

Theory of Order for the Copper Gold Alloy System

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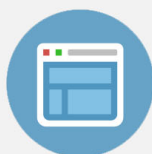
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The fact that equimolal high concentrations of added chlorides do not produce equal color changes serves to cast doubt upon the theory that complex ions, of the type CoCl_4^{--} are formed. That such color changes could be due to deformation of the chloride ions⁶ by strongly hydrating cations seems improbable, since pure concentrated solutions of aluminum chloride and of calcium chloride are colorless.

Absorption of energy in the visible region may be accomplished by the electrons¹³ within the cobalt atom. The change in color of a dilute aqueous solution of cobalt chloride from red to blue, upon adding strongly hydrating cations, may be explained on this basis. In dilute solutions, the cobalt ion is completely hydrated. Solvent molecules are held tightly bound¹⁴ and the solvent sheath prevents close approach of the cobalt and chloride ions. Electronic transitions in the unfilled third quantum group result from the

absorption of green wave-lengths and the solution is red. As strongly hydrating ions are added, they attract and orient solvent molecules. At high concentrations of the added salt, much of the solvent envelope about the cobalt ions is removed. Cobalt and chloride ions are then drawn more closely together by electrostatic attraction.

According to Lewis,¹⁵ the strongly electro-negative chloride ion tends to attract electrons of an ion near it. Thus, it is reasonable to assume that chloride ions distort the electronic system of the cobalt ion in such a way that the electrons in the third quantum group are capable of absorbing smaller quanta of energy. Hence, the yellow and red wave-lengths are absorbed and the solution becomes blue.

The blue color of concentrated solutions of pure cobalt chloride as well as of the anhydrous salt may also be explained in this way.

¹³ Taylor, *Treatise on Physical Chemistry* (D. Van Nostrand Co., 1931), pp. 1533, 1544.

¹⁴ Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

¹⁵ Lewis, *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Co., 1923), p. 139.

Theory of Order for the Copper Gold Alloy System

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The theory of order and disorder, in the form used by Bragg and Williams, is extended to arbitrary composition of the constituent elements. The work is based upon the nearest neighbor interaction assumption of Bethe and the connection between the Bethe and Bragg-Williams theory is shown. In order to extend the Bragg-Williams theory to compositions other than 25 and 50 atomic percent, new definitions of order are developed. The results are presented in terms of phase diagrams and curves showing energy *vs.* temperature, specific heat *vs.* temperature and state order *vs.* temperature. These results are of importance in giving a general picture of the order-disorder transformation for a wide composition range. They are not in detailed accord with experiment due to the rather idealized picture underlying the nearest neighbor assumption.

I. THE NEAREST NEIGHBOR ASSUMPTION

1. Introduction

The phenomenon of order and superlattice formation in alloys is of an energetic nature, being governed by forces which tend to establish atoms in an orderly array. Several theories have been developed based on various assumptions regarding the relationships between the orderliness of the alloy and its energy.

The best known of these is probably that of Bragg and Williams.¹ They gave a quantitative significance to the concept of order by introducing the idea of "right" and "wrong" positions for the atoms. If an alloy in an imperfect state of order is compared with the perfectly ordered alloy, it will be apparent that a certain fraction of the atoms are missing from their "right" positions—those

¹ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934); **A151**, 540 (1935); **A152**, 231 (1935).

which are occupied by atoms of their species in the ordered state—and occupy “wrong” positions. Complete disorder will correspond to a random arrangement of atoms so that the fraction of the atoms of a given species which are “right” will be equal to the atomic fraction of that species. The Bragg-Williams order parameter, S , is a linear function of the fraction of “right” atoms of such a form that $S=1$ corresponds to perfect order and $S=0$ to a random arrangement. From an intuitively appealing physical argument, Bragg and Williams concluded that the configurational energy, that is, the energy required to disorder the alloy from perfect order to order S , would be given by the expression $\frac{1}{2}W_0(1-S^2)$.

A weakness of the Bragg-Williams attack was its rather macroscopic character. It would be expected that more adequate theories would be developed by considering the atoms in detail and inquiring into the forces acting between them. Considerable progress in this direction has been made by Bethe,² whose work was later extended by Peierls.³ Bethe assumed that the atoms interacted in pairs, so that every two atoms had a mutual potential energy which, however, fell off rapidly with increasing separation of atoms. Bethe assumed that this falling off was so rapid that potential energies were appreciable only for those pairs of atoms which were nearest neighbors in the lattice.

The alloys of the Cu-Au system possess face-centered lattices—slightly distorted for some conditions of order—and each atom is surrounded by twelve nearest neighbors and hence has twelve non-negligible mutual potential energies. Since each of these is shared between a pair of atoms, there will be in all six potential energies per atom. The value of each potential energy will be V_{AuAu} if the pair of atoms to which it belongs are both Au, V_{CuCu} if both are Cu, and V_{AuCu} if the pair is mixed. In this work it will be assumed that these energy values are characteristic constants of the two elements; and no variations in their magnitudes, caused by change in order, composition, or state of strain, will be considered. This assumption will be referred to as the “nearest neighbor assumption”.

In terms of the nearest neighbor assumption a

formally simple expression for the energy of the alloy can be obtained. Let the number of pairs of nearest neighbors which are CuCu, CuAu, and AuAu be denoted by Q_{CuCu} , Q_{CuAu} , and Q_{AuAu} , respectively. Then associating with each pair its proper potential energy and summing these for all pairs in the lattice, we obtain

$$E = V_{\text{AuAu}}Q_{\text{AuAu}} + V_{\text{CuCu}}Q_{\text{CuCu}} + V_{\text{CuAu}}Q_{\text{CuAu}}. \quad (1)$$

In spite of the simplicity of the energy form the mathematical difficulties involved in a statistical mechanical treatment of it are so great that approximate and indirect methods are necessary. Bethe² has given a very satisfactory statistical mechanical treatment for a 50 atomic percent alloy having a simple type of lattice, but it is somewhat inappropriate to apply his results to CuAu. Peierls³ has carried out an appropriate extension to Cu_3Au . The improvement of their work over that of Bragg and Williams is considerable in some respects but much is still desired in the way of agreement with experiment.

In this paper we shall give an approximate treatment of the form (1) for all compositions of Cu-Au. It is shown, Part III, that this treatment reduces to that of Bragg and Williams for the compositions 25 and 50 atomic percent so that the latter may be regarded as an approximation to the nearest neighbor theory.

2. Some consequences of the nearest neighbor assumption

For the purposes of this paper it is convenient to use not the actual energy (1) of the lattice but the difference between its energy and the energy of two chemically pure crystals of its components. By methods given in Part III, this energy can be expressed in the very simple form,

$$E = -\frac{1}{2}VQ_{\text{CuAu}}. \quad (2)$$

$$\text{Here } V = V_{\text{AuAu}} + V_{\text{CuCu}} - 2V_{\text{CuAu}} \quad (3)$$

is a measure of the tendency of the alloy to order itself, giving the reduction in energy obtainable by putting unlike atoms together to form a superstructure rather than putting like atoms together to form pure metals. Two significant features of Eq. (2) should be noted: the replacement of the three potential energies by V , and the obvious symmetry between Au and Cu. The first shows that the nearest neighbor assumption

² H. A. Bethe, Proc. Roy. Soc. **A150**, 552 (1935).

³ R. Peierls, Proc. Roy. Soc. **A154**, 207 (1936).

leads to a theory involving only one adjustable parameter; hence the numerical determination of this parameter on the basis of a single experimental or theoretical item fixes all the quantitative predictions of the theory. The second means that all predictions based upon the nearest neighbor assumption alone will be symmetrical about 50 atomic percent, that is, the same behavior will be expected for any two alloys differing only in interchange of Cu and Au atoms. This prediction is in marked disagreement with experiment, for Cu_3Au readily forms ordered structures, whereas CuAu_3 does not. We shall return to this point briefly in Part II, Section 3.

It is not necessary to apply statistical mechanics to determine the limiting energies predicted by (2) for low and high temperatures; these correspond to minimum energy and random arrangement, respectively. These limiting values are shown as functions of the composition in Fig. 1(a), in which, as will be uniformly done in this paper, the composition is expressed in atomic percent. The unit of energy U_0 has been arbitrarily chosen so that,

U_0 = Change in configurational energy from perfect order to complete disorder for one gram atom of 50 atomic percent CuAu alloy.

