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An Approximate Theory of Order in Alloys*,**

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Short-range order parameters α_i are defined to express the interaction of a given atom in an alloy with the atoms of the ith shell of atoms surrounding it. From simple thermodynamic reasoning, involving a certain degree of approximation, equations relating the α_i with energy terms and the temperature are derived. Equations for the long-range order parameter, S, are obtained by considering the limiting case of i very large. The values of the long- and short-range order parameters obtained by solving these equations are in good agreement with experimental values recently found by x-ray diffraction methods. The theory is extended to the calculation of configurational energy and specific heat, and to the determination of order parameters for alloys of arbitrary composition in such binary systems as that of the copper-gold alloys. In these cases qualitative agreement with experimental observations is obtained.

INTRODUCTION

Of the many theoretical approaches to the phenomena of ordering in alloys, those which are mathematically rigorous have been applied only to simple cases, such as the two-dimensional square net,[1] and have not to date given results directly comparable with experiment. Various approximate theories have given predictions of long-range order and nearest-neighbor order for some special cases. Bragg and Williams[2] introduced the long-range order parameter, S, and devised a simple theory giving S as a function of temperature. Bethe[3] considered nearest-neighbor order, measured by the parameter σ, and determined long-range order and nearest-neighbor order for the case of AB alloys. Peierls[4] extended this theory to the case of the face-centered cubic A_3B alloys such as Cu_3Au. Similarly other approximate theories, such as that of Kirkwood[5] have given results for nearest-neighbor order and long-range order for a few special cases.

Recent advances in x-ray diffraction techniques have made possible the quantitative determination of the long-range order parameter, S, and short-range order parameters for several shells of neighbors. Thus, for the alloy Cu_3Au, Wilchinsky[6] measured S and the short-range order parameters for the first three shells, using powder diffraction methods. The present author has measured the short-range order parameters for the first ten shells of neighbors, using single-crystal techniques.[7] The x-ray diffraction methods involved may be applied equally well to a wide range of compositions in a number of alloy systems. For most of the results so obtainable, no theoretical results are available for comparison.

With this situation in mind, it seems worth while to present the following theory which, although admittedly of a very approximate nature, has shown good agreement with the available experimental data, and may be extended to the consideration of a wide range of structures and compositions without undue mathematical difficulty.

DEFINITION OF SHORT-RANGE ORDER PARAMETERS

For an alloy consisting of A and B atoms, present in the proportions m_A and m_B, we define the short-range order parameter for the atomic site with coordinates l, m, n with respect to a given B atom as $\alpha_{lmn}=1-p_{lmn}/m_A$ where p_{lmn} is the probability that the atomic site is occupied by an A atom. Then

$$p_{lmn}=m_A(1-\alpha_{lmn}).$$

If an A atom is taken as origin, $p_{lmn}=m_A+m_B\cdot\alpha_{lmn}$.

Alternatively, if the atom with coordinates l, m, n is considered to belong to the ith shell of neighbors surrounding a B atom, we may write $\alpha_i=1-n_i/m_Ac_i$, where n_i is the number of A atoms among the c_i atoms of the ith shell.

The short-range order parameters were initially defined in this way for convenience in considerations of the x-ray diffraction effects for alloys above the critical temperature of ordering, since the α_{lmn} are the coefficients of the three-dimensional Fourier series expressing the "scattering power" caused by short-range order as a function of the reciprocal-lattice coordinates. However, they were found to be very convenient for thermodynamic considerations also, and have been used in preference to parameters defined in analogy to Bethe's σ. They have the conventional properties of order parameters in that they are zero for the completely random state, and have a maximum (absolute) value for perfect order. The value for perfect order, α_i^0, is unity, however, only for even-numbered shells; for odd-numbered shells it is negative and fractional

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[1] G. H. Wannier, Rev. Mod. Phys. 17, 50 (1945).

[2] Bragg and Williams, Proc. Roy. Soc. A145, 699 (1934).

[3] H. A. Bethe, Proc. Roy. Soc. A150, 552 (1935).

[4] R. Peierls, Proc. Roy. Soc. A154, 207 (1936).

[5] J. G. Kirkwood, J. Chem. Phys. 6, 70 (1938).

[6] Z. W. Wilchinsky, J. App. Phys. 15, 806 (1944).

