Cu – Y (Copper – Yttrium)

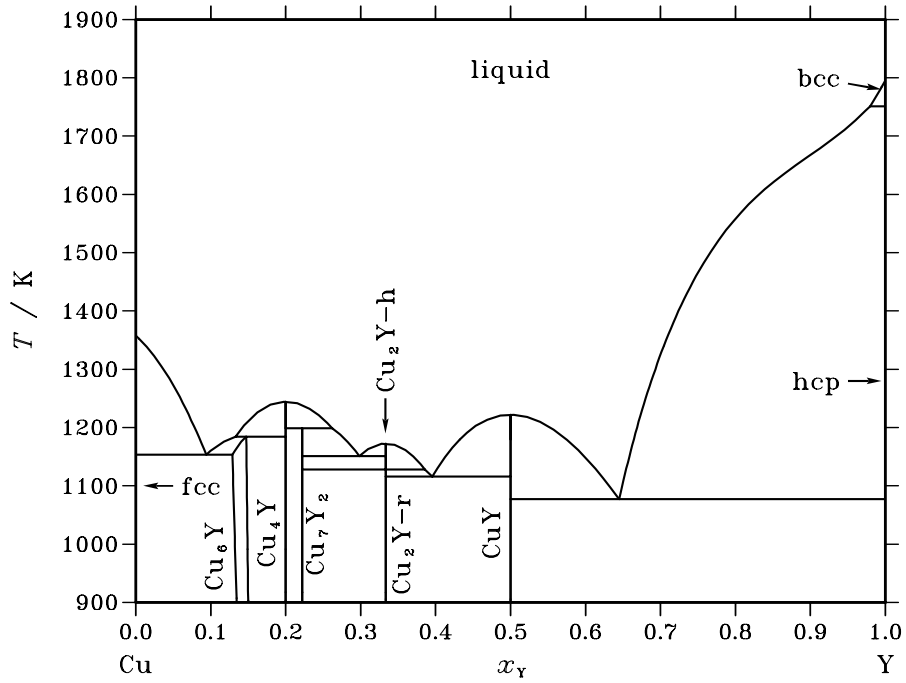

Fig. 1. Calculated phase diagram for the system Cu-Y.

The Cu-Y system is of interest as a subsystem of the Y-Ba-Cu-O high-temperature superconductors and also because both Cu and Y are components of Mg-based bulk metallic glasses with plasticity and high strength. The experimental data for the system have been reviewed by [81Cha] and an update is published by [92Oka]. Several thermodynamic assessments of the Cu-Y system have been reported [90Ita, 94Fri, 97Abe]. The thermodynamic dataset of [94Fri] is selected since it is based upon the most reliable experimental data, i.e., the invariant equilibrium temperatures and calorimetric measurements. The liquid, bcc, fcc, and hcp phases are modelled as simple substitutional solutions, the Cu_6Y compound is described by a two-sublattice model $(Cu)_5(Cu_2,Y)_1$, where two atoms of Cu substitute one atom of Y, whereas Cu_7Y_2, Cu_4Y, Cu_2Y, and CuY are treated as stoichiometric phases.

The calculated phase diagram reproduces very well the homogeneity range for the compound Cu_6Y and the temperature of a phase transition in Cu_2Y. The crystal structure of the high-temperature form of Cu_2Y (presumably hexagonal) has not been determined yet. There is an evidence for a homogeneity range of the Cu_4Y phase. It was not taken into account by [94Fri] since the corresponding phase boundaries are unknown.

A more recent assessment of [97Abe] is not recommended because Cu_6Y is modelled as a stoichiometric phase, the polymorphism of Cu_2Y is not taken into account, and the calculated phase diagram shows that compounds Cu_6Y and Cu_4Y are not stable down to 300 K. The new EMF measurements reported by [97Abe] are not in agreement with calculations of [94Fri].

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Cu,Y)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Cu,Y)_1$
Cu_6Y	···	···	$hP8$	$P6/mmm$	CU6Y	$Cu_5(Cu_2,Y)_1$
Cu_4Y	···	···	···	···	CU4Y	Cu_4Y_1
Cu_7Y_2	···	···	···	···	CU7Y2	Cu_7Y_2
Cu_2Y-r	···	$CeCu_2$	$oI12$	$Imma$	CU2Y_R	Cu_2Y_1
Cu_2Y-h	···	···	$hP*$	···	CU2Y_H	Cu_2Y_1
CuY	$B2$	CsCl	$cP2$	$Pm3m$	B2_CUY	Cu_1Y_1
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Cu,Y)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Cu,Y)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_Y			$\Delta_r H$ / (J/mol)
liquid + bcc $\rightleftharpoons$ hcp	degenerate	1751.1	0.980	1.000	1.000	−4886
liquid $\rightleftharpoons$ Cu_4Y	congruent	1244.5	0.200	0.200		−13963
liquid $\rightleftharpoons$ CuY	congruent	1222.2	0.500	0.500		−13029
Cu_4Y + liquid $\rightleftharpoons$ Cu_7Y_2	peritectic	1199.1	0.200	0.262	0.222	−4776
liquid + Cu_4Y $\rightleftharpoons$ Cu_6Y	peritectic	1184.6	0.133	0.200	0.147	−9676
liquid $\rightleftharpoons$ Cu_2Y-h	congruent	1172.9	0.333	0.333		−8092
liquid $\rightleftharpoons$ fcc + Cu_6Y	eutectic	1153.4	0.094	0.000	0.129	−11815
liquid $\rightleftharpoons$ Cu_7Y_2 + Cu_2Y-h	eutectic	1151.2	0.298	0.222	0.333	−9400
Cu_2Y-h + $\rightleftharpoons$ Cu_2Y-r	polymorphic	1128.0	0.333	0.386	0.333	−4512
liquid $\rightleftharpoons$ Cu_2Y-r + CuY	eutectic	1116.1	0.396	0.333	0.500	−11815
liquid $\rightleftharpoons$ CuY + hcp	eutectic	1077.1	0.645	0.500	1.000	−10208