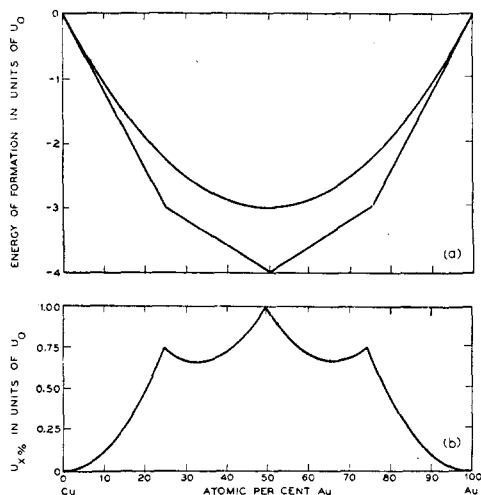


FIG. 1. (a) Energy of formation of one gram atom of best ordered (lower curve) or completely disordered (upper curve) Cu-Au alloy as a function of composition. (b) Difference of curves shows energy, U_X percent, required to transform one gram atom from best order to complete disorder. (The curves in this figure result directly from the "nearest neighbor assumption." They do not depend upon the approximations used in the statistical mechanical equilibrium theory which follows.)

In terms of the Loschmidt number N and the quantity V ,

$$U_0 = \frac{1}{2}NV. \quad (4)$$

(In the notation of Bragg and Williams⁴ $U_0 = NV_0/8$, and in that of Fowler⁵ $U_0 = \frac{1}{2}W_0$ per mole.) The curve 1b is the difference between the curves of 1a; it shows the dependence upon composition (denoted by X percent) of the entire change in configurational energy (U_X percent) between best order and complete disorder.

The remainder of this paper is devoted to examining the details of the transition from the state of minimum energy to the state random arrangement.

II. THE APPROXIMATE EQUILIBRIUM THEORY

Definitions and approximations

1. *Definition of the state of order.*—The Bragg-Williams definition of order is given in terms of the number of right and wrong atoms in the lattice—i.e., those which are or are not in positions appropriate to their species in the state of perfect order. This definition, although very convenient for alloys of simple composition, is unsuitable for this problem, because as the composition is varied the lattice points which are right and wrong do not remain the same. Furthermore, it may introduce artificial distinctions: in Cu_3Au one lattice point out of four is right for Au, but the choice of the set of right points is somewhat arbitrary since any one of four possibilities is physically equivalent.

For this case it proves best to define order in terms of the atoms located upon four sublattices. The face-centered lattice can be divided into four simple cubic sublattices which we shall refer to as L_1, L_2, L_3 and L_4 (Fig. 2a). If the fraction of the L_1 lattice points which are occupied by Au atoms is f_{Au} then a , the order parameter of L_1 , is defined by the equation $a = 2f_{\text{Au}} - 1$. In terms of a the fractions of Au and Cu in L_1 are $(1+a)/2$ and $(1-a)/2$, respectively; so that $a = +1$ corresponds to a pure Au partial lattice, $a = -1$ to pure Cu, and $a = 0$ to a 50 atomic percent mixture. The order parameters b, c and d of L_2, L_3 and L_4

⁴ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **151**, 540 (1937), p. 556.

⁵ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936), p. 794.

L_3 , and L_4 are similarly defined. Giving the values of the four order parameters will be regarded as specifying "the state of order." The total fractions of Au and Cu present, F_{Au} and F_{Cu} , respectively, are, of course, the averages for the sublattices:

$$\begin{aligned} F_{Au} &= \frac{1}{2} + \frac{1}{8}(a+b+c+d), \\ F_{Cu} &= \frac{1}{2} - \frac{1}{8}(a+b+c+d). \end{aligned} \quad (5)$$

It is readily seen from the figure that each atom is surrounded by twelve nearest neighbors. These are divided four to each of the three other sublattices with none in the same sublattice as the central atom. These facts prove of considerable convenience in setting up the energy expressions.

There are five readily distinguishable types of order which can be expressed by these parameters. First, the disorder type, in which no superlattice is detectable, and hence $a=b=c=d$. We denote this by the symbol (4) meaning that all four order parameters have the same value. Next there is a type for which three order parameters have one value and the other has a different value; this is denoted by (31). Examples of it are furnished by Cu_3Au , which has, in the perfectly ordered state, the parameter value -1 thrice (i.e., 3 pure Cu sublattices) and $+1$ once; the somewhat disordered state of Cu_3Au with values -0.8 thrice and $+0.4$ once is also represented by (31). Similarly, there is a type (22) for which ordered $CuAu$ with $+1$ and -1 each twice is an example. When three distinct values of the parameters are allowed there is only one possibility (211), and also for four values—(1111).

The types of order possess different crystallographic symmetries. In Fig. 2 the different types are indicated schematically, sublattices marked in different ways having different order parameters. The order type (4), which would correspond to the same symbol upon every lattice point, is not shown; it will clearly give rise to a macroscopic cubic symmetry. The order type (31), Fig. 2(b), has cubic symmetry as is indicated by the presence of three fourfold symmetry axes represented by heavy arrows. Types (22) and (211) have tetragonal symmetry, while (1111) has orthorhombic symmetry. (These are, so to speak, maximum possible symmetries; they will, however, probably occur for the Cu-Au alloys since

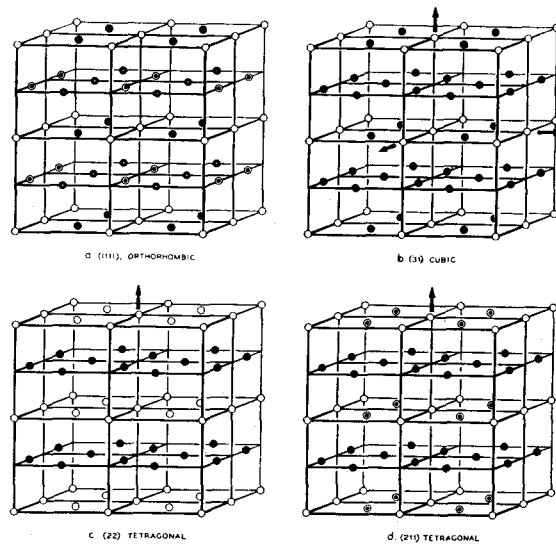


FIG. 2. Diagrams for discussing types of order for Cu-Au alloys. (a) Resolution of face-centered lattice into four simple cubic sublattices L_1 \circ , L_2 \bullet , L_3 \odot , L_4 \ominus . This also represents the order type (1111) for which all four order parameters have different values. (b) Order type (31), with $a \neq b = c = d$ as the example. Heavy arrows indicate fourfold axes. This also represents the known ordered state of Cu_3Au . (c) Order type (22), with $a = b \neq c = d$ as the example. This also represents ordered state of $CuAu$. (d) Order type (211), with $a \neq b \neq c = d \neq a$ as the example.

the free ions of these noble metals are known to possess spherical symmetry.) All three symmetry types have been observed in Cu-Au alloys.⁶ The theory presented here predicts all but the orthorhombic type; however, there is reason to believe that its absence is due to mathematical approximations.

2. *The mathematical approximation: the connection between the configurational energy and the state of order.*—There are, of course, a great number of ways of distributing the atoms for a fixed state of order $abcd$. If there are N atoms in the lattice altogether and $n(=N/4)$ on each sublattice, then the number of arrangements is easily shown to be

$$W(abcd) = \frac{n!}{[\frac{1}{2}(1+a)n]![\frac{1}{2}(1-a)n]!} \cdots \frac{n!}{[\frac{1}{2}(1+d)n]![\frac{1}{2}(1-d)n]!} \quad (6)$$

⁶ C. H. Johansson and J. O. Linde, Ann. d. Physik **25**, 1 (1936), who discovered the orthorhombic phase, do not, however, find the (1111) type of order.