[7] J. M. Cowley, J. App. Phys. (to be published).

except in the case of some AB alloys. Thus, for Cu_3Au, $\alpha_i^0=1$ for i even, and $-1/3$ for i odd. For the case of AB alloys, the α_{lmn} are equivalent to the parameters r_{hkl} defined by Zernike[8] and used by him in theoretical considerations of ordering at this composition. For β-brass, CuZn, at the 50:50 composition, $-\alpha_1=-\alpha_{111}=r_{111}=\sigma(=1$ for perfect order).

Long-range order may be said to exist in an alloy if the value of the parameter α_i does not tend to zero, but approaches a finite limiting value as i becomes very large. The relation between the limiting value of the short-range order parameter and the long-range order parameter depends on the nature of the ordered structure and the composition of the alloy. As an example, the derivation of the relation will be indicated for an alloy of arbitrary composition forming a face-centered cubic lattice such as that of Cu_3Au.

The long-range order parameter S for the face-centered cubic lattice may be defined as the average of the values of S for the four simple-cubic lattices of which the face-centered lattice is composed. If three of the simple-cubic lattices are considered to be α-sites, properly occupied by A atoms, and the other one is considered to consist of β-sites, properly occupied by B atoms,

$$S=\frac{3}{4}\left(\frac{r_\alpha-m_A}{1-m_A}\right)+\frac{1}{4}\left(\frac{r_\beta-m_B}{1-m_B}\right),$$

where r_α and r_β are the fractions of α and β-sites rightly occupied. By summing the total number of A or B atoms, one derives the relation, $r_\beta=3r_\alpha+4m_B-3$, from which it follows that $r_\alpha=(4/3)m_Am_BS+m_A$ and $r_\beta=4m_Am_BS+m_B$.

In order to establish the relationship between the imiting value of the α-coefficients and S, we consider a lattice with long-range order S. If we pick an atom at random as origin, there is a relative probability $r_\beta/4$ that it is a B atom on a β-site, in which case $\alpha_{i\text{ even}}\rightarrow 4m_BS$. The probability that the origin is a B atom on an α-site is $\frac{3}{4}(1-r_\alpha)$, and for this case $\alpha_{\text{even}}\rightarrow -4m_BS/3$. Similarly, if the origin chosen is an A atom. Taking the weighted average of the limiting values of α_{even} for the various cases, we get, for the whole lattice,*

$$\alpha_{\text{even}}\rightarrow\frac{16}{3}m_Am_BS^2.$$

The limiting value for $\alpha_{i\text{ odd}}$ is equal to $-\alpha_{\text{even}}/3$.

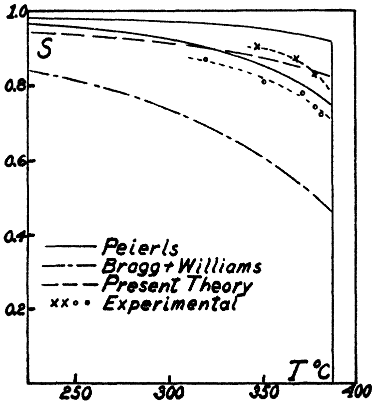

FIG. 1. Variation of long-range order with temperature for Cu_3Au, theoretical and experimental.

In the same way it can be shown that, if the numbers of α and β-sites are equal, $\alpha_{\text{even}}\rightarrow 4m_Am_BS^2$.

THEORY FOR SHORT-RANGE ORDER

In a crystal having zero long-range order, the atomic sites are occupied at random in that each site is occupied by an A atom with probability m_A, and by a B atom with probability m_B. To investigate the influence of one atom on its neighbors, we choose a particular atom as origin—that is, increase the probability of a particular site being occupied by an A, or a B, to unity, and consider the associated change in free-energy. The free-energy change is given by $F-F_0=(U-U_0)-T(S-S_0)$, where U is the configurational energy of the lattice, and S is the entropy of configuration.

The configurational energy is made up of the energies of interaction between pairs of atoms. We denote by $V_{AB,\,lmn,\,l'm'n'}$ the energy of interaction between an A atom with coordinates l, m, n and a B atom with coordinates l', m', n'. For convenience, we substitute the symbol I for the coordinates l, m, n in the subscript, so that the symbol I represents the atom with coordinates l, m, n, which is considered to be a particular atom of the ith shell of atoms about the origin. Similarly we replaced l', m', n' by the symbol J, and the atom with these coordinates is considered to be a particular atom of the jth shell. Similarly we define $V_{AA,\,IJ}$ and $V_{BB,\,IJ}$ as the energies of interaction of pairs of A and B atoms at these particular sites. For considerations of ordering, it is necessary to deal with only the linear combination,

$$V_{IJ}=\tfrac{1}{2}(V_{AA,\,IJ}+V_{BB,\,IJ})-V_{AB,\,IJ},$$

which represents the average change of energy when a pair of like atoms is replaced by two unlike atoms at the same positions.

