the theoretically predicted rate of 1.95 °C/kbar, as derived from the Clausius-Clapeyron equation [74Iwa]. Measurements extended to 100 kbar using electrical resistivity showed a linear relation between pressure and the transition temperature. Phenomenological discussion of the effect of pressure on the relative stability of the AuCu(II) and AuCu(I) phases is given by [75Sat].

Pressure also increases the order-disorder temperature in $AuCu_3$. [67Fra] reported the change at the rate of 2.1 K/kbar between 7 and 21 kbar. Relevant electrical resistivity measurements were made at high temperatures and pressures.

Thermodynamics

Liquidus and Solidus. The enthalpy of mixing for the liquid phase was reported by [56Edw], [56Ori], [69Nec], [70Hag], [71Ita], and [84Top] (Fig. 8). The value assessed by [Hultgren, B] is nearly identical to the results of [71Ita] and [75Yaz]. [84Top] expressed their calorimetric results, measured at 1106 °C, in the form:

$$\Delta H = X(1 - X)(-21\,748 - 16\,614\,X + 9\,541\,X^2)\ \text{J/mol}$$

Very early results of [30Kaw] were roughly $\Delta H/X(1 - X) = 0$ with approximately ±50 J/mol scatter (not shown in Fig. 8). The assessed Gibbs energy of mixing (ΔG^{ex}) for the liquid phase, determined at 1277 °C by [Hultgren, B] on the basis of the data of [35Mei], [56Edw], [56Ori], [65Sch], [69Nec], and [70Hag], is about $-24X(1 - X)$ kJ/mol (Fig. 9).

The assessed thermodynamic properties (ΔG^{ex}, ΔH, ΔS^{ex}) for the solid phase, determined at 527 °C by [Hultgren, B] on the basis of the data of [32Wag], [36Syk2], [39Wei], [40Sch], [51Hal], [51Hir1], [51Hir2], [52Chi], [54Bal], [55Bal], [54Ori], [55Rub], [56Kuc], [57Hir], [57Nes], [58Ori1], [58Ori2], [60Orr1], [60Orr2], [61Dhe], [66Her], and [67Her] are shown in Fig. 10 to 12, where the more recent results of [79Lan] and [82Nay] obtained from emf measurements are also included.

Thermodynamic Model. Table 9 summarizes the thermodynamic model adopted in the present assessment, together with the earlier models of [75Bha], [76Bha], [76Boy], [78Tar], and [79Agr]. The temperature dependence of the ΔH and ΔS^{ex} functions has not been considered in the present model.

The entropy of mixing for the liquid phase was accepted from the most recent work of [84Top]. The excess entropy of mixing is assumed to be zero in the present model, because the magnitude of the ΔH value (as a function of X) is about the same as that of the ΔG^{ex} value at 1277 °C, assessed by [Hultgren, B]. Also, it is unlikely that the ΔG^{ex} function is symmetric (as suggested in [Hultgren, B]) if the ΔH function is assumed to be nonsymmetric.

Fig. 11 $\Delta H/X(1 - X)$ for the fcc Solid Solution as a Function of Mole Fraction of Cu