Among these many arrangements there will be a great variety of energies depending upon the particular way in which neighboring atoms are placed in the various sublattices. It may readily be shown, however, that for a large number of atoms there is a very narrow range of energy, centered about the average energy, to which all but a very small fraction of the arrangements correspond. The approximation made in this work consists of lumping together all of the arrangements for a given state of order and assigning to them a single definite energy—the average energy. We shall calculate this quantity in Part III and represent it here by the symbol $E(abcd)$.

This approximation is equivalent to that used by Bragg and Williams throughout their work, in which the energy was taken to be a definite function of the long distance order and independent of the particular arrangement. Rather serious errors are produced by this process; in particular no anomalous specific heat occurs above the disordering temperature of the alloy. Methods of improving it have been devised by various writers. The work of Bethe and of Peierls in which the basic concept is that of the arrangement of nearest neighbors—short distance order—has been mentioned. Another method has been developed by Kirkwood⁷ which appears very promising. In the first approximation Kirkwood's method reduces to that used here; however, it can readily be formulated in terms of higher approximations, the second of which apparently has an accuracy comparable to that of Bethe while the third should be somewhat better. Due to the mathematical difficulties involved in getting solutions to Kirkwood's second approximation, the first has been used here. However, in view of the possibility of its predicting the appearance of an orthorhombic phase, it would be very interesting to carry out the calculations.

3. *The condition for thermodynamic equilibrium.*—The condition for thermodynamic equilibrium state of an alloy at a given temperature is that the free energy F must be a minimum. (The effect of the pV term, which is small for a solid, is

neglected.) The free energy may conveniently be thought of as arising from three sources: the lattice vibrations, whose energy may be expressed in terms of the Debye temperature; the electrons, whose free energy is related to the degeneracy temperature of the electron gas; and the state of order, which gives rise to the "configurational free energy." In all treatments of order and disorder, it has been assumed that the contributions from the first two sources are independent of the state of order. If this is true, then they can be disregarded, and the equilibrium state of order will be found by minimizing the configurational free energy.

Some preliminary work by F. C. Nix and the writer has shown that the dependence of vibrational free energy upon the state of order may be quite important in the Cu-Au system and has an influence in the right direction to explain the difference in behavior of Cu_3Au and CuAu_3 . We shall neglect this effect here and consider only the configurational free energy.

The approximation introduced in the last section enables us to give a simple expression for the configurational free energy. Both the energy $E(abcd)$ and the entropy $S(abcd) (= k \ln W(abcd))$ are known functions of the state of order. We must therefore minimize $F = E - TS$ while holding the temperature and composition constant.⁸ The resultant values of $abcd$ will then specify the equilibrium state of order.

Results

4. *Phase diagram.*—When the equilibrium state problem described above is solved (the details of the solution are given in Section III), it is found that the free energy depends upon composition in a distinct way for three different kinds of order. We may conveniently think of these as phases. They are the (4) type cubic disordered phase ξ , the (31) type cubic ordered phase η , and the tetragonal phase ζ , which consists of two distinguishable types ζ_1 and ζ_2 corresponding to (211) and (22) respectively. ζ_1 and ζ_2 join continuously as regards state of order to each other, and for most purposes can be lumped into the single phase ζ . Due to the

⁷ J. G. Kirkwood, remarks made at the Symposium on the Structure of Metallic Phases, Cornell University, July, 1937. *J. Chem. Phys.* **6**, 70 (1938.)

⁸ G. Borelius, *Ann. d. Physik* **20**, 57 (1934) and **24**, 489 (1935), has discussed in a general way the order-disorder phenomenon in these thermodynamic terms. Our work is of a much more specific and detailed nature.

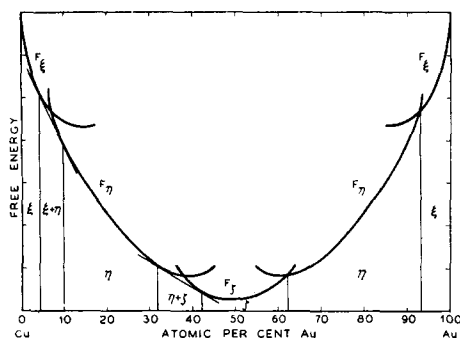


FIG. 3. Schematic representation of free energy vs. composition, showing the difference in free energy for the different phases, the crossing points, and the method of finding phase boundaries.

intrinsic symmetry resulting from the nearest neighbor assumption, the same symbols have been used for phases which differ only by interchange of Cu and Au.

The dependence of free energy upon composition for a typical temperature is shown in Fig. 3. (This curve is schematic; in an exact plot the reentrant portions near the crossing points are much less prominent.) It is seen that in different composition ranges different phases are stable. In the neighborhood of the intersection points of the free energy curves, common tangents can be drawn. For compositions between the points of tangency the most stable state of the alloy will be a mixture of two phases having compositions corresponding to the points of tangency.⁹ After similar calculations are made for different temperatures a phase diagram can be constructed (Fig. 4). For convenience phase boundaries have been shown on the left while crossing points of the free energy curves are shown on the right. This explains the apparent lack of symmetry. (The extra division of the η phase is not significant and is included for use with Part III.) The temperature T_0 , chosen as the unit of temperature in this work, is defined as follows:

T_0 = Temperature above which the 50 percent CuAu alloy is completely disordered.

The relationship between T_0 and U_0 , derived in Part III, is

$$RT_0 = 2U_0. \quad (7)$$

⁹ For a discussion of this point see N. F. Mott and H. Jones *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), p. 24.

($T_0 = T_c$ in the notations of Bragg and Williams⁴ and of Fowler.⁵ The equations analogous to (7) are $T_c = V_0/4k$ and $T_c = W_0/Nk$, respectively.)

If an alloy of, say, 40 percent Au is cooled from the disorder phase ξ so slowly that it is in the equilibrium state, it will at a certain temperature commence to acquire a second phase of the η type with a composition of more than 40 percent Au. As it is cooled through the two-phase region the η phase becomes more abundant and its composition approaches 40 percent until at the lower boundary a phase of pure η results. A similar transition from η to ζ will occur at lower temperature.

In actual experiments, the times required to produce equilibrium are frequently very long. For this reason certain experimental effects were at first considered to be hysteresis whereas they really represented a nonequilibrium behavior.¹⁰ These effects depended mainly upon establishing an equilibrium state in a single phase. The process of producing two phases of different composition, requiring first of all the formation of nuclei for growth of the new phase and involving the transport of an appreciable fraction of the atoms across phase boundaries, will, of course, be much slower; and for this reason will be very difficult to observe.

If the formation of two phases with different compositions does not have time to occur, then the behavior of the alloy is to be predicted from the right side of Fig. 4. Here an alloy of 40 percent Cu when cooled from the ξ phase passes abruptly into the η phase with the production of

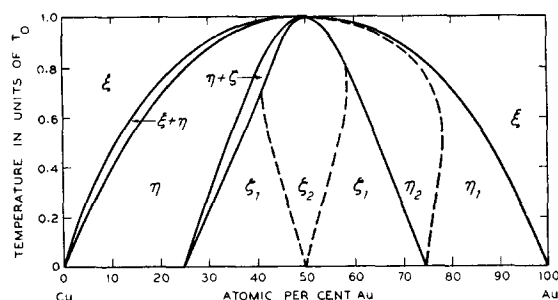


FIG. 4. Phase diagram: Left half conventional; right half alloy restrained to one phase of prescribed composition. Both diagrams when shown in full are symmetrical about 50 atomic percent.

¹⁰ G. Borelius, *Proc. Phys. Soc.* **49**, 77 (1937), however, refers to some experimental effects which are apparently true hysteresis.

a latent heat. Further cooling again produces an abrupt transition to the ζ phase with another latent heat.

Even the single phase type of transition may be prevented from taking place due to the effective freezing out of atomic interchange at low enough temperatures. Anomalous specific heat, attributable to ordering processes, has been observed by Sykes and Jones¹¹ at temperatures as low as 60°C. However, at this temperature only changes in the degree of order in a phase take place and apparently no change of order type is possible. It is probable that only for temperatures in the top third of Fig. 3 (above 200°C in the actual case) will the ordering process be rapid enough to allow realization of changes of phase.

The latent heats per gram atom in making the transitions from ξ to η and η to ζ are represented by the upper and lower curves, respectively, of Fig. 5.

