Cu-Pd (Copper-Palladium)

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Equilibrium Diagram

The equilibrium phases in the assessed Cu-Pd phase diagram (Fig. 1) are: (1) the liquid, L; (2) the fcc continuous solid solution, (Cu,Pd); (3) ordered Cu_3Pd, occurring in the solid solution phase field with a composition range of homogeneity; and (4) ordered CuPd, also existing in the solid solution phase field with a range of homogeneity. This evaluation of the Cu-Pd system updates the phase diagram assessed by [Hansen].

Liquidus and Solidus

The Cu-Pd system was first investigated by [06Rue] by thermal analysis and metallography. Subsequently, [49Nem] determined the Cu-Pd liquidus on the basis of thermal analysis data. The liquidus and solidus in the diagram of [Hansen] were drawn from the data of [06Rue] and [49Nem]. There have been no other investigations of the Cu-Pd liquidus and solidus. Therefore, the assessed liquidus and solidus in Fig. 1 are based on the data of [06Rue] and [49Nem], with modifications in the temperatures so that the melting points of Cu and Pd conform to the accepted values of 1084.87 and 1555 °C, respectively, from [Melt]. Table 1 shows the experimental liquidus and solidus data for the Cu-Pd system.

(Cu,Pd) Solid Solution

The (Cu,Pd) continuous solid solution has been investigated by numerous researchers. Various physical properties were determined—electrical conductivity and resistivity [24Sed, 27Joh, 28Bor, 32Sve, 33See, 34See, 34Tay, 36Jau1, 73San], magnetic susceptibility [32Sve, 36Jau1, 78Bel], X-ray methods [24Hol, 25Joh, 32Lin, 35Gra, 54Gei, 54Jon, 55Sch, 56Jau1, 57Hir, 69Pre, 71Rau, 73San, 78Ima], thermoelectric emf [49Nem, 52Rud, 56Rud1] (also see [56Rud2]), hardness [54Gei, 56Jau1, 69Pre, 73San], absolute thermopower [56Jau1], short-range order [59Wat, 67Kat, 73Ohs, 76Ohs, 78Bel], diffusivity [52Tho, 66Mar, 68Bor, 69Bad, 74Ten], density [69Pre], optical absorption [72Spr], and thermal conductivity (compiled by [78Ho]). (Also see the sections on "Short-Range Order" and "Thermodynamics.")

Order-Disorder Transformations

Order-disorder transformations occur in Cu_3Pd and CuPd.

Cu_3Pd

Early investigations of the transformation from disordered to ordered Cu_3Pd on the basis of electrical resistivity [27Joh, 28Bor, 32Sve, 33See, 34Tay, 36Bel], magnetic susceptibility [32Sve], thermal analysis [34Tay, 36Bel, 49Nem], and X-ray methods [27Joh, 32Lin] indicated that ordered Cu_3Pd forms with $AuCu_3$-type structure over the entire composition range 10 to 25 at.% Pd. [28Bor] and [36Bel] found maxima in the transformation temperature at 578 and 620 °C, respectively, and the stoichiometric composition 25 at.% Pd. On the other hand, [34Tay] observed the maximum transformation temperature to lie at 500 °C and the off-stoichiometric composition 15 at.% Pd. On the basis of resistivity, X-ray, and specific heat measurements, [39Jon] observed that $AuCu_3$-type ordering is present only in alloys with less than ~20 at.% Pd. For alloys containing 20 to 25 at.% Pd, tetragonal structure was observed. [39Jon] proposed the Cu_3Pd phase boundaries as accepted in [Hansen] on the basis of the transformation data of [34Tay], in combination with their own resistivity and X-ray data.

Subsequently, [54Jau] confirmed the existence of ordered $AuCu_3$ structure in 10 to 19 at.% Pd and ordered tetragonal structure in 19 to 27 at.% Pd on the basis of X-ray and resistivity measurements. [54Gei] reported a "2-high inverted" Ni_4Mo-type structure, with space group $P4_2/m$, for an alloy containing 20 at.% Pd. [54Jon] studied the temperature variation of the tetragonality of an ordered Cu-25 at.% Pd alloy, and proposed the following relationship between the degree of order (W) and the axial ratio (c/a) of the tetragonal cell: $c/a = 1 - 0.015W$.

Based on powder X-ray data, [54Sch] and [55Sch] proposed the existence of one-dimensional antiphase domain (1D APD) structure (or long-period superlattice, LPS) in alloys containing 18.5 to 25 at.% Pd, and a "complex" APD structure in 25.5 to 30 at.% Pd alloys. Subsequently, [55Wat] and [56Wat] determined the structure of alloys with 18 to ~28 at.% Pd (α' phase) by electron diffraction measurements in thin oriented films and by X-ray diffraction (XRD) of single crystals. They observed that in alloys

Table 1 Experimental Cu-Pd Liquidus and Solidus Data

Reference	Composition, at.% Pd	Temperature(a), °C Liquidus	Solidus
[06Rue]	0	1084.87	...
	6.2	1093	1088
	13.0	1104	1094
	20.4	1125	1110
	28.5	1148	1128
	32.8	1180	1145
	37.4	1197	1167
	42.2	1215	1180
	47.3	1230	1205
	58.2	1289	1264
	70.5	1375	1335
	84.3	1459	1419
	100	1555	...
[49Nem]	10	1107	...
	20	1119	...
	30	1150	...
	50	1241	...
	70	1351	...
	80	1416	...
	90	1479	...

(a) The temperatures are adjusted so that the melting points of Cu and Pd correspond to the accepted values of 1084.87 and 1555 °C [Melt], respectively.