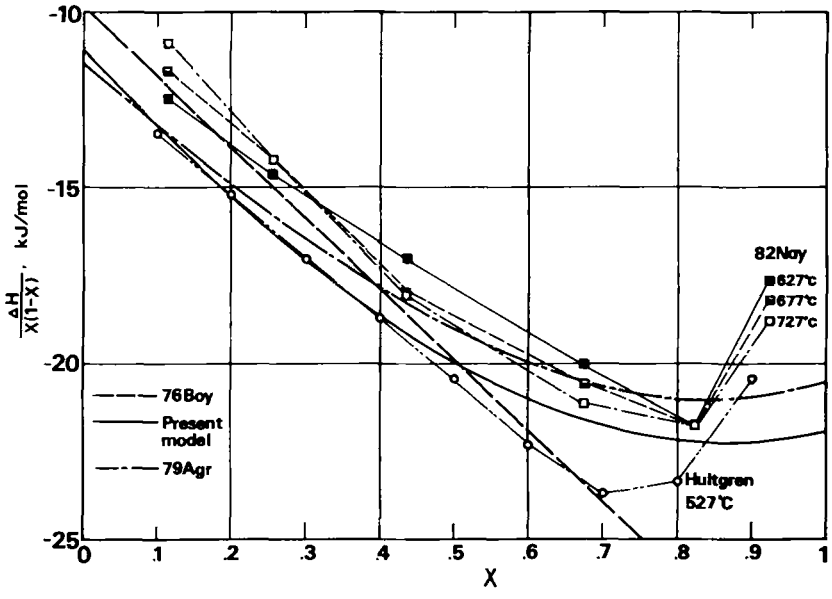

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Fig. 12 $\Delta S^{ex}/X(1 - X)$ for the fcc Solid Solution as a Function of Mole Fraction of Cu

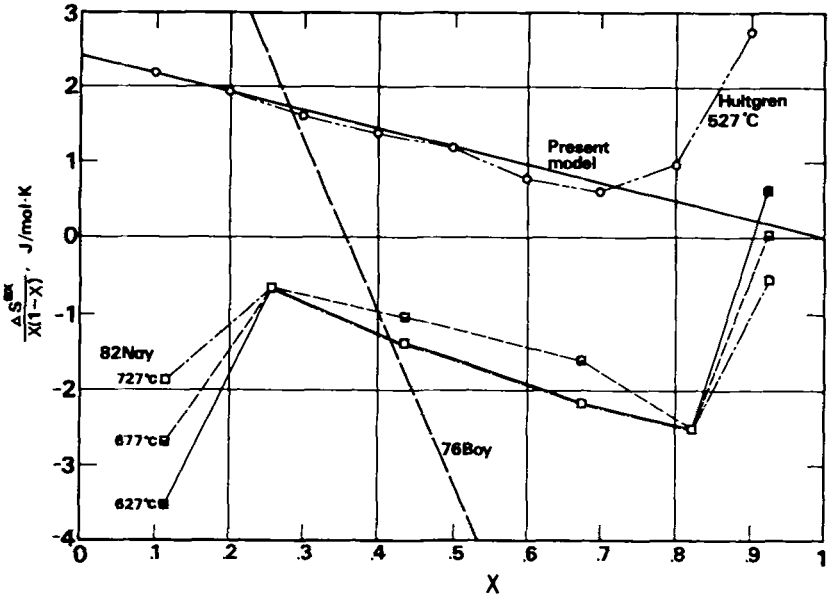

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Table 9 Au-Cu Thermodynamic Models

Function	[75Bha]	[76Boy]	[79Agr]	Present Model
Enthalpy and excess entropy of mixing, liquid phase				
$\frac{\Delta H}{X(1-X)}$	−27 230	−42 568 + 46 808X	−15 500 − 4 000X	−21 748 − 16 614X +9 541X^2 [84Top]
$\frac{\Delta S^{ex}}{X(1-X)}$	0	−13.253 + 32.333X	5.7 − 2.7X	0
Enthalpy and excess entropy of mixing, solid phase				
$\frac{\Delta H}{X(1-X)}$	−20 290	9794 − 20 203X	−11 500 − 17 500X +1500X^2 + 7000X^3	−11 053 − 22 878X +8000X^2 + 4000X^3
$\frac{\Delta S^{ex}}{X(1-X)}$	0	7.965 − 22.415X	2.1 − 1.8X − 0.3X^2 + 2.4X^3 (a)	2.4 − 2.4X
Lattice stability parameter				
G^0(Au, L)	0	0	...	0
G^0(Cu, L)	0	0	...	0
G^0(Au,fcc)	−12 760 + 9.551 T	−12 550 + 9.393 T	...	−13 000 + 9.719 T
G^0(Cu,fcc)	−13 055 + 9.623 T	−13 055 + 9.623 T	...	−13 050 + 9.6096 T