5. Behavior of various fixed compositions with temperature.—The behavior of a given composition as a function of temperature is of particular

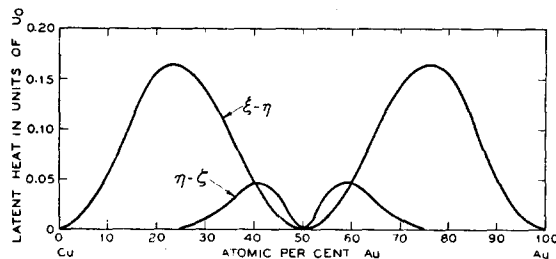


FIG. 5. The latent heats of transformation per gram atom from ξ to η and η to ζ as functions of composition.

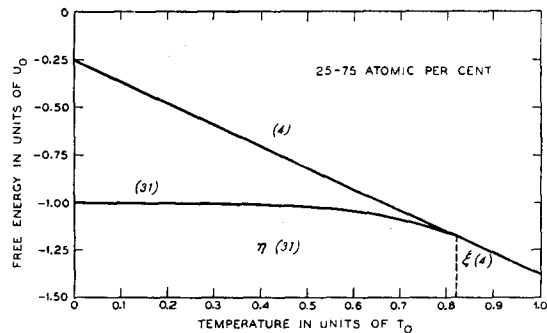


FIG. 6. Free energy per gram atom vs. temperature for the various phases of an alloy having 25 percent of one element and 75 percent of the other. The crossing point of the free energy curves give the transition temperature.

¹¹ C. Sykes and F. W. Jones, Proc. Roy. Soc. **157**, 213 (1936).

interest as it has close correspondence with experimental work. In this treatment, the possibility of two phase regions is disregarded for the reasons given previously.

Figure 6 shows the dependence of the free energy upon temperature for an atomic ratio of 1:3 (either Cu_3Au or CuAu_3 being implied since the symmetry about 50 atomic percent makes them equivalent). We see that at low temperatures the free energy is less for the (31) or η phase than for the (4) ξ phase. At $T=0.82T_0$, the curves cross and (4) is less than (31); hence at this temperature there is a transition from the η to the ξ phase. Since the slope of the free energy curve is minus the entropy, the latent heat is T times the difference in the slopes of the two curves at the crossing point.¹² Similar curves have been analyzed for other compositions. (The free energies of Fig. 6 differ from F by additive constants; they are actually $\psi/4$ as defined in Part III.)

As pointed out previously, these curves should be modified by adding to them the order-dependent part of the other free energies, such as that of lattice vibrations. Near the crossing points there is very little difference between the various free energy curves like those of Fig. 6. For this reason, we may expect a consideration of vibrational free energy to modify considerably the results presented here.

The behavior of the configurational energy as a function of temperature is shown for several compositions in Fig. 7. Of the two percentages on each figure, either may refer to the Cu and the other to the Au. The energies are given in terms of U_x percent, the entire difference in energy between order and disorder. The actual change in terms of U_0 , as determined from Fig. 1(b), is also indicated. We note that all compositions except 50 percent show a latent heat. Both 37.5 and 45 percent show two latent heats, which are very small for 45 percent.

The absence of a latent heat at 50 atomic percent is due mathematically to the smooth joining of the free energy curves, like those of Fig. 6. If we include the dependence of vibrational free energy upon order, there is no reason to suppose that the curves will still join without a break in slope.

¹² $dF/dT = dE/dT - TdS/dT - S = C_v - TC_v/T - S = -S$.
 $\Delta E = T\Delta S$.

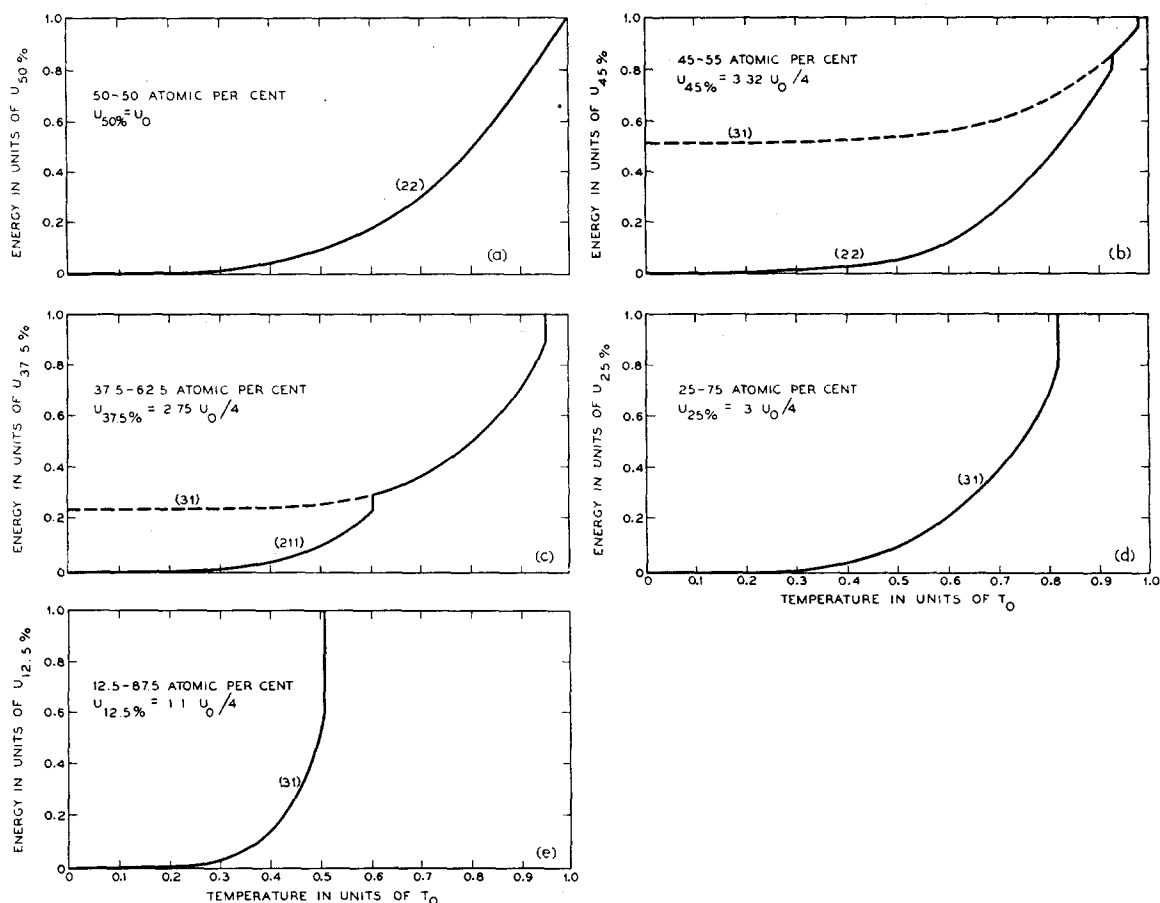


FIG. 7. Energy per gram atom due to disordering *vs.* temperature for fixed compositions. The unit on the energy scale has been chosen as the energy necessary to disorder completely the alloy. The value of this quantity in terms of U_0 is also shown.

For CuAu it is observed experimentally that there is a discontinuity in lattice constants at the critical temperature⁶ and it is natural to expect an associated energy discontinuity and latent heat.

Figure 8 shows the specific heat per gram atom for the same set of compositions.

Figure 9 shows the change in order as a function of temperature. The number next to each curve indicates the number of order parameters which have the value corresponding to the ordinate of the curve. The larger atomic percentages refer to Cu in this case. For corresponding Au percentages, the vertical scale should be reversed in sign.

The compositions 25 percent and 50 percent have been previously treated by Bragg and Williams and the results here are repetitions

except for correlation of the respective critical temperatures and energy changes.

6. Dependence of state of order upon composition at fixed temperature.—For temperatures above T_0 the behavior of the order parameters as functions of composition is very simple. Fig. 4(d) shows that each sublattice has the same composition as the whole sample. A calculation of energy for this case leads to the upper curve of Fig. 1(a).