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containing ~18 to 25 at.% Pd, the lattice consists of fct cells built in terms of the original disordered fcc cell. Moreover, the splitting of superlattice reflections indicated the presence of 1D APD's with a periodicity of $2M_3$ along the tetragonal axis of the fct cell, where M_3 is the half period and varies with Pd content. In alloys with ~25 to 28 at.% Pd, the reflections indicated a two-dimensional (2D) APD structure, wherein the atoms have two kinds of step shifts occurring at every M_3th and M_1th atom along the z and x directions, respectively, where M_3 and M_1 are the half periods in the two directions.

The resulting 2D APD structure was observed to have lattice parameters $2M_1a_1$, a_2, and a_3, where a_1, a_2, and a_3 correspond to the lattice vectors of the fundamental fcc cell. The space group

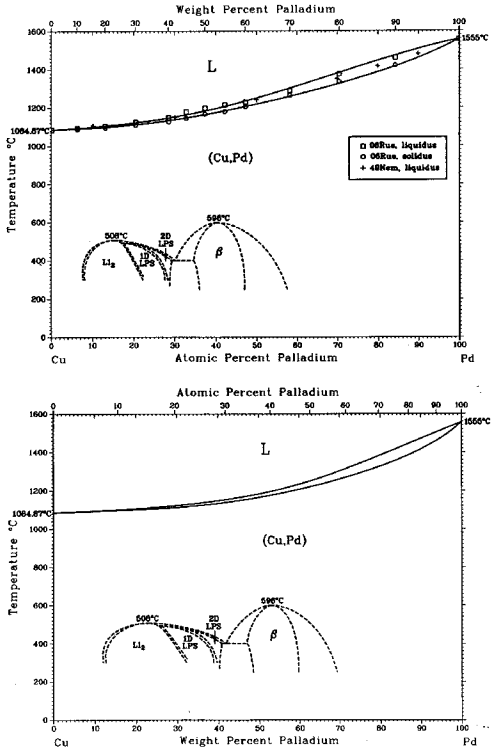

Fig. 1 Assessed Cu-Pd phase diagram.

symmetry of such a cell (as shown, for example, in [56Wat]) is not orthorhombic, but rather monoclinic. Furthermore, [55Wat] and [56Wat] observed that the length of the APD's depend on Pd concentration. These results confirmed the earlier observations of [55Sch], with the complex APD structure of [55Sch] corresponding to the 2D APD structure of [55Wat]. In addition, [56Wat] observed that the tetragonality of the ordered phase disappears along with the APD structure in alloys containing less than ~18 at.% Pd. Table 2 lists the values for the half periods in the 1D LPS and 2D LPS Cu_3Pd (α'') alloys at various Pd concentrations; the half periods, in general, decrease with increasing Pd contents.

[56Jau2] studied the annealing behavior of quenched and cold worked Cu-Pd alloys containing 6 to 30 at.% Pd from room temperature to 450 °C. [56Jau1] measured various physical properties of 6 to 30 at.% Pd alloys as a function of the degree of order. Based on isothermal annealing and X-ray data, [56Jau2] concluded that the ordering is a nucleation and growth process. In the light of their observations, [56Jau2] proposed that the entire ordered region from 10 to ~28 at.% Pd has tetragonal structure, with the axial ratio close to unity for 19 at.% Pd. [56Jau1] concluded that Cu_4Pd is the most favorable composition for ordering, and that it has the tetragonal structure proposed by [54Gei]. However, [57Hir] indicated that the experimental results of [54Gei] can be interpreted in terms of the 1D APD structure.

On the basis of thermal emf investigations, [49Nem], [52Rud], and [56Rud1] proposed the existence of ordered structures corresponding to the stoichiometries Cu_5Pd (16.67 at.% Pd) and Cu_5Pd_3 (37.5 at.% Pd). Similarly, [69Pre] suggested the formation of ordered Cu_6Pd and Cu_5Pd. However, in view of the substantial evidence for the existence of ordered Cu_3Pd and CuPd,

Table 2 Values for the Half Period in the LPS Cu_3Pd (α'') Alloys at Various Pd Concentrations

Reference	Composition, at.% Pd	Temperature, °C	Half period(a) M_1	Half period(a) M_2
[54Sch]	18.0	430	...	9
	25.0	430	...	4
[55Wat]	22.0	200	...	7
	27.0	200	4	3
[55Sch](b)	18.5	430	...	8.5
	19.0	430	...	8.1
	19.5	430	...	8.5
	20.5	430	...	7.1
	21.0	430	...	7.3
	21.5	430	...	6.0
	22.5	300	...	5.6
	23.0	430	...	5.2
	24.0	430	...	4.5
	25.0	430	...	4.2
	25.5	430	6.8	4.1
	26.0	430	6.2	4.1
		380	...	4.0
	26.5	430	5.4	3.8
	27.0	430	4.7	3.7
	27.5	430	4.5	3.6
		380	4.8	3.5
	28.0	380	3.9	3.3
	28.5	380	4.0	3.3
	29.0	380	3.9	3.2

(continued)

(a) In the 1D LPS, M_1 is the half period along the tetragonal axis of the fundamental cell; in the 2D LPS, M_1 and M_2 are the half periods in the x and z directions, respectively, of the fundamental cell. (b) Calculated from the fault densities listed in [Pearson2], based on the data of [55Sch]. (c) Annealed at various temperatures between 200 and 450 °C and slowly cooled to room temperature.