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[8] F. Zernike, Physica 7, 565 (1940).

* B atom on a β-site, relative probability $r_\beta/4$.

With respect to this position shells with i=even represent β-sites.

$$\alpha_{i\text{ even}}\rightarrow 1-\frac{P_{lmn}}{m_A}=1-\frac{(1-r_\beta)}{m_A}=4m_BS.$$

B atom on an α-site, relative probability $3/4(1-r_\alpha)$.

With respect to this position shells with i=even represent α sites.

$$\alpha_{i\text{ even}}\rightarrow 1-\frac{P_{lmn}}{m_A}=1-\frac{r_\alpha}{m_A}=-\frac{4m_BS}{3}.$$

Weighted average of $\alpha_{i\text{ even}}$ for all B atoms as origin

$$\alpha_{i\text{ even}},\frac{(r_\beta/4)4m_BS-\frac{3}{4}(1-r_\alpha)(4m_BS/3)}{r_\beta/4+\frac{3}{4}(1-r_\alpha)}=\frac{16}{3}m_Am_BS^2.$$

If the atom in the position denoted by J is in the kth shell of atoms with respect to the atom I, we write $V_{IJ}=V_k$.

The change in configurational energy involved in the fixing of an A or B atom as origin may be found by summing the average values of the energy changes for all possible pairs of atoms. With respect to the origin, the probabilities of the atoms I and J being A or B atoms are given in terms of α_I and α_J, and the average change in the energy of interaction between these atoms may be found in terms of α_I, α_J, and V_{IJ}. The total configurational energy change for the whole lattice when one atom is fixed as origin is then found to be, on the average,

$$U-U_0=m_Am_B\sum_I\sum_J \alpha_I\cdot\alpha_J\cdot V_{IJ},$$

where a summation with respect to I or J is a summation over every atom in the lattice, that is, over all possible values of the coordinates l, m, n or l', m', n'.

The change of entropy involved in fixing an A or B atom as origin may be expressed as $S-S_0=k\ln W-k\ln W_0$, where k is Boltzman's constant, W is the number of ways of arranging the atoms so that the short-range order parameters will have the values α_i, and W_0 is a constant. In the ith shell about a B atom at the origin, on the average $c_im_A(1-\alpha_i)$ of the c_i atoms will be A atoms.

This arrangement may be obtained in

$$W_{B,i}=\frac{c_i!}{[c_im_A(1-\alpha_i)]![c_i(m_B+m_A\alpha_i)]!}\text{ ways.}$$

This term is multiplied by similar terms for all values of i to give W_B, the total number of arrangements when the origin is a B. Analagous expressions are obtained considering an A at the origin. The entropy-change may thus be found. The simple method of its calculation involves the approximation that only the average distributions have been considered, and fluctuations in the distribution of atoms have been ignored.

For equilibrium, the values of the variables α_I will be such as to make the free-energy a minimum, so that $\delta F=\delta U-T\delta S=0$.

Substituting the expressions obtained for the energy and entropy in this equation gives

$$m_Am_B\sum_I\delta\alpha_I\left[2\sum_J V_{IJ}\alpha_J+kT\ln\left\{\frac{(m_A+m_B\alpha_i)(m_B+m_A\alpha_i)}{m_Am_B(1-\alpha_i)^2}\right\}\right]=0,$$

where the atom I is taken as a particular atom of the ith shell, so that $\alpha_I=\alpha_i$, and Stirling's approximation has been used to simplify the entropy terms.