At absolute zero the behavior, shown in Fig. 10a, is also fairly simple. Starting with pure Cu and adding Au, the process consists of converting first one entire sublattice to Au. This is complete at 25 percent Au, and during the process the order type is (31), the η phase. Next another sublattice is converted to Au ending at 50 percent Au; during this the order type is (211), ζ_1 phase,

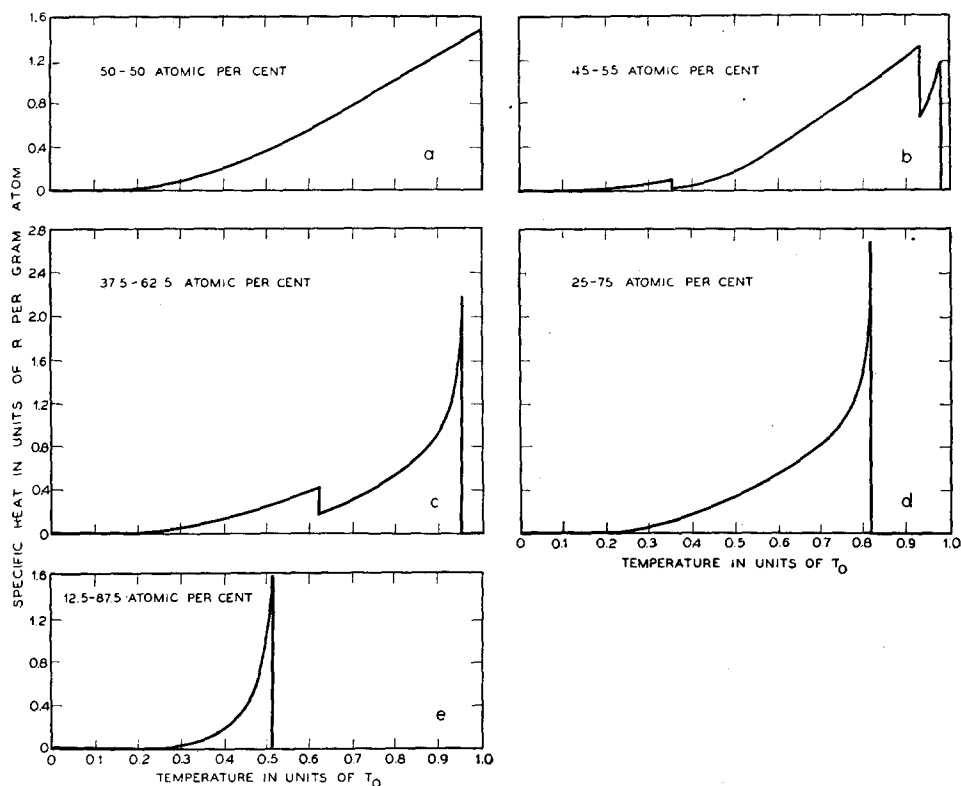


FIG. 8. Heat capacity per gram atom vs. temperature for fixed compositions.

Two more such processes result in pure Au. At any stage in the process three of the sublattices are purely Au or else Cu, while the fourth is in an intermediate stage. These situations lead to the lower curve of Fig. 1(a). (See III, 2 for a proof that this is the lowest possible curve.) It is realized that some of the aspects of this description are too detailed and result only from the mathematical approximation. Thus for composition less than 25 percent, the state of lowest energy can be realized without any long distance order.

For an intermediate temperature $T=0.4T_c$, for example, the behavior is more complicated. From the phase diagram, neglecting the two-phase possibility, Fig. 4, we see that from 0 percent to 10 percent Au we have the disordered ξ phase, hence the state of order is the same as for $T>T_0$. Between 10 percent and 33 percent the alloy is in the η or (31) state; hence three order parameters have one value and one a different value. It is seen in Fig. 10b which shows quantitatively the effects discussed above, that for the η phase up to 25 percent Au the

equilibrium order differs only slightly from the $T=0$ state of order. Above 25 percent instead of going at once to (211) order, ξ_1 type, which corresponds to $T=0$, the η type persists considerably modified up to 33 percent, when a shift over to (211) order takes place. The (211) order holds only up to 44 percent, when it is replaced, without any break in state of order, by (22).

At $T=0.8T_c$ the behavior is generally similar. The difference from $T=0$ order is more marked and the (211) region, ξ_1 , has been swallowed up by (31), η , which has moved to higher compositions, and (22), ξ_2 , which has widened its range.

For still higher temperatures the η and ξ regions move closer about 50 percent and nearer to the line of complete disorder, until at last at T_c only the latter remains.

III. MATHEMATICAL DETAILS

1. Simplification of the energy expression

Since the results derived in this section depend only on the nearest neighbor assumption and

apply to any binary alloy, we shall substitute A and B for Cu and Au. Consider a lattice containing N atomic sites each surrounded by z nearest neighbors; the total number of pairs will then be

$$Q = \frac{1}{2}zN. \quad (8)$$

Let Q be made up of Q_{AA} , Q_{BB} , and Q_{AB} pairs of the different types. Next imagine that a model of the alloy, consisting of wooden balls and wooden rods representing the atoms and the lines between pairs, is pulled apart into pairs, each pair carrying with it $1/z$ th of a ball at either end. Each AA pair then has the fraction $(2/z)$ of a A ball, etc. If the total numbers of A and B balls in the model are $F_A N$ and $F_B N$ then we must have

$$F_A N = (2/z)Q_{AA} + (1/z)Q_{AB}, \quad (9a)$$

$$F_B N = (2/z)Q_{BB} + (1/z)Q_{AB}. \quad (9b)$$

We can solve these for the like neighbor pairs:

$$Q_{AA} = F_A Q - \frac{1}{2}Q_{AB}, \quad (10a)$$

$$Q_{BB} = F_B Q - \frac{1}{2}Q_{AB}. \quad (10b)$$

Let us next consider the energy of the alloy as compared to the energy of two pure crystals of A and B from which it could be made. The energy of a crystal of pure A with $F_A N$ atoms will be V_{AA} times the number of pairs, which is $(z/2)F_A N = F_A Q$. Hence the energy in question is

$$E = V_{AA}Q_{AA} + V_{BB}Q_{BB} + V_{AB}Q_{AB} - F_A V_{AA}Q - F_B V_{BB}Q, \quad (11)$$

which reduces to

$$E = [V_{AB} - \frac{1}{2}(V_{AA} + V_{BB})]Q_{AB}. \quad (12)$$

It is best to define a new quantity

$$V = V_{AA} + V_{BB} - 2V_{AB}. \quad (13)$$

In terms of V the energy is

$$E = -\frac{1}{2}VQ_{AB}. \quad (14)$$

The meaning of V is indicated in the diagram below:

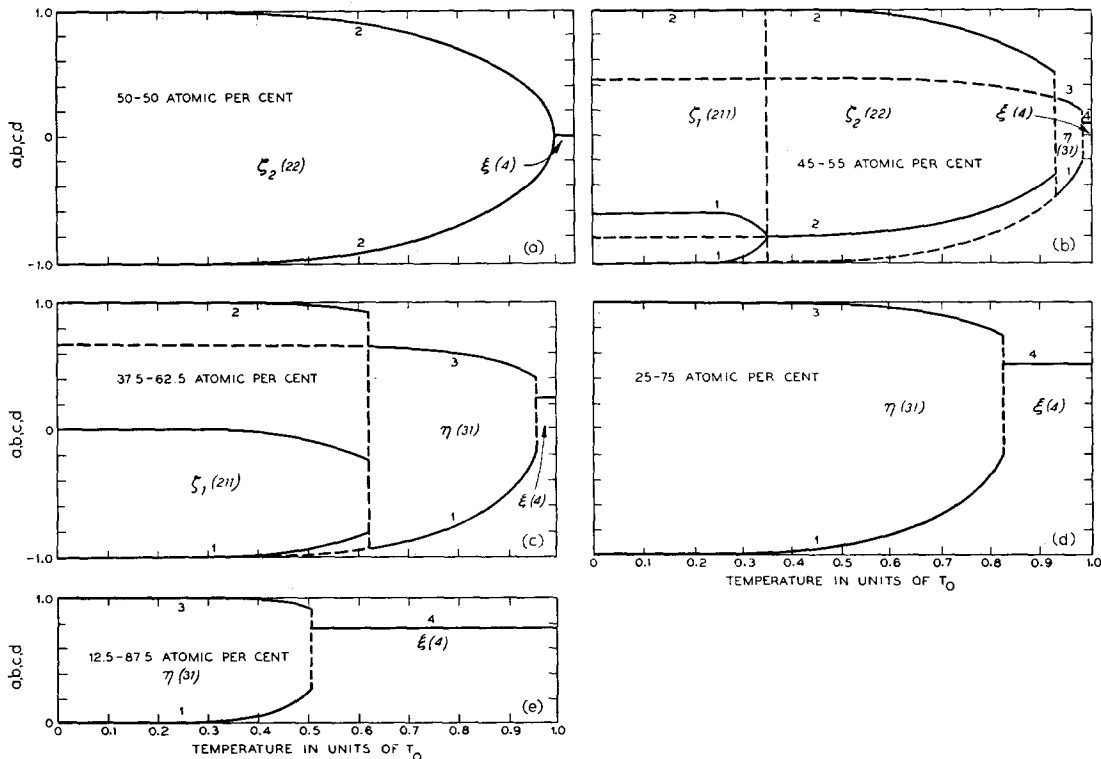
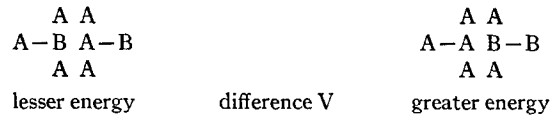