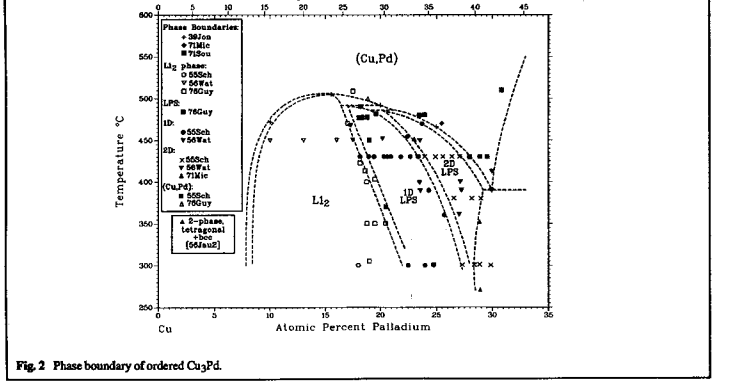

Fig. 2 Phase boundary of ordered Cu_3Pd.

Table 2 Values for the Half Period in the LPS Cu_3Pd (α') Alloys at Various Pd Concentrations (continued)

Reference	Composition, at.% Pd	Temperature, °C	Half period(a) M_1	Half period(a) M_3
[56Wat]	18.0	490	...	9.9
		470	...	10.5
		450	...	10.5
	21.0	490	...	6.8
		470	6.8	5.6
		450	...	6.4
		250	7.6	5.7
	25.0	450	5.3	3.8
		400	5.4	3.7
		390	5.3	3.8
		250	5.4	3.7
		230	5.5	3.7
	28.0	400	3.6	3.2
		390	3.5	3.2
		360	3.6	3.1
		250	3.5	3.2
	30.0	400	3.3	3.1
		390	3.2	3.1
		250	3.3	3.1
[57Hir]	20.8	(c)	...	7.0
	25.2	(c)	...	4.4
	25.8	(c)	...	4.2
	27.3	(c)	4.0	3.2
	28.5	(c)	3.8	3.5
[59Wat]	18.0	470	...	10.8
		440	...	9.4
	25.0	462	...	4.0
		453	...	3.9
		451	...	3.7
		442	...	3.8
	28.0	413	...	3.1
		395	...	3.2
[70Oka]	25.8	...	...	3.5
[71Mic]	24.5	365	...	4.3
		450	5.8	4.3
[76Guy]	18.5	475	...	12.0
	19.0	475	...	11.7
		450	...	11.5
	19.5	475	...	9.4
	20.5	370	...	7.1
[81Ter]	28.0	400	4.3	3.4
[85Fon]	20.0	457	...	8.0

(a) In the 1D LPS, M_3 is the half period along the tetragonal axis of the fundamental cell; in the 2D LPS, M_1 and M_3 are the half periods in the x and z directions, respectively, of the fundamental cell. (b) Calculated from the fault densities listed in [Pearson2], based on the data of [55Sch]. (c) Annealed at various temperatures between 200 and 450 °C and slowly cooled to room temperature.

the conclusions of [56Rud1] and [69Pre] are not justified. [63Pre] studied the temperature variation of the lattice parameter of a Cu-28.8 at.% Pd alloy and reported the presence of a disordered fcc phase above 750 °C, an ordered fcc phase between 350 and 375 °C, a tetragonal phase between 475 and 600 °C and a phase with unknown structure between 675 and 700 °C. The existence of the latter two phases within the temperature range specified by [63Pre] is quite unlikely; moreover, the authors themselves noted that there was considerable uncertainty in the observed temperature range of stability of the various phases.

Single-crystal and powder XRD studies [57Hir, 70Oka, 70Sou, 71Mic, 71Sou, 81Egu], electron diffraction studies [59Wat, 70Sou, 71Sou], and transmission electron microscopy (TEM) studies [81Ter, 81Egu, 83Egu] confirmed the existence of 1D APD structures in the range ~18 to ~27 at.% Pd and 2D APD structures in the range ~27 to ~30 at.% Pd. Moreover, [59Wat], [71Mic], [73Kub], and [76Guy] observed that the relative stability of the two types of long-period structures is dependent on temperature. According to [57Hir], [59Wat], and [71Mic], a transition from 1D to 2D APD structure with increasing temperature might explain the specific heat vs temperature data for Cu_3Pd from [39Jon], which show a maximum at around 400 °C. [70Oka] tentatively proposed the space group *P4mm* for the 1D APD structure. Investigations by [70Oka], [81Ter], and [81Egu] showed that the antiphase half periods of the long-period structures are nonintegral and represent an average of integral periods of domains over the entire crystal. [85Fon] interpreted the long-period superstructures in Cu_3Pd in terms of the axial next nearest neighbor (ANNI) model. On the basis of this model, they proposed a schematic ANNI phase diagram, wherein the phase region corresponding to the long-period structures comprises a number of "incommensurate" polytypes.

Phase diagrams showing the Cu_3Pd order-disorder transformation were proposed by [28Bor], [34Tay], [39Jon], [55Sch], [56Jau2], [71Mic], [71Sou], [76Guy], and [85Fon]. However, the proposed temperature and composition range of existence of the various ordered structures do not agree with one another. The phase diagrams of [71Sou] and [85Fon] showed the formation of the phase with the 1D LPS through a peritectoid reaction between the $L1_2$-type α' phase and the (Cu,Pd) solid solution, and that with the 2D LPS through a peritectoid reaction between the 1D LPS and the disordered (Cu,Pd) solid solution. In addition, [56Jau2]

Table 3 Cu-Pd Crystal Structure Data

Phase	Composition, at.% Pd	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Cu,Pd)	0 to 100	*cF4*	*Fm3m*	*A1*	Cu	[King1]
Cu_3Pd (α')	~7.6 to ~22	*cP4*	*Pm3m*	*L1₂*	$AuCu_3$	[39Jon]
Cu_3Pd (α'')						
1D APD(a)	~17 to ~28	*tP28*	*P4mm*	...	Cu_3Pd	[55Wat]
2D APD(b)	~19 to ~31	...	...	...	...	[55Wat]
CuPd (β)	~36 to ~47	*cP2*	*Pm3m*	*B2*	CsCl	[39Jon]