If it is assumed that all the α_I are independent variables, it follows that all the terms in the square brackets must be zero, so that

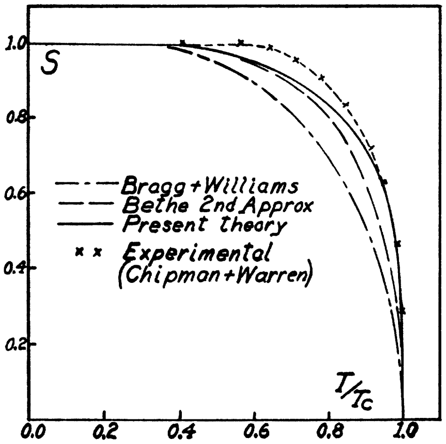

FIG. 2. Variation of long-range order with temperature for CuZn, theoretical and experimental.

$$2\sum_J V_{IJ}\alpha_J+kT\ln\left\{\frac{[m_A/m_B)+\alpha_i][(m_B/m_A)+\alpha_i]}{(1-\alpha_i)^2}\right\}=0. \quad (1)$$

The assumption that the α_I are independent is not strictly valid, and must be regarded as a rough approximation only. It is justified in the present case only in that it leads directly to the Eqs. (1) which appear to represent the relations between the order coefficients and energy terms with fair accuracy.

There is an equation of the type (1) for every value of i, and the summation over J is the summation over all atoms of the lattice of the product of the α-coefficient of each atom and its interaction energy with a particular atom of the ith shell.

For Cu_3Au the equations are:

$$-kT\ln\left\{\frac{(\frac{1}{3}+\alpha_1)(3+\alpha_1)}{(1-\alpha_1)^2}\right\}=2V_1(1+4\alpha_1+2\alpha_2+4\alpha_3+\alpha_4)+2V_2(2\alpha_1+2\alpha_3+2\alpha_5)+\cdots,$$

$$-kT\ln\left\{\frac{(\frac{1}{3}+\alpha_2)(3+\alpha_2)}{(1-\alpha_2)^2}\right\}=2V_1(4\alpha_1+4\alpha_3+4\alpha_5)+2V_2(1+4\alpha_4+\alpha_8)+\cdots,$$

$$-kT\ln\left\{\frac{(\frac{1}{3}+\alpha_3)(3+\alpha_3)}{(1-\alpha_3)^2}\right\}=2V_1(2\alpha_1+\alpha_2+2\alpha_3+2\alpha_4+2\alpha_5+\alpha_6+2\alpha_7)+2V_2(\alpha_1+2\alpha_3+2\alpha_7+\alpha_9)+\cdots.$$

On the right-hand side of the first equation, V_1 is multiplied by the α-coefficients of all the atoms which are nearest neighbors of a particular atom of the first shell, V_2 is multiplied by the α's of all atoms which are second-nearest neighbors of an atom in the first shell, and so on.

For any temperature T, this infinite set of equations could be solved to give short-range order parameters for given values of the energy terms. Conversely, the energy terms may be calculated from experimental values of the short-range order coefficients. This has been done for Cu_3Au using the values for the first ten order coefficients found from x-ray diffraction measurements,[7] assuming that only V_1, V_2, and V_3 were appreciable. The values obtained, $V_1=358k$, $V_2=-34k$, $V_3=-19k$, are of the right order of magnitude.

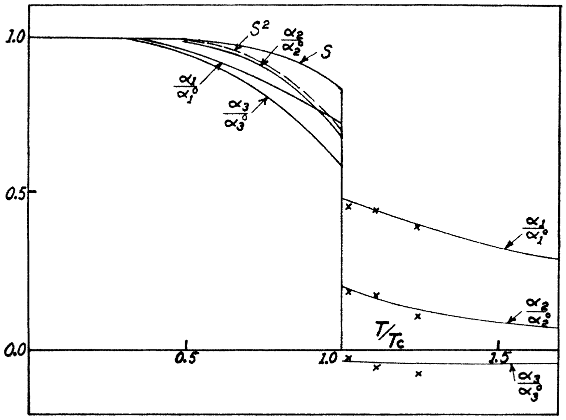

FIG. 3. Short-range order parameters for the first three shells of neighbors, for Cu_3Au, as functions of temperature.