Table IIIa. Integral quantities for the liquid phase at 1823 K.

x_Y	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−11020	−9960	0.581	−6093	−2.122	0.000
0.200	−17823	−16994	0.455	−10239	−3.706	0.000
0.300	−21806	−21233	0.314	−12547	−4.765	0.000
0.400	−23392	−22886	0.278	−13191	−5.318	0.000
0.500	−22917	−22240	0.372	−12411	−5.392	0.000
0.600	−20709	−19659	0.576	−10508	−5.020	0.000
0.700	−17110	−15587	0.836	−7851	−4.243	0.000
0.800	−12457	−10541	1.051	−4873	−3.110	0.000
0.900	−6996	−5121	1.028	−2068	−1.674	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Cu(liquid), Y(liquid)

Table IIIb. Partial quantities for Cu in the liquid phase at 1823 K.

x_{Cu}	ΔG_{Cu} [J/mol]	ΔH_{Cu} [J/mol]	ΔS_{Cu} [J/(mol·K)]	G^E_{Cu} [J/mol]	S^E_{Cu} [J/(mol·K)]	a_{Cu}	γ_{Cu}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2583	−1479	0.606	−986	−0.270	0.843	0.937
0.800	−7214	−5779	0.788	−3832	−1.068	0.621	0.777
0.700	−13627	−12519	0.608	−8221	−2.358	0.407	0.581
0.600	−21387	−21089	0.163	−13644	−4.084	0.244	0.407
0.500	−29904	−30641	−0.405	−19397	−6.168	0.139	0.278
0.400	−38474	−40099	−0.891	−24585	−8.510	0.079	0.198
0.300	−46367	−48150	−0.979	−28117	−10.989	0.047	0.156
0.200	−53105	−53252	−0.081	−28710	−13.463	0.030	0.150
0.100	−59786	−53628	3.378	−24885	−15.767	0.019	0.194
0.000	−∞	−47268	∞	−14973	−17.715	0.000	0.372

Reference state: Cu(liquid)

Table IIIc. Partial quantities for Y in the liquid phase at 1823 K.

x_Y	ΔG_Y [J/mol]	ΔH_Y [J/mol]	ΔS_Y [J/(mol·K)]	G^E_Y [J/mol]	S^E_Y [J/(mol·K)]	a_Y	γ_Y
0.000	−∞	−114482	∞	−70868	−23.925	0.000	0.009
0.100	−86951	−86294	0.361	−52050	−18.784	0.003	0.032
0.200	−60259	−61856	−0.876	−35864	−14.257	0.019	0.094
0.300	−40889	−41563	−0.370	−22640	−10.380	0.067	0.225
0.400	−26401	−25581	0.450	−12512	−7.169	0.175	0.438
0.500	−15930	−13838	1.148	−5424	−4.616	0.350	0.699
0.600	−8866	−6033	1.554	−1123	−2.693	0.557	0.929
0.700	−4572	−1631	1.614	834	−1.352	0.740	1.057
0.800	−2296	136	1.334	1087	−0.521	0.859	1.074
0.900	−1130	269	0.767	467	−0.109	0.928	1.031
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Y(liquid)

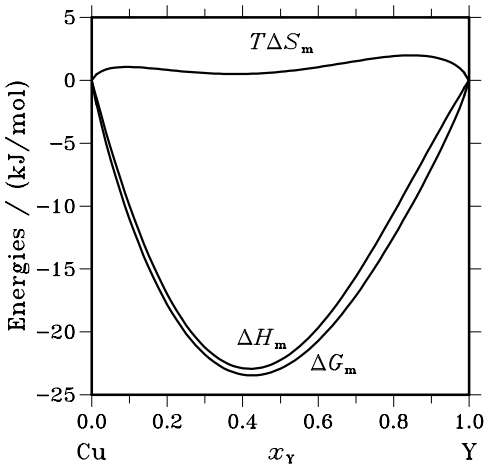

Fig. 2. Integral quantities of the liquid phase at T=1823 K.

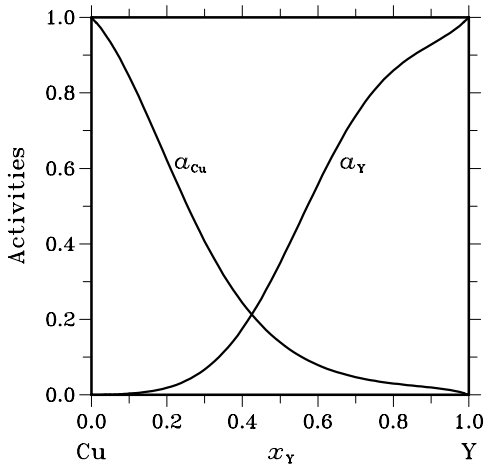

Fig. 3. Activities in the liquid phase at T=1823 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Y}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
Cu_6Y	0.155	−13593	−13892	−1.002	0.000
Cu_4Y_1	0.200	−17374	−17866	−1.650	0.000
Cu_7Y_2	0.222	−18209	−18724	−1.730	0.000
Cu_2Y-r	0.333	−21175	−21775	−2.012	0.000
Cu_2Y-h	0.333	−17856	−17263	1.988	0.000
CuY	0.500	−21694	−22308	−2.061	0.000

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