(a) The 1D APD cell has lattice parameters a and $2M_3c$, where a and c are the lattice vectors of the fundamental cell, and M_3 is the half period and varies with Pd concentration. (b) The 2D APD cell has lattice parameters $2M_1a_1$, a_2, and $2M_3a_3$, where a_1, a_2, and a_3 correspond to the lattice vectors of the fundamental cell, and M_1 and M_3 are half periods and vary with Pd concentration. The space group symmetry of this cell is monoclinic.

and [71Sou] showed the existence of a eutectoid equilibrium between ordered Cu_3Pd and CuPd at lower temperatures.

Figure 2 shows the tentative phase diagram for ordered Cu_3Pd, proposed on the basis of selected data from [39Jon], [55Sch], [56Wat], [71Mic], [71Sou], and [76Guy]. In view of the large degree of scatter in the data, this phase diagram for Cu_3Pd should be regarded as a compromise, with minimum uncertainties on the order of ±10 °C for the transformation temperatures, and ±2% for the composition range of stability of the various structures.

Table 4 Lattice Parameter Data for the (Cu,Pd) Solid Solution

Composition, at. % Pd	Lattice parameter, nm	Composition, at. % Pd	Lattice parameter, nm
From [24Hol]		**From [56Jau2](c)**	
0	0.3627	6.4	0.3635
19.4	0.3662	9.7	0.3645
36.4	0.3732	11.3	0.3651
51.9	0.3763	12.6	0.3656
54.4	0.3758	13.9	0.3659
70.2	0.3820	14.7	0.3663
100	0.3905	16.7	0.3668
		17.0	0.3670
From [32Lin]		19.5	0.3678
0	0.3615	20.9	0.3682
6.9	0.3639	22.7	0.3687
14.8	0.3663	26.6	0.3698
17.0	0.3669	29.0	0.3704
19.0	0.3680		
25.0	0.3695	**From [57Hir]**	
30.8	0.3718	15.5	0.3663
45.5	0.3753	16.3	0.3667
49.9	0.3767	20.8	0.3680
51.9	0.3774	25.2	0.3695
54.4	0.3779	25.8	0.3696
59.3	0.3789	27.3	0.3699
78.4	0.3839	28.5	0.3701
88.7	0.3862		
100	0.3892	**From [69Pre](d)**	
		3.0	0.3626
From [35Gra]		4.5	0.3631
43.0	0.3728	5.0	0.3633
50.0	0.3758	6.3	0.3637
		7.7	0.3640
From [39Jon](a)			
30(b)	0.3709	**From [71Rau](e)**	
35(b)	0.3716	35.0	0.3723
50(b)	0.3767	37.5	0.3734
55(b)	0.3781	40.0	0.3740
60	0.3794	41.0	0.3740
		42.5	0.3738
From [54Gel]		45.0	0.3758
20	0.3682	50.0	0.3768
From [55Sch]		**From [73San]**	
18	0.3672	40.0	0.3730
24	0.3692		
28	0.3697	**From [78Ima]**	
29	0.3698	40.0	0.3733
30	0.3702		
		From [Massalski2]	
		0	0.36146
		100	0.38903

(a) Lattice parameters calculated from atomic volume data of [39Jon]. (b) Alloys lie in the two-phase α + β region. (c) Read from lattice parameter vs composition graph; alloys quenched from 800 °C. (d) Read from lattice parameter vs composition graph. (e) Alloys heat treated at 650 °C. (f) At 25 °C, compilation.

CuPd

The composition range of stability of CsCl-type CuPd was studied by X-ray [27Joh, 32Lin, 34Tay, 39Jon], magnetic susceptibility [32Sve], and electrical resistivity measurements [27Joh, 28Bor, 32Sve, 34Tay, 36Bel]. On the basis of electrical resistivity measurements, [28Bor] observed in the phase boundary of CuPd a maximum at ~670 °C and 50 at.% Pd. [34Tay] determined that the transformation from disordered (Cu,Pd) solid solution to ordered CuPd occurs over the range 35 to 50 at.% Pd, from thermal analysis, metallography, and electrical resistivity measurements. Moreover, [34Tay] noted that the CuPd phase boundary shows a maximum at 596 °C and that it occurs at the off-stoichiometric composition 40 at.% Pd. This maximum was subsequently confirmed by [39Jon] from resistivity measurements on a Cu-40 at.% Pd alloy. From the temperature variation of the enthalpy of formation of a 40 at.% Pd alloy, [62Ori] determined that the order-disorder transformation for this alloy occurs at ~600 °C, in agreement with the data of [34Tay] and [39Jon]. The reports of [49Nem] and [56Rud1] showing the existence of ordered Cu_5Pd_3, instead of CuPd, have not been corroborated.

The phase diagram of [56Jau2] showed the existence of a eutectoid equilibrium between ordered CuPd and Cu_3Pd, based on X-ray data on a Cu-29 at.% Pd alloy that was slowly cooled to 275 °C. Similarly, [68Dzh] investigated alloys containing 26.4 to 28.8 at.% Pd and reported the eutectoid decomposition of (Cu,Pd). The diagram proposed by [71Sou] also indicated this eutectoid equilibrium. However, their diagram was constructed by extrapolating the Cu_3Pd and CuPd phase boundaries from higher temperatures.