FIG. 9. State of order vs. temperature for fixed compositions. The number near each curve shows the number of order parameters whose common value is given by the ordinate. (The larger percentages refer to Cu.)

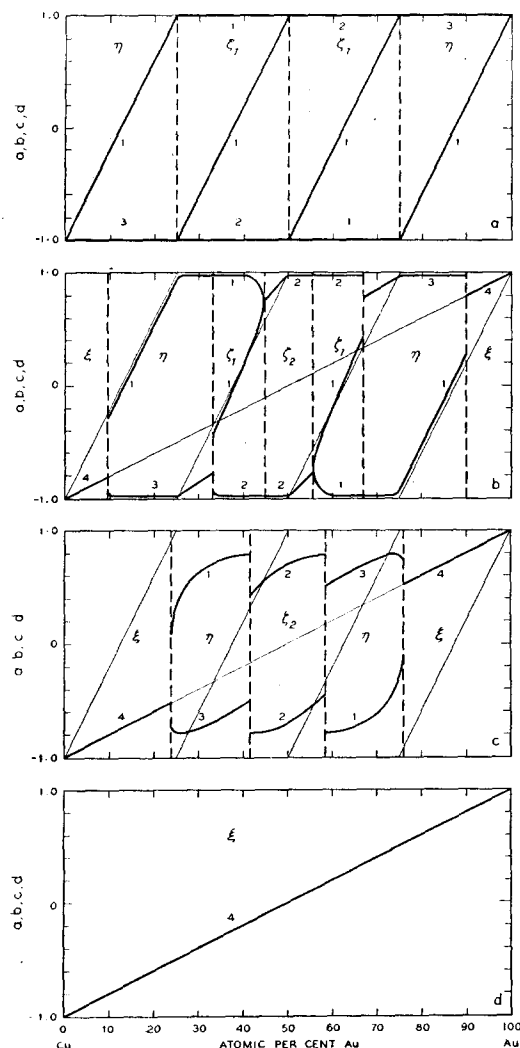


FIG. 10. Dependence of state of order upon composition for several fixed temperatures: *a*, $T=0$; *b*, $T=0.4T_0$; *c*, $T=0.8T_0$; *d*, $T>T_0$. The numbers next to the heavy lines indicate the number of order parameters whose values are given by the ordinates.

We see that V must be positive or else there will be a tendency at low temperature for the alloy to separate into two components of pure A and B, contrary to the assumption that we are dealing with an alloy which forms a superlattice at low temperatures.

2. Determination of the curves of Fig. 1

The determination of the high temperature curve of Fig. 1(*a*), which corresponds to random arrangements and hence to the state of order represented by Fig. 10*d*, is postponed to the next section where $E(abcd)$ is treated. There is no

difficulty in connection with it since random order can be clearly defined and the average energy readily calculated. The situation is quite different for the lowest energy curve, for in its case we must prove that the best possible arrangement can only give a certain number of CuAu pairs, namely that indicated by the lowest curve of Fig. 1(*a*).

Consider again a wooden model of the alloy in which for the moment nothing is specified about the arrangement of the balls. Let this be divided into cubes the corners of which are the mid-point of balls upon one of the sublattices. Every one of these cubes will have one-eighth of a ball at each of its eight corners and one-half a ball on each of its faces—4 balls in all—there will be twelve rods in its body and twenty-four half rods lying in its faces—24 rods in all. One may easily show that Eqs. (9) and (10) apply to this case with $N=4$ and $Q=24$. There are $N/4$ of these cubes and we number them with integers 1, 2, \dots , i , \dots , $N/4$. Now let the number of Cu balls in cube i be n_i , where n_i may have any value from 0 to 4 in steps of $\frac{1}{8}$. Let the number of CuAu rods be q_i . Then we have

$$F_{\text{Cu}}N = \sum n_i, \quad (15)$$

$$Q_{\text{CuAu}} = \sum q_i. \quad (16)$$

Next we consider a particular cube having n Cu's. By actual trial (rearranging the n Cu's, divided into half balls and eighth balls among all the corners and faces) we find that there is a certain maximum possible number of CuAu pairs, $q(n)$, for each value of n . This number is shown in Fig. 11 as a function of n . Since q_i must

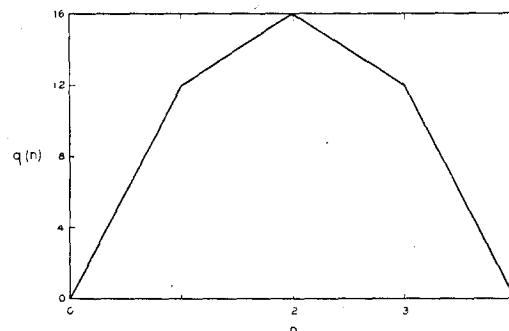


FIG. 11. Plot of the maximum possible number of AuCu pairs, $q(n)$, for one of the cubic cells as a function of the number of Cu atoms in the cell n . This function is defined only for values of n which are integer multiples of $\frac{1}{8}$; the straight lines are drawn through such points.

be less than or equal to $q(n_i)$ we may write

$$Q_{\text{CuAu}} \leq \Sigma q(n_i). \quad (17)$$

Suppose now that two cubes have different numbers n_i and n_j . If n_i and n_j lie on different sides of a kink in Fig. 11, then bringing them nearer together while keeping $n_i + n_j$ constant (thus preserving (15)) will increase $q(n_i) + q(n_j)$. The maximum value of $\Sigma q(n_i)$ will then be obtained by choosing all n_i in the same range between two of the kinks. This will give

$$Q_{\text{CuAu}} \leq (N/4)q(\bar{n}), \quad (18)$$

where $\bar{n} = 4F_{\text{Cu}}$.

This argument does not show that such a high value of Q_{CuAu} can be obtained. However, the type of order given in Fig. 10a leads to just this optimum result and hence the curve of Fig. 1a, drawn on that basis, is the true minimum.