LONG-RANGE ORDER FOR PARTICULAR COMPOSITIONS

If, in the lattice of a binary alloy, two kinds of sites are available in exactly the same ratio as the two kinds of atoms, an equation for the long-range order parameter, S, is obtained by considering the limiting case of Eq. (1) for i very large. For example, for Cu_3Au the limiting values of α_i for i large are S^2 if i is even and $-S^2/3$ for i odd. The long-range order parameter is defined by considering the correlation of atoms in a given simple-cubic sub-lattice and the atoms on the same simple-cubic sub-lattice as the origin are those contained in shells with i even. Hence S is given by the limiting form of the equations for α_i with i even. This limiting form is

$$\ln\left\{\frac{(\frac{1}{3}+S^2)(3+S^2)}{(1-S^2)^2}\right\}=+\frac{8S^2}{kT}(V_1-3/2V_2+\cdots).$$

This equation predicts a "critical temperature," T_c at which the long-range order drops to zero. By considering $S\rightarrow 0$ one finds

$$T_c=\frac{3}{2k}(V_1-3/2V_2+\cdots).$$

Substituting for the energy terms in the first equation, we have an equation giving S in terms of the ratio T/T_c only, thus,

$$\ln\left\{\frac{(\frac{1}{3}+S^2)(3+S^2)}{(1-S^2)^2}\right\}=\frac{16}{3}\cdot\frac{T_c}{T}\cdot S^2.$$

In Fig. 1 the values of S from this equation are plotted against temperature, assuming $T_c=390°C$, and compared with the values predicted by the theories of Bragg and Williams[2] and Peierls,[4] and experimental values obtained by the present author.[7] The present theory appears to agree with experiment within the limits of experimental error.

For a body-centered cubic structure such as that of β-brass, the analogous equation is

$$\ln\left\{\frac{1+S^2}{1-S^2}\right\}=2\cdot\frac{T_c}{T}\cdot S^2.$$

The values of S found from this equation are plotted against the ratio T/T_c in Fig. 2. It is seen that the present theory is in better agreement with the experimental values of Warren and Chipman[9] than the Bragg and Williams theory or Bethe's second approximation for this case.

CALCULATION OF SHORT-RANGE ORDER COEFFICIENTS

The short-range order parameters α_i may be found for any temperature by solving the Eqs. (1), if the energy terms are known. The values of the first three order parameters for Cu_3Au have been calculated for a number of temperatures with the use of certain simplifying assumptions. It was assumed that for temperatures greater than the critical temperature all $\alpha_i=0$ for i greater than 5, and for temperatures less than the critical temperature all α_i had the limiting value of S^2 or $-S^2$ for i greater than 3. All V_i were assumed zero for i greater than 2, and V_2 was taken as $-V_1/10$, as found by calculation from experimental order coefficients. Both V_1 and V_2 could then be expressed in terms of the critical temperature by use of the relation given in the previous section. For T greater than T_c, the equations to be solved were then

$$\begin{aligned}
-f(\alpha_1)&=1.160T_c/T\cdot(1+3.8\alpha_1+2\alpha_2\\
&\qquad+3.8\alpha_3+\alpha_4-0.2\alpha_5),\\
-f(\alpha_2)&=1.160T_c/T\cdot(-0.1+4\alpha_1+4\alpha_3-0.4\alpha_4+4\alpha_5),\\
-f(\alpha_3)&=1.160T_c/T\cdot(1.9\alpha_1+\alpha_2+1.8\alpha_3+2\alpha_4+2\alpha_5),\\
-f(\alpha_4)&=1.160T_c/T\cdot(\alpha_1-0.2\alpha_2+4\alpha_3+2\alpha_5),\\
-f(\alpha_5)&=1.160T_c/T\cdot(0.1\alpha_1+\alpha_2+2\alpha_3+\alpha_4+1.9\alpha_5),
\end{aligned}$$

where

$$f(\alpha_i)=\ln\left\{\frac{(\frac{1}{3}+\alpha_i)(3+\alpha_i)}{(1-\alpha_i)^2}\right\}.$$

This set of equations was solved by trial-and-error methods through a series of successive approximations

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[9] Warren and Chipman, Phys. Rev. 75, 1629 (1949).

leading to a consistent set of parameters. Three equations of the same sort, but involving the values of S^2, were solved for T less than T_c.

The curves so obtained, giving the order parameters as functions of temperature, are shown in Fig. 3. For convenience the values of α_i/α_i^0 rather than α_i have been plotted, α_i^0 being the value of α_i for the case of perfect order. Thus all variables plotted vary from zero for zero order to unity for perfect order. The experimental values obtained by x-ray diffraction methods for temperatures of 405, 460, and 550°C,[7] are added for comparison. The agreement is within the limits of experimental error. In particular, the theory agrees with experiment in giving a negative value for α_3/α_3^0, that is, a positive value for α_3, for T greater than T_c. From the experimental observations of this, and other, reversals of sign it was deduced[7] that there was a "liquid-like" distribution of atoms about a given atom, with the tendency for defect or excess of one kind of atom being more dependent on the radial distance from the origin than on the lattice coordinates. It appears that such a distribution is predicted directly by the theory, and may be regarded as a natural consequence of the structure and energy relations within the crystal lattice. This prediction, and the general magnitudes found for the order parameters are not affected by any reasonable change in the value assumed for the ratio of V_2 to V_1.