Order-disorder transformations in CuPd have also been studied by [70Ell], [72San], [73San], [78Ima], [78Iwa], [78Bel], [81Tel], [81Iwa], and [83Syu]. [70Ell] observed that any type of deformation induced a transformation from ordered CsCl structure to dis-

Table 5 Lattice Parameters of Ordered $L1_2$-type Cu_3Pd (α')

Composition, at. % Pd	Lattice parameter, nm	Composition, at. % Pd	Lattice parameter, nm
From [32Lin]		**From [69Pre](b)**	
10.8	0.3655	9.1	0.3645
14.8	0.3662	10.0	0.3647
17.0	0.3671	11.1	0.3652
19.0	0.3680	12.5	0.3655
		14.3	0.3661
From [39Jon](a)		16.7	0.3667
10	0.3646	20.0	0.3675
15	0.3662	25.0	0.3689
18	0.3672		
		From [76Guy]	
From [55Sch]		17.5	0.3670
18.00	0.3670	19.0	0.3674
18.25	0.3672	19.5	0.3676
		20.5	0.3676

(a) Lattice parameters calculated from atomic volume data of [39Jon]. (b) Read from lattice parameter vs composition graph.

ordered (Cu,Pd) solid solution, with the degree of transformation depending on the degree of deformation. This evidence led [74War] to suggest that the disorder-order transformation is martensitic in nature.

[78Bel] investigated the ordering process in a Cu-41.3 at.% Pd alloy by electron diffraction, metallography, and magnetic susceptibility measurements. Their results showed that the ordered phase forms by nucleation along the grain boundaries of the parent disordered phase and subsequent growth of the randomly oriented nuclea, with the complete absence of APD's in the ordered state. Subsequently, [81Tel] investigated the order-disorder transformation in a 40 at.% Pd alloy by TEM, metallography, and XRD. Their results confirmed the observations of [78Bel] in that the ordering process involves nucleation and growth of ordered phases, with no definite orientation relationship to the parent disordered phase. [78Iwa] and [81Iwa] studied the effect of pressure on the CuPd phase field, and observed that the application of pressure displaced the CuPd phase field toward the ideal equiatomic composition. Moreover, studies on a Cu-41 at.% Pd alloy showed that the application of pressure raises the order-disorder transformation temperature at the rate of 1.4 °C/kbar.

The assessed CuPd phase boundaries in Fig. 1 and 3 are drawn from the data selected by [39Jon] from the resistivity measurements of [34Tay].

Table 6 Lattice Parameters of Ordered Cu_3Pd (α')

Composition, at.% Pd	Lattice parameters, nm a	c	Comment
From [39Jon]			
24.9	0.3715	0.3663	...
From [54Gel]			
20.0	0.3685	0.3664	...
From [54Jon]			
25.0	0.3710	0.3654	At 18 °C
From [55Sch]			
18.5	0.3679	0.3661	Annealed at 430 °C
19.0	0.3679	0.3665	Annealed at 430 °C
19.5	0.3681	0.3660	Annealed at 430 °C
20.5	0.3685	0.3659	Annealed at 430 °C
21.5	0.3686	0.3654	Annealed at 430 °C
22.5	0.3696	0.3655	Annealed at 300 °C
23.0	0.3693	0.3657	Annealed at 430 °C
24.0	0.3701	0.3666	Annealed at 430 °C
25.0	0.3703	0.3655	Annealed at 300 °C
25.5	0.3698	0.3667	Annealed at 430 °C
26.0	0.3700	0.3677	Annealed at 430 °C
26.5	0.3699	0.3679	Annealed at 430 °C
From [56Jau2]			
19.5	0.3687	0.3659	Quenched from 400 °C
	0.3688	0.3655	Quenched from 275 °C
20.9	0.3694	0.3657	Quenched from 400 °C
	0.3695	0.3654	Quenched from 275 °C
22.9	0.3700	0.3659	Quenched from 400 °C
	0.3703	0.3653	Quenched from 275 °C
26.6	0.3702	0.3683	Quenched from 400 °C
	0.3703	0.3670	Quenched from 275 °C
From [57Hir]			
20.8	0.3691	0.3659	...
25.2	0.3707	0.3665	...
25.8	0.3708	0.3660	...
27.3	0.3711	0.3677	...
28.5	0.3710	0.3682	...
From [68Dzh]			
28.8	0.3736	0.3680	(a)
From [70Oka]			
25.8	0.3710	0.3665	...
From [76Guy]			
18.5	0.3678	0.3660	
19.0	0.3680	0.3668	(b)
19.5	0.3680	0.3664	(b)
20.5	0.3680	0.3669	(b)

Note: Lattice parameters given in terms of the fundamental cell. (a) Annealed between 450 and 475 °C. (b) Annealed between 475 and 480 °C.

The assessed CuPd phase boundaries in Fig. 1 and 3 are drawn from the data selected by [39Jon] from the resistivity measurements of [34Tay].

