Copper-Gold

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Abstract

Among transition metal alloys the CuAu system has a special significance since it has atomically-ordered phases at lower temperatures.The Cu-Au system has been the favorite object for experimental as well as theoretical order-disorder transformation studies; accordingly vast amount of literature on the constitution of the system and its properties are published . In this review a collection of some transport and equilibrium proerties are presented.

CuAu alloys can exist in two phases-atomically disordered(U) or atomically ordered(G). In the U phase the alloys are totally miscible, and their properties show a smooth variation with alloy concentration.Over wide concentration ranges near the stoichiometries of 3:1, 1:1, and 1:3 a transformation to a G phase occurs.

1 Phase Diagram and Crystal Structures

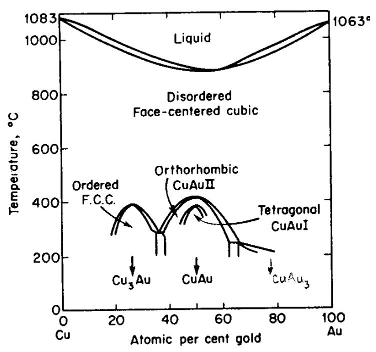


Figure 1: *The copper-gold phase diagram.*

The phase which lies between the liquid and the peaks around 400^oC is the disordered solid phase and the crystal structure is fcc.The region below the left peak at 390^oC is the Cu_3Au ordered structure as shown in Fig.2(left)[1]. The center part of Fig.1 is the CuAu ordered structure, except for the slight complication that CuAu occurs in two forms: CuAu I has a tetragonal structure while CuAu II has an orthorhombic(psuedo- tetragonal) structure(Fig 2(right)). In copper-gold there are sheets of copper and gold along the cube axes and since there is a preference for opposite nearest neighbours the sheets are closer together than the atoms in the sheets. As a result the fcc crystal structure distort into face-centred tetragonal with c/a=0.925.

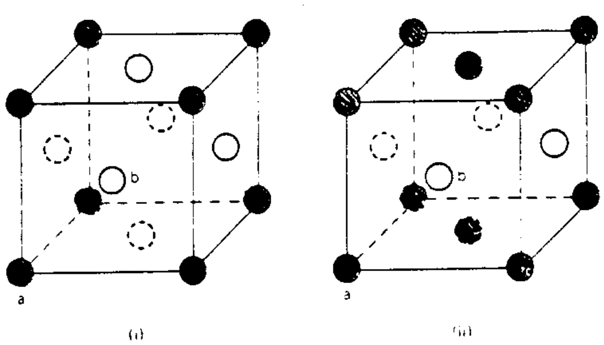


Figure 2: *Fig.2 (i) Cu_3Au structure and (ii) CuAu structure. A white circle is Cu and a shaded one is Au*

Another important feature of the phase diagram which is not shown on Fig.1 is that the transition between the disordered phase and each one of the ordered phases is the first order; that means there is a discontinuity in entropy at the transition.

material (reference)	$\rho(-295K)$ $\mu\Omega$-cm	$\rho_t h(-295K)$ $\mu\Omega - cm$	$S(-295K)$ $\mu V/K$	$R_H(-295K)$ 10^-11m^3/ASec	γ mJ/mole K^2	χ $10^-6e\mu/mole$
Cu	1.55	1.55	1.85	-5.0	0.695	-5.3
Au	2.02	2.02	1.89	-7.1	0.70	-28.0
$Cu_{0.75}Au_{0.25}$	.	.	.	.	.	.
[2]G	3.9	3.1	.	.	.	.
U	11.3	2.1	.	.	.	.
[1]G	7.34	3.14	-0.96	.	.	.
U	11.37	2.27	0.45	.	.	.
[3]G	9.66	3.36	-1.11	.	.	-15
U	14.06	1.36	0.71	.	.	-12.5
[4]G	6.9	-0.95	.	.	.	.
U	11.1	.	0.65	.	.	.
[5]G	4.8	.	.	3.7	.	.
U	11.5	.	.	-0.6	.	.
[6]G	.	.	.	1.72	.	.
U	.	.	.	-6.4	.	.
[7]G	.	.	.	.	0.651	.
U	.	.	.	.	0.679	.
$Cu_{0.25}Au_{0.75}$	.	.	.	.	.	.
[2]G	11.87	3.57	.	.	.	.
U	11.2	3.23	.	.	.	.
[1]G	11.87	3.08	.	.	.	.
U	11.4	2.37	.	.	.	.
[8]G	.	.	.	.	.	-21.6
U	.	.	.	.	.	-23
[7]G	.	.	.	.	0.723	.
U	.	.	.	.	0.681	.