3. Calculation of the energy, E ($abcd$)

We shall now specialize upon a face-centered lattice containing N atoms in all of mixed Au and Cu and in a state of order $abcd$. We wish to know the average value of the energy E when we average over all arrangements of the atoms keeping $abcd$ fixed. Consider a pair consisting of atoms in L_1 and L_2 . During the averaging process, the atom of L_1 is Au in a fraction $\frac{1}{2}(1+a)$ of the arrangements and the atom of L_2 is Cu in a fraction $\frac{1}{2}(1-b)$ of the arrangements. Hence this pair is $L_1\text{Au}L_2\text{Cu}$ in a fraction $(1+a-b-ab)/4$ of the arrangements. Similarly the situation $L_1\text{Cu}L_2\text{Au}$ occurs in a fraction $(1-a+b-ab)/4$. Hence an L_1L_2 pair is of AuCu type in $(1-ab)/2$ of the arrangements. Of the entire Q pairs in the lattice, $\frac{1}{8}$ are between L_1 and L_2 . Hence in the average the contribution of L_1L_2 to Q_{CuAu} will be

$$(1/12)(1-ab)Q \quad (19)$$

and the average value of Q_{CuAu} will be

$$\bar{Q}_{\text{CuAu}} = (1/12)[6 - (ab + ac + ad + bc + bd + cd)]Q. \quad (20)$$

This expression can be simplified by introducing the quantity

$$C = a + b + c + d. \quad (21)$$

C is a parameter which represents the composition of the alloy. In terms of C

$$F_{\text{Au}} = (4+C)/8, \quad (22a)$$

$$F_{\text{Cu}} = (4-C)/8. \quad (22b)$$

and

$$\bar{Q}_{\text{CuAu}} = (1/24)[12 - C^2 + (a^2 + b^2 + c^2 + d^2)]6N. \quad (23)$$

Hence the energy is given by

$$E = -\frac{1}{2}V\bar{Q}_{\text{CuAu}} \\ = (NV/8)[- (a^2 + b^2 + c^2 + d^2) + C^2 - 12]. \quad (24)$$

4. Calculation of the entropy, S ($abcd$)

The logarithm of one term in the entropy expression is

$$\ln \frac{n!}{[\frac{1}{2}(1+a)n]! [\frac{1}{2}(1-a)n]!} \\ = -\frac{n}{2}[2\ln 2 - (1+a)\ln(1+a) - (1-a)\ln(1-a)] \\ = (N/8)\eta(a), \quad (25)$$

where $\eta(a)$ is the quantity in the square brackets. Hence the entropy is

$$S = \frac{1}{8}kN[\eta(a) + \eta(b) + \eta(c) + \eta(d)]. \quad (26)$$

5. New units and the free energy

Before dealing with free energy we shall introduce some convenient units of temperature, energy, and entropy. The new temperature, t , is measured in units of V/k and from (4) and (7), which can be regarded as definitions of U_0 and T_0 at present, we obtain

$$t = T/(V/k) = T/(NV/R) = T/T_0. \quad (27)$$

We next restrict N to mean Loschmidt's number so that we have to do with one gram atom. A new energy, u , and free energy, f , measured in units of $V/8$ per atom are related to E and F as follows:

$$u = 8E/NV = 4E/U_0, \quad (28)$$

$$f = 8F/NV = 4F/U_0. \quad (29)$$

Hence quarter units on energy scales measured in units of V_0 are now units for u and f .

The value of entropy in units of $k/8$ per atom is s so that

$$s = 8S/R. \quad (30)$$

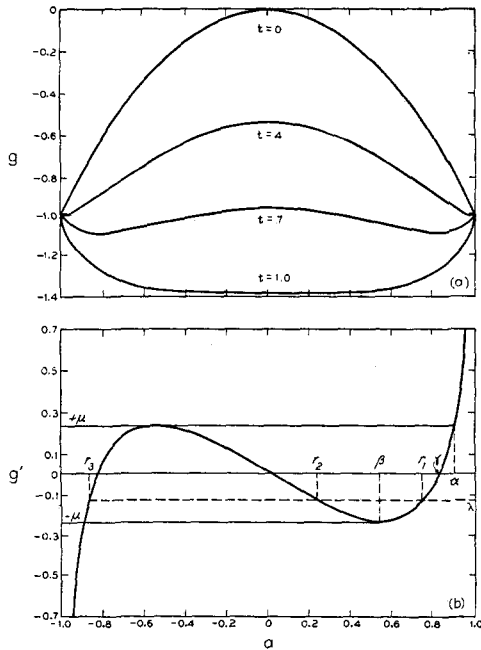


FIG. 12. (a) Plot of $g(a) = -a^2 - t\eta(a)$ vs. a with t as a parameter for four values of t . (b) Plot of $g'(a) = dg/da$ for $t=0.7$ showing the meaning of α , β , γ , μ , λ , r_1 , r_2 , r_3 .

The values of u , f and s are found to be

$$u = -(a^2 + b^2 + c^2 + d^2) + C^2 - 12, \quad (31)$$

$$f = u - t(\eta(a) + \eta(b) + \eta(c) + \eta(d)), \quad (32)$$

$$s = \eta(a) + \eta(b) + \eta(c) + \eta(d). \quad (33)$$

6. Minimization of the free energy

Our problem is therefore to minimize f while keeping C constant. For this purpose we may omit the $C^2 - 12$ from f . Writing

$$g(a) = -a^2 - t\eta(a), \quad (34)$$

we have

$$\psi = f - C^2 + 12 = g(a) + g(b) + g(c) + g(d). \quad (35)$$

The method of La Grange multipliers at once yields the equations

$$g'(a) = g'(b) = g'(c) = g'(d) = \lambda. \quad (36)$$

Figure 12 shows the behavior of $g(x)$ with t as a parameter and also the shape of the derivative $g'(x)$ for $t=0.7$.

We see that for $\mu > \lambda > -\mu$, there are three roots $r_1 r_2 r_3$ of the equation

$$g'(x) = \lambda. \quad (37)$$

The La Grange equations unfortunately do not show which order parameters have which roots. They show merely that for the minimum conditions the values of the four-order parameters must be chosen from the three roots of Eq. (37). There are in all 15 distinct ways of assigning three different values to a set of four numbers. Let the number of order parameters assigned to value r_1 be n_1 , to r_2 be n_2 , to r_3 be n_3 . Then each distinct set of values of the triplet $n_1 n_2 n_3$ corresponds to one of the 15 ways of satisfying Eq. (36). In Table I the 15 different triplets are classified according to the type of order. For example, the triplet 202 means that two order parameters are equal, having value r_1 , and are different from the other two which are also equal, having value r_3 ; this situation corresponds to the type of order (22). There appears to be no way of telling *a priori* which triplet gives the lowest free energy for a given C . Hence we proceed by calculating the functions

$$\psi(n_1 n_2 n_3 \lambda) = n_1 g(r_1(\lambda)) + n_2 g(r_2(\lambda)) + n_3 g(r_3(\lambda)), \quad (38)$$

$$C(n_1 n_2 n_3 \lambda) = n_1 r_1(\lambda) + n_2 r_2(\lambda) + n_3 r_3(\lambda), \quad (39)$$

which give the values of ψ and corresponding values of C when the order parameters are chosen according to the possibilities shown in the table. The values of ψ are then plotted *versus* C ; the lowest ψ for a given C represents the true minimum for that composition, while the other curves represent only virtual minima, for which $\delta\psi=0$ for small changes in order satisfying $\delta C=0$.

The results of plotting all fifteen realizations of the 4 kinds of orders are shown in Fig. 13.

Certain features of this figure should be pointed out. For $\lambda = -\mu$, $r_1 = r_2 = \beta$ and $r_3 = -\alpha$, and hence the curves 400, 310, 220, 130, and 040 have the common values $\psi = 4g(\beta)$, $C = 4\beta$. Similarly 301, 211, 121, 031 meet at $\psi = 3g(\beta) + g(\alpha)$, $C = 3\beta - \alpha$; 202, 112, 022 at $\psi = 2g(\beta) + 2g(\alpha)$, $C = 2\beta - 2\alpha$; 103 and 013 at $\psi = g(\beta) + 3g(\alpha)$, $C = \beta - 3\alpha$; the curve 004 is at $\psi = 4g(\alpha)$, $C = -4\alpha$. This set of branch points are

TABLE I.

TYPE OF ORDER	CORRESPONDING TRIPLETS
(4)	400, 040, 004
(31)	310, 301, 130, 031, 103, 013
(22)	220, 202, 022
(211)	211, 121, 122
(1111)	Impossible

colinear and will be referred to as the $-\mu$ series. When λ equal $+\mu$, the $+\mu$ series of branch points is obtained for which triplets $n_1 n_2 n_3$ with a common value of n_1 meet.