Short-Range Order

[59Wat] investigated 13 to 28 at.% Pd alloys by high-temperature electron diffraction measurements at temperatures above the order-disorder transformation point. They observed that in alloys with the 2D APD structure, diffuse scattering corresponding to short-range order exists at 100 to 150 °C above the transformation point. The resulting domain structure consists of large pockets of completely disordered regions between ordered domains. Diffuse X-ray scattering, indicative of short-range order, was observed by [67Kat] in a Cu-15 at.% Pd alloy that had been deformed and annealed at various temperatures. Diffuse electron scattering was also observed by [73Ohs] in 12.6 to 60.6 at.% Pd alloys that had been quenched from above their respective transformation temperatures. Furthermore, hot-stage electron microscopy of 25 to 29.4 at.% Pd alloys at ~500 °C showed that the dis-

Table 7 Lattice Parameters of Ordered CsCl-Type CuPd

Composition, at.% Pd	Lattice parameter, nm	Composition, at.% Pd	Lattice parameter, nm
From [24Hol]		**From [39Jon](a)(cont.)**	
45.5	0.2980	50.0(b)	0.2977
		55.0(b)	0.2978
From [32Lin]			
38.9	0.2960	**From [55Sch](c)**	
39.7	0.2958	41.0	0.2966
45.5	0.2973		
47.3	0.2977	**From [71Rau](d)**	
		40.0	0.2961
From [35Gra]		41.0	0.2965
43.0	0.2966	42.5	0.2967
50.0	0.2996	45.0	0.2973
From [39Jon](a)		**From [72San]**	
30.0(b)	0.2955	40.0	0.2954
35.0(b)	0.2955		
40.0	0.2965	**From [78Ima]**	
45.0	0.2970	40.0	0.2962

(a) Lattice parameters calculated from atomic volume data of [39Jon]. (b) Alloys lie in the two-phase $\alpha + \beta$ region. (c) Annealed at 410 °C. (d) Alloys heat treated at 500 °C.

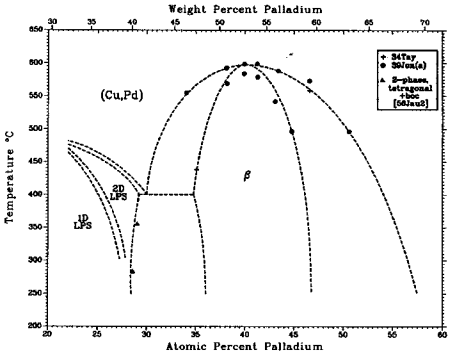

Fig. 3 Phase boundary of ordered CuPd. (a) Selected by [39Jon] from the data of [34Tay].

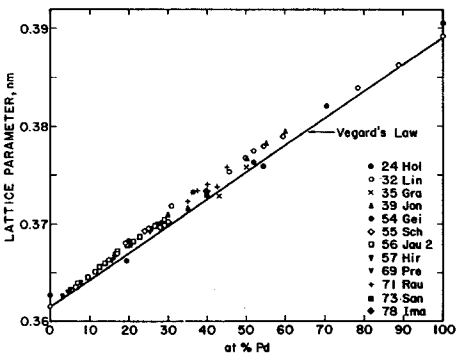

Fig. 4 Variation of lattice parameters of the disordered (Cu,Pd) solid solution with composition.

tribution of short-range order diffuse scattering in these alloys is similar to that observed in the quenched alloys. [76Ohs] determined the short-range order parameters for a disordered 29.8 at.% Pd alloy by XRD measurements on single crystals that had been quenched after annealing at 500 °C. The existence of short-range order in quenched alloys with 35 to 41 at.% Pd was reported by [78Bel]. Also, high-resolution electron microscopy investigation on a disordered Cu-30 at.% Pd alloy by [83Ten] revealed the existence of microdomains in the alloy, suggesting the presence of short-range order. [84Tan] observed the presence of lattice fringes in electron micrographs of disordered Cu-21 and -29.8 at.% Pd alloys. They concluded that these fringes are related to short-range order diffuse streaks, indicating the existence of localized ordered domains in the disordered alloys. [68Sat] studied the effects of short-range order on low-temperature specific heats of Cu-Pd alloys containing 58, 67.5, and 75 at.% Pd.

Crystal Structures and Lattice Parameters

The crystal structures of Cu-Pd phases are listed in Table 3. Lattice parameters of the (Cu,Pd) solid solution phase measured by [24Hol], [32Lin], [35Gra], [39Jon], [54Gei], [55Sch], [56Jau2], [57Hir], [69Pre], [71Rau], [73San], and [78Ima] are summarized in Table 4 and Fig. 4, along with data for the pure elements from [Massalski2]. In general, the lattice parameter data show good agreement in the range 0 to 30 at.% Pd, whereas there is a small degree of scatter in the range 30 to 60 at.% Pd. Almost all the data show positive deviation from Vegard's law. [54Jon] determined the temperature dependence of the lattice parameters in a Cu-25 at.% Pd alloy from high-temperature X-ray data. [71Rau] measured lattice parameters of both ordered and disordered CuPd alloys in the range 35 to 50 at.% Pd between 400 and 700 °C.

Lattice parameters of ordered $L1_2$-type Cu_3Pd (α'), ordered Cu_3Pd (α''), and ordered CsCl-type CuPd (β) phases are listed in Tables 5, 6, and 7, respectively.

Thermodynamics

Solid (Cu,Pd) Solution

Thermodynamic properties of solid Cu-Pd alloys were determined by chemical equilibrium studies [40Sch, 51Sch], emf measurements [58Vec, 60Vec, 63Vec, 69Bug], tin solution calorimetry [62Gua, 62Ori], and vapor pressure measurements [68Myl]. [Hultgren, B] assessed the various thermodynamic data for solid Cu-Pd alloys based on the above-mentioned experimental reports. In all instances, the data show negative enthalpies of mixing for the solid. Moreover, the enthalpy and Gibbs energy data show an asymmetry with respect to composition, with a minimum between 40 and 45 at.% Pd. This asymmetry in the thermodynamic functions, in combination with the large negative enthalpies of mixing, could explain the tendency for ordering observed at lower temperatures. Figures 5 and 6 show the composite of all available data for the normalized enthalpies of mixing, $\Delta H/X(1-X)$, and normalized excess entropies of mixing, $S^{ex}/X(1-X)$, respectively, for the solid Cu-Pd alloys (where X is the atomic fraction of Pd). [71Sha] applied the subregular model and a quasichemical model to derive analytical expressions for the enthalpies of mixing of solid Cu-Pd alloys, based on the selected values of [Hultgren, B]. These expressions are also represented in Fig. 5.