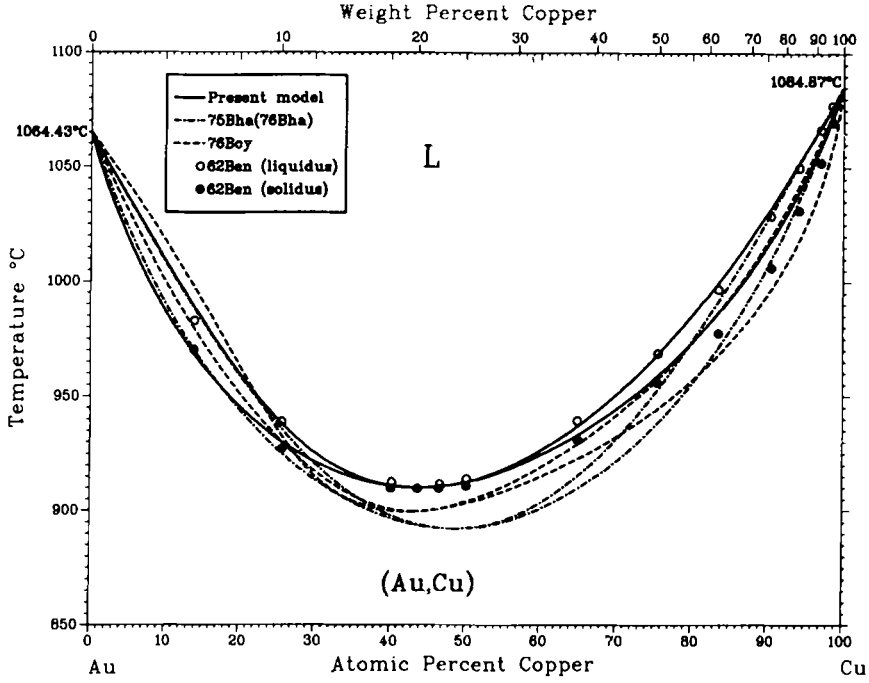
Note: T is in K and X is atomic fraction of Cu.
(a) From table in [79Agr]. Disagrees with the plot in the original paper.

The ΔS^{ex} function for the solid phase was assumed to be $2.4X(1 - X)^2$ J/mol·K based on the assessed value of [Hultgren, B] (Fig. 12). If the positive deviation at $X > 0.8$ is considered, the calculated phase diagram tends to agree less with the experimental data of [62Ben]. For better fitting, the ΔH function must be expressed with higher order terms than in the present model. The ΔH function for the solid phase in the form of $X(1 - X)(a + bX + cX^2 + dX^3)$ was derived from the modeled ΔG function for the liquid phase and the assessed phase diagram. The congruent temperature was assumed to be 910 °C, but the composition (43.0 at.% Cu) was chosen in such a way that the rest of the diagram can be reproduced with the best possible agreement with the data points of [62Ben]. Figures 10 and 11 show that the present thermodynamic model agrees reasonably well with the assessed values of [Hultgren, B] and the recent experimental ΔG^{ex} values of [79Lan], especially for the composition range $X < \sim 0.6$.

[71Sha] expressed the assessed ΔH values of [Hultgren, B] for the liquid and solid phases in terms of the subregular and quasichemical models without taking into account the phase diagram.

Phase Diagram Calculation. The liquidus and solidus calculated on the basis of the present thermodynamic model are shown in Fig. 13. The calculated solidus temperatures on the Cu-rich side are slightly higher (maximum ~10 °C) than the experimental values of [62Ben]. It is possible to attain better fitting by introducing higher order terms in

Fig. 13 Au-Cu Calculated Liquidus and Solidus Boundaries vs Experimental Data



Experimental data from [62Ben].