Table 1: Table I

2 Transport and Eqilibrium Properties

Table I contains a summary of transport property and equilibrium data near 3:1 and 1:3 stoichometries. Since any attempt to list all the studies done on this alloy would clearly exceed the allotted space, I have attempted to present a representative summary. To minimize complications due to short-range order, data for totally disordered phases and for totally ordered phases are presented.For the purpose of comparision, data for pure Cu, and Au have also been included in the table.

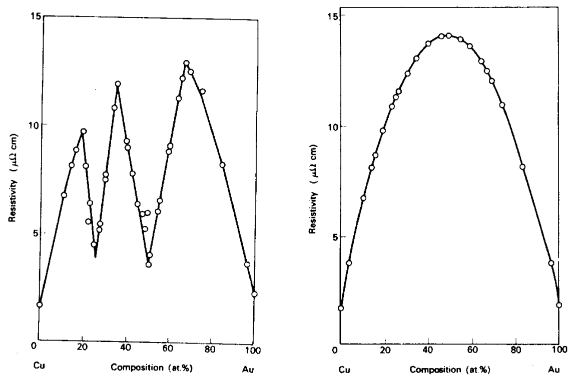


Figure 3: *Fig.3 Resistivity of ordered(right) and disordered(left) copper-gold alloys.*

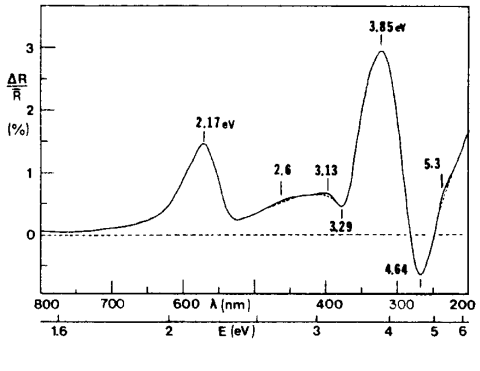
The resistivity data in column 2 show that generally the disordered phase(U) has the larger resistivity and any decrease in resistivity indicate the presence of atomic order.The values from different studies seldom agree quantitatively, but the trends do agree. In Fig.3 the resistivity of disordered Cu-Au alloys as a function of concentration indicate prominent minima at the formation of ordered alloys Cu_3Au and CuAu[1]. Notice that $CuAu_3$ is an interesting exception where the ordered alloy(G) appears to have large resistivity. This raises a (very interesting) problem that our later and more precise theories of the order-disorder phenomena must explain[2] .

The data in column 3 exhibit clear trends with a semi quantitative agreement for different studies.ρ_{th} is defined as $\rho(295^0K)$-$\rho(4.4^0K)$ is a measure of phonon scattering. Two features of the ρ_th data deserve comment. First, for both Cu_3Au and $CuAu_3$ in whatever state of order, the magnitude is comparable to that for Cu, and Au(where there is no s to d scattering). Second,ρ_th is greater in the ordered phase.Generally the quantitative agreement for ρ_th values from different studies is much better than the agreement for ρ.

Thermoelectric power S in column 4 and the Hall coefficient R_H in column 5 are comparable for different studies. Thermoelectric power data give a striking illustration of how atomic order can modify a given property. For Cu_3Au both S and R_H seem to have a sign reversal as a function of atomic order. These sign reversals are usually claimed as evidence of new zone gaps and often the sign of the property is used to infer whether electron or hole transport is dominant at the Fermi surface. At the present time it is unclear whether these signs are caused by the presence of new zone gaps,by the presence of optical mode scattering as well as acoustic mode scattering, by phonon enhanced domain-boundary scattering, or by some blend of these possibilities.