[62Ori] determined the temperature variation of the enthalpy of formation of a Cu-40 at.% Pd alloy in ordered and disordered states by differential solution calorimetry. They observed that the order-disorder transformation occurs with negligible enthalpy and entropy changes. However, according to [Hultgren, B], this type of behavior is inconsistent with the thermal effects observed during the order-disorder transition. [68Sat] and [70Sat] measured the low-temperature specific heats of various Cu-Pd alloys and determined the variation of the electronic specific heat coefficient and Debye temperature with Pd concentration.

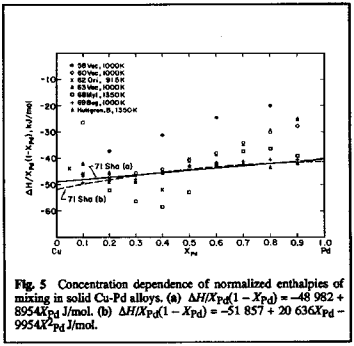

Fig. 5 Concentration dependence of normalized enthalpies of mixing in solid Cu-Pd alloys. (a) $\Delta H/X_{Pd}(1-X_{Pd}) = -48\,982 + 8954X_{Pd}$ J/mol. (b) $\Delta H/X_{Pd}(1-X_{Pd}) = -51\,857 + 20\,636X_{Pd} - 9954X^2_{Pd}$ J/mol.

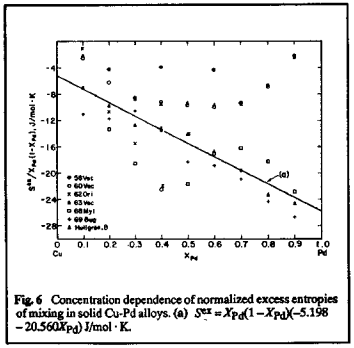

Fig. 6 Concentration dependence of normalized excess entropies of mixing in solid Cu-Pd alloys. (a) $S^{ex} = X_{Pd}(1-X_{Pd})(-5.198 - 20.560X_{Pd})$ J/mol·K.

Liquid Cu,Pd

[71Vat1] and [71Vat2] determined the activities of Cu and Pd in liquid alloys by emf and vapor measurements, respectively. [71Vat1] concluded from the resulting entropy values that the excess entropy of mixing of the liquid is close to zero. [71Ukh] calculated the activities of Cu and Pd in liquid Cu-Pd melts from vapor pressures determined by the Knudsen method. The calculated activities are reported to be in good accord with the results obtained from emf measurements by [69Tim] (not available to the authors). The activity data show positive deviations from Raoultian behavior, indicating that the liquid solution forms with positive heats of mixing. Partial enthalpies of Cu and Pd in liquid solutions, determined by [74Ser] on the basis of a cluster model, were reported to be in good agreement with corresponding experimental values from [59Ukh]. [81Arp] determined the enthalpies of mixing of liquid Cu-Pd alloys at 1600 K by high-temperature calorimetry. Their results indicated that the composition variation of the enthalpies is similar to that observed for solid alloys.

The resulting data, given in Table 8 and Fig. 7, show negative enthalpies of mixing with a minimum value of approximately –15 kJ/mol at X_{Pd}~0.35. [81Arp] explained the large negative values on the basis of a strong mutual exchange between Cu and Pd in the liquid state. In addition, [81Arp] reported that liquid enthalpies of mixing calculated on the basis of a modified association model agree well with their experimental data. Although the data of [81Arp] are in contradiction to the positive enthalpies of mixing of [71Vat1], [71Vat2], [71Ukh], and [74Ser], they are consistent with the form of the Cu-Pd phase diagram and therefore are accepted in the present evaluation.

Thermodynamic Modeling

The lattice stability parameters of elemental Cu and Pd are given in Table 9. The ΔH function for the solid, based on the selected data of [Hultgren, B], is taken from the subregular model of [71Sha] as:

$$\Delta H(s) = X(1-X)(-48\,982 + 8954X)\ \text{J/mol} \qquad \text{(Eq 1)}$$

The assessed S^{ex} values for the solid from [Hultgren, B] were fitted by the least-squares approximation to give:

$$S^{ex}(s) = X(1-X)(-5.198 - 20.560X)\ \text{J/mol}\cdot\text{K} \qquad \text{(Eq 2)}$$

The resulting plots of the ΔH and S^{ex} values are compared in Fig. 5 and 6, respectively, with the various experimental data. [81Arp] fitted their experimental values for the enthalpy of mixing of the liquid to analytical expressions based on the subregular model as:

$$\Delta H(L) = X(1-X)(-87\,824 + 63\,054X)\ \text{J/mol} \qquad \text{(Eq 3)}$$

and on a quasichemical model as:

$$\Delta H(L) = X(1-X)(-81\,380 + 9296X + 81\,568X^2)\ \text{J/mol} \qquad \text{(Eq 4)}$$

The resulting ΔH vs concentration curves are shown in Fig. 7, along with the experimental data. No entropy data are available for the liquid.

An initial attempt to reproduce the phase diagram consisted of optimizing the experimental phase boundaries with the thermodynamic data for the solid from [Hultgren, B] (Eq 1 and 2), together with the enthalpy function for the liquid from [81Arp] (Eq 3) to derive the following function for the excess entropy of mixing of the liquid:

$$S^{ex}(L) = X(1-X)(-28.419 + 13.861X)\ \text{J/mol}\cdot\text{K} \qquad \text{(Eq 5)}$$

The calculated liquidus and solidus data, based on the above approach, show a reasonable accord with the assessed phase diagram at high Pd concentrations. However, the calculated phase boundaries lay well below the experimental data at low Pd concentrations. As a result, this approach was deemed inappropriate for calculating the phase boundaries.