The slope $d\psi/dC$ along the curves is equal to λ , as may be verified at once:

$$\begin{aligned} \frac{d\psi(n_1 n_2 n_3)}{d\lambda} &= n_1 g'(r_1) \frac{dr_1}{d\lambda} + n_2 g'(r_2) \frac{dr_2}{d\lambda} + n_3 g'(r_3) \frac{dr_3}{d\lambda} \\ &= \lambda \left[n_1 \frac{dr_1}{d\lambda} + n_2 \frac{dr_2}{d\lambda} + n_3 \frac{dr_3}{d\lambda} \right] \\ &= \lambda (d/d\lambda) [n_1 r_1 + n_2 r_2 + n_3 r_3] \\ &= \lambda (d/d\lambda) C(n_1 n_2 n_3). \end{aligned} \quad (40)$$

Hence

$$d\psi/dC = (d\psi/d\lambda) / (dC/d\lambda) = \lambda. \quad (41)$$

This accounts for the fact that all curves have the same slope $-\mu$ on the $-\mu$ series and $+\mu$ on the $+\mu$ series.

Another regular array of points is produced by $\lambda=0$. For these points

$$\psi(n_1 n_2 n_3) = (n_1 + n_3)g(\gamma) + n_2 g(0), \quad (42)$$

$$C(n_1 n_2 n_3) = (n_1 - n_3)\gamma. \quad (43)$$

At them $d\psi/dC = \lambda$ is 0. These are called the $\lambda=0$ array.

As a curve goes from a point of the $-\mu$ array the slope $d\psi/dC$ increases from $-\mu$ to a value zero, at a point of the $\lambda=0$ array, and then to $+\mu$ when the curve reaches the $+\mu$ series. Next suppose C attains values not between those of its end points on the $\pm\mu$ series; then if we follow the curve in the sense of continually increasing λ , we reach a point where C is an extremum. At this point $d\psi/dC$ must lie between $+\mu$ and $-\mu$, and when the curve turns back it does so with a finite slope, thus producing a sharp point on the curve.

Investigations can also be carried out to determine the direction of the curves as they pass through points of the $\lambda=0$ array, and also to see which leave with greater curvature at points of the $\pm\mu$ series. With this information, reasonably accurate plots like that of Fig. 13 can be drawn using only these limiting values of λ . This has been the procedure adopted for values of t except 0.7, for which quite complete calculations were made.

The curves of Fig. 13 are symmetrical about $C=0$, that is 50 atomic percent. The division

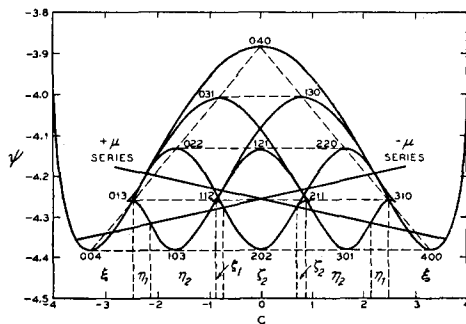


FIG. 13. Plot of ψ vs. C , showing the phases having lowest free energy for each composition.

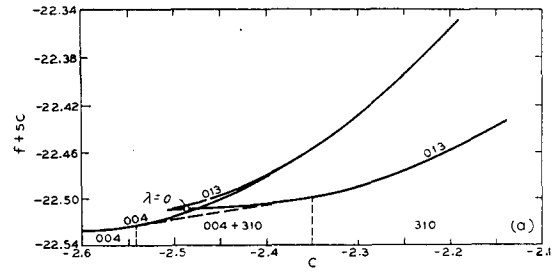


FIG. 14. Free energy f plus a linear term in composition vs. composition, showing the method of determining phase boundaries and two phase regions.

into stable states is indicated in the same notation as is used in connection with the phase diagram.

7. Calculation of the phase boundaries

Figure 13 cannot conveniently be used to find phase boundaries. A tangent to the minimum points of the ψ curves, being a parabola in the f vs. composition plane, does not give phase boundaries. Fig. 14 shows an enlargement of the region including $\xi+\eta$; the linear term in C added to f has been chosen so as to facilitate plotting and does not, as does the C^2 term by which ψ differs from f , distort the relations derived from the tangency. For values of t other than 0.7 the width of the two-phase region has been estimated roughly. The behavior near $t=0$ and $t=1$ is generally correct.

8. Behavior of various fixed compositions with the temperature

The work with the fixed compositions was carried out somewhat differently. For points in the $\xi(4)$, $\eta(31)$, and $\xi(22)$ regions there is only one independent order parameter, the second being determined in terms of the first and the composition. Thus for $\eta(31)$ we have $abbb$ for the state of order. For composition value C we can derive the equations

$$b = (C-a)/3 \quad (44)$$

$$\text{and } \psi(31) = -a^2 - 3b^2 - t[\eta(a) + 3\eta(b)]. \quad (45)$$

Hence for equilibrium

$$d\psi/da = 0$$

$$\text{or } t = \frac{2}{3 \ln [(1-a)(1+b)/(1+a)(1-b)]} \quad (46)$$

From this relationship t was found as a function of a and then ψ was computed and plotted versus t . The intersection with

$$\psi(4) = -\frac{1}{4}C^2 - 4t\eta(C/4) \quad (47)$$

gives the critical temperature. The energy content, $\mu = -(a^2 + 3b^2)$, and the state of order were also plotted.

The specific heat was found by differentiating (46), obtaining

$$\frac{dt}{da} = + \left[\frac{8 - 2a^2 - 6b^2}{(1-a^2)(1-b^2)} t - 8 \right] \div 3 \ln \frac{(1-a)(1+b)}{(1+a)(1-b)}. \quad (48)$$

Combining this with

$$du/da = 2(b-a) \quad (49)$$

and transforming to E and T , we obtain

$$C_v = \frac{dE}{dT} = \frac{(NV/8)du}{(V/k)dt} = \frac{R}{8} \frac{(du/da)}{(dt/da)}. \quad (50)$$

Similar calculations applied to $\xi(22)$ yield

$$b = C/2 - a, \quad (51)$$

$$\psi(22) = -2(a^2 + b^2) - 2t[\eta(a) + \eta(b)], \quad (52)$$

$$t = \frac{C - 4a}{\ln [(1-a)(1+b)/(1+a)(1-b)]}, \quad (53)$$

$$\frac{dt}{da} = [4 - t(4 - 2a^2 - 2b^2)/(1-a^2)(1-b^2)] \div \ln [(1+a)(1-b)/(1-a)(1+b)], \quad (54)$$

$$du/da = 4(b-a). \quad (55)$$

This method when applied to Cu_3Au and CuAu is mathematically identical with the work of Bragg and Williams and the results are in harmony with theirs.

The values needed for (211) with compositions 37.5 percent and 45 percent were estimated from

the ψ vs. C curves for various temperatures. They are not very accurate, but since the entire set of calculations must be viewed with regard to suggested trends rather than high accuracy, they are probably quite good enough.

9. Latent heat curves

The latent heats for the $\xi-\eta$ transformation were taken from the work at constant C . The regions near $C=4$ and $C=0$ were obtained, respectively, from Fig. 1b and from an analytic expansion of $\psi(4)$ and $\psi(31)$. Two values for the $\eta-\xi$ transformation were found from detailed work at $t=0.7$ and 0.6 . The behavior near $C=0$ was found analytically.

IV. CONCLUSIONS

The "nearest neighbor assumption" is capable of giving a coherent description of the $\text{Cu}-\text{Au}$ alloy system showing how the ordered structures of Cu_3Au and CuAu are related by an intermediate series of phases. It cannot possibly describe the behavior in correct detail because it requires symmetry about 50 atomic percent which does not actually exist. One simple modification which will effect improvement (inclusion of vibrational free energy) is mentioned.

Two new features are brought out by this work: a definition of the "state of order" which is applicable to a wide composition range; and the theoretical possibility of two transition temperatures with two latent heats.

The writer is indebted to Professor J. G. Kirkwood, Dr. F. Seitz, and Dr. L. P. Bouckaert for several interesting discussions which were helpful in crystallizing the ideas presented here, and to Drs. C. J. Davisson and F. C. Nix for their continued interest and encouragement in the progress of this work. Sincere thanks are due also to Miss E. C. Kempfer who carried out the computational work and Mr. H. M. Yates who furnished the figures.