In the same way, values of the order parameters have been calculated for AB alloys with structures that are simple-cubic, body-centered cubic, and face-centered cubic. No experimental results are available for comparison. For the hypothetical case of an AB alloy with simple-cubic structure, values of α_i were calculated on the assumption that all α_i with i greater than 3 had the limiting values of zero for T greater than T_c, or $\pm S^2$ for T less than T_c, and $V_i=0$ for i greater than 1. The values found for $-\alpha_1$ are compared with the values of $\sigma(=-\alpha_1)$ given by Bethe's second approximation for this structure, in Fig. 4. The present theory gives a much sharper drop in the value of $-\alpha_1$ for temperatures just below the critical temperature.

CONFIGURATIONAL ENERGY AND SPECIFIC HEAT

The average energy of ordering associated with a particular pair of atoms, one of which is one of the ith—nearest neighbors of the other, is given by $2m_Am_BV_i\alpha_i$. There are $Nc_i/2$ such pairs of atoms in the system. Hence the total configurational energy for the whole system, referred to the state zero order, is given by

$$E'=Nm_Am_B\sum_i c_i\alpha_iV_i.$$

If, as is usual, the energy is referred to the perfectly ordered state, we may write

$$E=E'+E_0=Nm_Am_B\sum_i c_iV_i(\alpha_i-\alpha_i^0).$$

Since the energy terms V_i decrease rapidly with i, the summation contains very few terms of appreciable magnitude, and both the configurational energy and the configurational specific heat, given by dE/dT, may be calculated readily from the values found for the order parameters.

In Table I the values, obtained from such calculations, for various energies and relevant ratios are compared with the values obtained from other theories and experimentally, as reported by Nix and Shockley.[10]

A failing common to most theories of order is that the value of the specific heat predicted by them for alloys such as CuZn is much too low for temperatures just below the critical temperature. Thus the table shows that the values given by Bethe and Kirkwood are less than half the experimental value for CuZn. The present theory gives a much sharper decrease in the order coefficients in this temperature range, and so gives a higher value for the specific heat. It can be shown, in fact, that the order coefficients given by the Eqs. (1) decrease infinitely fast just at T_c, so that the specific heat increases without limit, although there is no discontinuity in energy, and so no latent heat. Such an infinity in the specific heat could not be observed in practice. In any measurement the value of the specific heat obtained is an average taken over the range of fluctuation in temperature and composition in the specimen. Hence the maximum observable specific heat will be finite. For example, for an effective temperature fluctuation of $0.01T_c$, the maximum specific heat observable for CuZn would be $7R$.

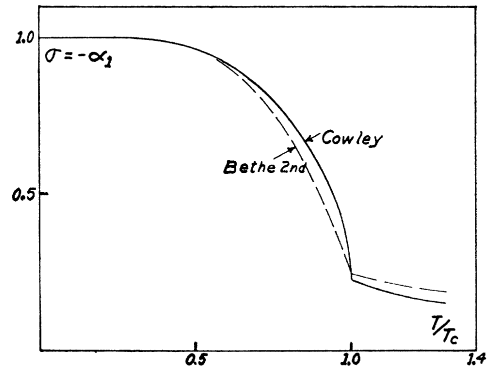

FIG. 4. Nearest neighbor order parameter for simple-cubic lattice.

VARIATION OF ORDER WITH COMPOSITION

For temperatures above the critical temperature, the general Eqs. (1) are valid for all compositions, and may be solved for various values of the ratio m_A/m_B to give the order parameters as functions of composition for given values of the energy terms and temperature. This has been done for the Cu—Au system assuming the value of V_1 found for Cu_3Au, and disregarding other energy terms.