An alternate calculation was performed on the basis of the following assumptions:

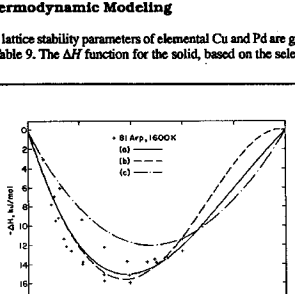

Fig. 7 Enthalpy of mixing of liquid Cu-Pd alloys as a function of Pd concentration. (a) $\Delta H(L) = X_{Pd}(1-X_{Pd})(-87\,824 + 63\,054X_{Pd})$ [81Arp]; see Eq 3. (b) $\Delta H(L) = X_{Pd}(1-X_{Pd})(-81\,380 + 9296X_{Pd} + 81\,568X^2_{Pd})$ [81Arp]; see Eq 4. (c) $\Delta H(L) = X_{Pd}(1-X_{Pd})(-52\,656 + 9626X_{Pd})$; present model.

Table 8 Enthalpy of Mixing of Liquid Cu-Pd Alloys at 1600 K

Composition, atomic fraction Pd	Enthalpy of mixing, J/mol	Composition, atomic fraction Pd	Enthalpy of mixing, J/mol
0.060	–3018	0.296	–15 036
0.091	–7798	0.298	–12 248
0.102	–6894	0.298	–15 768
0.107	–9535	0.385	–13 730
0.118	–9167	0.394	–15 136
0.124	–6019	0.397	–15 907
0.139	–11 352	0.465	–13 780
0.149	–12 106	0.493	–13 508
0.169	–12 629	0.497	–13 847
0.210	–9347	0.543	–13 362
0.213	–14 014	0.599	–11 382
0.215	–13 805	0.601	–12 612

From [81Arp].

- The excess entropy of the liquid is the same as that for the solid.
- The enthalpy of mixing of the liquid has a concentration variation similar to that observed for the solid.

These assumptions are fairly reasonable, in view of the fact that the phase diagram shows the presence of a continuous solid solution of Cu and Pd at lower temperatures and a very narrow two-phase coexistence region for the solid and liquid at higher temperatures. Based on the enthalpy and entropy data for the solid from Eq 1 and 2, respectively, the enthalpy function for the liquid was determined as:

$$\Delta H(L) = X(1-X)(-52\,656 + 9626X)\ \text{J/mol} \qquad \text{(Eq 6)}$$

The calculated ΔH values are compared with the experimental data of [81Arp] in Fig. 7, where it is observed that the resulting deviation of the calculated values is on the same order of magnitude as the scatter manifested in the experimental data themselves. Nevertheless, the calculated coefficients for $\Delta H(L)$ should be viewed only as fitting parameters and not as actual thermodynamic quantities. The various thermodynamic data for the Cu-Pd system are summarized in Table 9. The calculated liquidus and solidus, shown in Fig. 8, are in reasonable agreement with the experimental phase boundaries at all Pd concentrations.

[80Gop] derived the Cu-Pd phase diagram on the basis of a regular-solution model, with the following empirical interaction parameters for the liquid and solid:

$$W_L = -42\,578\ \text{J/mol}$$

and

$$W_{fcc} = -41\,744\ \text{J/mol}$$

The resulting liquidus and solidus, shown at selected temperatures in Fig. 8, lie well above the experimental data.

Table 9 Thermodynamic Parameters for the Cu-Pd System

Lattice stability parameters for Cu [Hultgren,E]

$G^0(Cu,L) = 0$
$G^0(Cu,fcc) = -13\,054 + 9.613\,T$

Lattice stability parameters for Pd [83Cha]

$G^0(Pd,L) = 0$
$G^0(Pd,fcc) = -17\,560 + 9.606\,T$

Solid phase

$\Delta_{mix}H(s) = X(1-X)(-48\,982 + 8954X)$ [71Sha]
$S^{ex}(s) = X(1-X)(-5.198 - 20.560X)$ [Present model]

Liquid phase

$\Delta_{mix}H(L) = X(1-X)(-52\,656 + 9626X)$ [Present model]
$S^{ex}(L) = X(1-X)(-5.198 - 20.560X)$ [Present model]
Standard states: pure liquid Cu and pure liquid Pd.

Note: Quantities in J/mol, J/mol · K, X is the atomic fraction of Pd, and mol refers to the atom as the elementary entity.

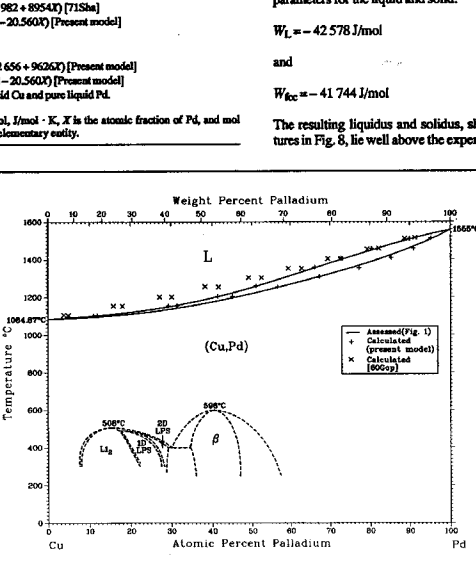

Fig. 8 Assessed vs calculated Cu-Pd phase diagram.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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