Columns 11 and 12 give equilibrium properties;electron specific heat(γ) and magnetic susceptibility(χ).The fact that Cu-Au is diamagnetic and its γ's are comparable to that for Cu makes the presence of unfilled d-bands unlikely. Interpreting these data on a single particle model, both γ and χ are directly proportional to density of states at the Fermi energy.Thus, in this simplest model γ and χ would be expected to exhibit parallel changes with atomic order[8] .

3 Optical Properties



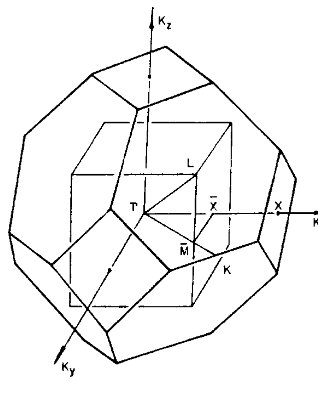


Figure 4: *Fig.4.Differential reflectogram of ordered* Cu_3Au*(left) and First Brillouin zone of an fcc lattice (right).*

We have seen that the resistivity decreases when solute atoms of an alloy are periodically arranged on the regular lattice site. Thus, ordering has an effect on the electronic structure and hence on the electronic properties of alloys.The onset of interband transitions and the structure of the imaginary part of the dielectric constant as a function of energy, $\varepsilon_2(\omega)$, are evidences of the energies for transitions between the electronic states. The situation for Cu_3Au is summarized in a recent study by [8]. Their data leads to the following features: (i)A sharp absorption edge occurs at 2eV in both the ordered and disordered samples(Fig.4(left)). (ii)For the disordered phase there is no indication of interband transitions below this edge. However, in the ordered phase, weaker but substantial interband transitions are evident from 0.7 to 1.5 eV(not shown in Fig.4(left)). (iii) Above the 2eV absorption edge, $\varepsilon_2(\omega)$ in the disordered phase has a general shape similar to that in pure Cu. For the ordered phase the major change in $\varepsilon_2(\omega)$ above 2eV is the appearence of a new peak near 3.6eV.

These have been explained by refrring to Fig.4(right) which depicts the first Brillouin zone of the disordered fcc lattice in which a simple cubic Brillouin zone, representing the superlattice, is inscribed. The $\Gamma - X$ direction of the fcc Brillouin zone is bisected by the face of the cubic Brillouin zone at the point $\bar{X}$. The point X is then thought to be folded back to the point Γ. A new transition from the d-bands take place. Folding along other directions, explains the other transitions[8] .

References

[1] J. Goff, The effect of ordering on the Lattice Thermal Conductivity of Cu_3Au, Intl. Conference on Phonon Scattering, Albany, editor, 122(1972).

[2] M. Hirabayashi, Electrical resistance of Cu-Au Alloys at Low Temperatures, Acta Metall, **9**, 489-503(1961).

[3] D. Larch, Measuring the Thermopower of Ordered and Disordered Alloys, unpublished thesis, (1978).

[4] F.F. Jaumot ,and A. Sawatzky, Order-Disorder and Cold-Work Phenomena in Cu-Pd Alloys, Acta Met. **4**, 127 (1956).

[5] A.R. Neida and R. Gordon, Change in the Hall Coefficient During ordering of Cu_3Au, Philos. Mag. **7**, 1129(1962).

[6] W. Love, Hall Effect in Cu and Cu_3Au at Low Temperatures, Jour. Phys. Chem. Solids **9** ,281-284(1979).

[7] L. M. Martin , Specific Heat of Copper-Gold Alloys Below 30k, Phys. Rev. **B14**,369-385 (1986).

[8] C. L. Foiles , Use of Optical Data to Determine Individual Contributions to the Magnetic Susceptibility of Metals, AIP Conference Proceedings. **24**, 17-19 (1976).

[9] H. Myers and L. Wallden, Some Optical properties of CuPd, AgPd, AuPd, and CuMn, AgMn Alloys, Philos. Mag. **18** , 725(1978).