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some of the thermodynamic functions (ΔH) or ΔS^{ex}, for the liquid or solid phase. However, such efforts are unnecessary until more detailed experimental data are available. In particular, the ΔH, and consequently the ΔG^{ex} function for the solid phase may change abruptly at about $X = 0.7$ (see assessed values by [Hultgren, B] in Fig. 11). The emf measurements of [70Tro] indicated trends similar to those in [Hultgren, B] where ΔH_{Cu} is slightly positive at 90 to 95 at.% Cu, although the ΔH values of [70Tro] are less endothermic—$\Delta H/X(1 - X) = -12.5 \pm 1$ kJ/mol at $X = 0.6$, according to the Gibbs-Duhem integration of the original data. The present polynomial model for the ΔH function cannot express satisfactorily the abrupt change in the slope of $\Delta H/X(1 - X)$ at $X = \sim 0.7$, as indicated by [Hultgren, B] or [70Tro].

Earlier Thermodynamic Calculations. A qualitative derivation of the minimum melting point for the Au-Cu system can be found in many standard textbooks, but quantitative models are few. The regular solution model for both solid and liquid phases by [75Bha] and [76Bha] shows that the roughly averaged thermodynamic values lead to liquidus and solidus curves that are in fairly good agreement with the presently assessed phase diagram (Fig. 13). The thermodynamic functions in Table 9 and Fig. 9 to 12 were derived from the set of coefficients for the α functions given by [76Boy] and [78Tar]. Both the thermodynamic functions and the calculated phase boundaries (Fig. 13) leave room for further improvement.

Early attempts by [50Geg] and [54Wag] at thermodynamic modeling of this system may need further refinement if the same methods are to be used. The congruent temperature calculated by [50Geg] is about 150 °C too high when compared with the present assessment. [51Heu] modeled the heats of mixing for the liquid and solid phases from the atomic volume standpoint. Values with reasonable magnitudes were obtained.

Thermodynamic Data of Solid Phases. Specific heat and enthalpy of formation results for both AuCu and $AuCu_3$ phases from [50Bor], [50Nys], [51Hir1], [57Ray], [58Ori2], [68Mar], and [70Haw] are presented in [Hultgren, B]. A summary of subsequent works on the thermodynamic properties is presented below.

Au_3Cu. The enthalpy of transformation associated with the order-disorder transition is 1782 J/mol at 299 K [77Den, 78Den].

AuCu and $AuCu_3$. [72Nog] measured specific heats at liquid helium temperatures and derived results for the electronic specific heat coefficient, γ, and Debye temperature, θ_D, for AuCu (disordered), AuCu(I), and AuCu(II) phases as given in Table 4. Also included are similar data for three Cu-rich disordered alloys from [72Del], the variation of the Debye temperature with composition as calculated from elasticity data by [72Del], and data from [60Fli] for $AuCu_3$. Detailed tabulated specific heat results for different phases are presented by [76Mar]. [78Tis] estimated enthalpy values from DTA measurements for the reactions, AuCu (disordered) → AuCu(II) and AuCu(II) → AuCu (disordered), as − 2050 and 1320, respectively. [78Tis] reported similar data for the $AuCu_3$ (disordered) → $AuCu_3$ and $AuCu_3$ → $AuCu_3$ (disordered) reactions; results were −2350 J/mol and 860 J/mol, respectively. [71Pre] reported the enthalpy of formation for $AuCu_3$ as 480 J/

mol. [72Yoo] measured heat capacities of $AuCu_3$ in both ordered and disordered conditions and observed that below 130 K C_p for the ordered state was lower by up to 6%, whereas above that temperature the reverse was true. Similar results were found by [71Haw] for AuCu, where the temperature of reversal was 100 K.

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01Mae: E. Maey, "Specific Volume as Determination Characteristics of Chemical Bonding of Alloys," *Z. Phys. Chem., 38*, 292-306 (1901) in German. (Equi Diagram; Experimental)

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*Indicates key paper.
#Indicates presence of a phase diagram.

Au-Cu evaluation contributed by **H. Okamoto**, ASM INTERNATIONAL, Metals Park, OH 44073; **D.J. Chakrabarti**, Alcoa Laboratories, Alcoa Center, PA 15069; and **D.E. Laughlin** and **T.B. Massalski**, Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213. Work was supported by the International Gold Corporation, the International Copper Research Association, Inc., ASM INTERNATIONAL, and the Department of Energy through the Joint Program on Critical compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data, National Bureau of Standards. Literature searched through 1985. Part of the bibliographic search was provided by ASM. Professor Massalski is the ASM/NBS Data Program Editor-in-Chief for the Binary Alloy Program and is also Co-Category Editor for the binary gold alloys with Dr. Okamoto. Professor Laughlin is the Category Editor for binary copper alloys.

The Cr-Si (Chromium-Silicon) System

51.996 28.0855

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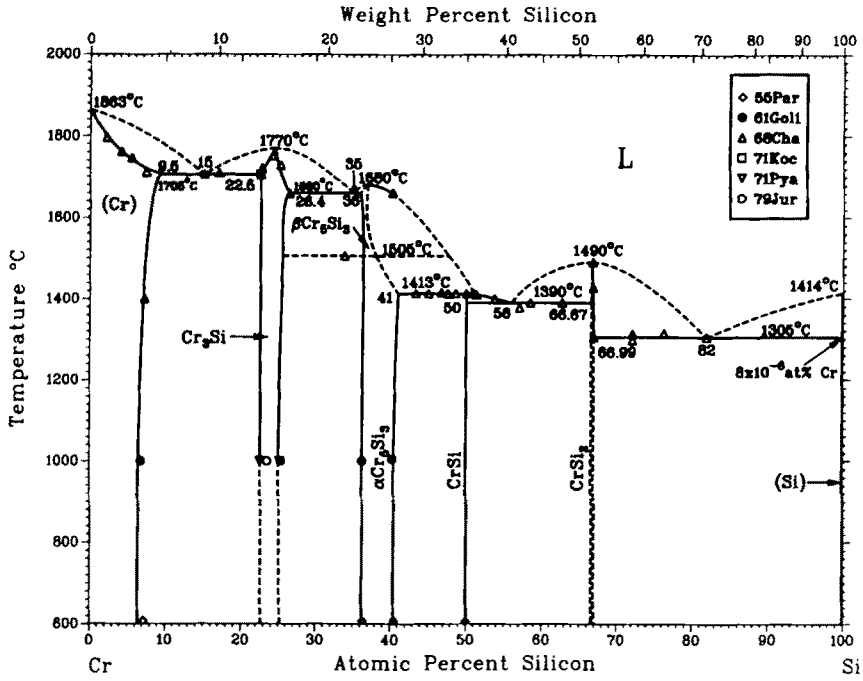
Equilibrium Diagram

The Cr-Si system is technologically interesting because its intermediate phases possess useful thermoelectric properties. The assessed equilibrium phase diagram of the Cr-Si system is shown in Fig. 1. The following stable phases are present in the system: (1) the liquid, L; (2) the terminal solid solution of Si in (Cr), with a maximum solubility of approximately 9.5 at.% at the eutectic temperature of 1705 °C; (3) the terminal solid solution of Cr in (Si), with a maximum solid solubility of approximately 8×10^{-6} at.% at the eutectic temperature of 1305 °C; (4) the cubic intermediate phase Cr_3Si, which melts congruently at 1770 °C; (5) the tetragonal intermediate phase Cr_5Si_3,

Fig. 1 Assessed Cr-Si Phase Diagram



A.B. Gokhale and G.J. Abbaschian, 1987.