If the same value of V_1 is assumed for all compositions, the values of α_i are symmatrical about the 50:50

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[10] Nix and Shockley, Rev. Mod. Phys. **10**, 1 (1938).

composition. However, it seems probable that V_1 varies rapidly with the average distance between neighboring atoms, and in the Cu—Au system the unit-cell dimension varies approximately linearly from 3.61*kX* for pure copper to 4.07 *kX* for pure gold. For the calculation of order parameters it was assumed that V_1 was proportional to the inverse sixth power of the unit cell dimension, and so of the average distance between atoms. The results for α_1 and α_2 for $T=770°\text{C}$ are shown in Fig. 5. The maximum values occur at about 45 percent gold. The experimental values plotted are values of α_1 calculated by Professor B. Averbach from the emf data given by Weibke and Quadt[11] for the same temperature.

The case of long-range order in an alloy of arbitrary composition has been treated by Easthope[12] and by Shockley.[13] Both treatments lead to the prediction of only one maximum in the value of the critical temperature for Cu—Au alloys; that at the 50:50 composition. No indication of the experimentally observed maximum at the 3:1 composition was obtained.

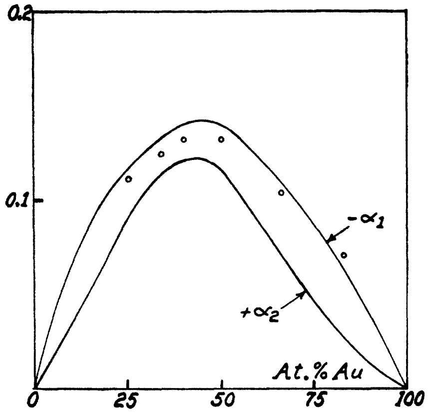

FIG. 5. Variation of short-range order parameters with composition in Cu-Au system for $T=770°\text{C}$.

If a direct substitution of the limiting values of α_i, as worked out above, is made in the general Eq. (1), the resulting equations for S give a critical temperature varying parabolically with m_A or m_B, with a maximum at the CuAu composition, as found by Shockley. However, this direct substitution involves the assumption that for any composition a super-lattice exists for which two kinds of atomic sites are present in exactly the same ratio as the two kinds of atoms. For the face-centered cubic structure of the Cu—Au alloys, the available sites can be divided only in the ratios 1:1 or 3:1 unless a super-structure "unit-cell" consisting of two or more face-centered cubic cell is considered. The formation of such a multiple "unit-cell," however, would involve, in effect, an ordering of atoms separated by distances greater than the nearest-neighbor distance in the lattice. Hence the ordering energies involved would be small, and the formation of a multiple unit-cell super-lattice would not take place except at temperatures too low for the rate of formation to be observable. Hence it may be assumed that the available atomic sites may be divided only in the ratios 1:1 or 3:1. For an arbitrary composition, then, limitations are imposed on the values of the order parameters by the conditions that r_α and r_β, the fractions of α- and β-sites rightly occupied, cannot exceed unity. The relation between the limiting value of α_i and S then varies with the amount of long-range order present.

For example, for an alloy near the 3:1 composition, but with an excess of A atoms, the restriction that r_α is less than unity leads to the conditions, $S<3/4m_A$, and the limiting value of α_i for i even, $\alpha_{\text{even}}<3m_B/m_A$. When the amount of long-range order present is very small the restriction is ineffective, and we may write as before, $\alpha_{\text{even}}=(16/3)m_Am_BS^2$. For the maximum value of long-range order, $S=3/4m_A$, the second term of Eq. (1)

TABLE I. Comparison of the values for various energies and relevant ratios as obtained from various theories and by experiment.*

Structure	Source	E_0	$\frac{RT_c}{E_0}$	$\frac{E(T_c-)}{E_0}$	Q/R	$\frac{E(T_c+)}{E_0}$	$E_c(\sigma)$	$\frac{RT_c}{E(T_c+)}$	$\frac{C(T_c-)}{R}$	$\frac{C(T_c+)}{R}$
AB alloy Simple cubic	$B+W$	$NV_0/8$	2.0	1.0	0	1.0	0	2.0	1.50	0
	Bethe no. 1	$3NV/2$	1.65	0.80	0	0.800	0.200	2.06	1.90	0.119
	Bethe no. 2	$3NV/2$	1.581	0.754	0	0.754	0.246	2.10	2.14	0.203
	Kirkwood	$3NV/2$	1.577	0.789	0	0.789	0.211	2.00	4.23	0.134
	Present	$3NV/2$	2.0	0.780	0	0.780	0.220	2.56	∞	0.17
AB alloy Body-centered cubic	Bethe no. 1	$2NV$	1.738	0.857	0	0.857	0.143	2.03	1.78	0.081
	Kirkwood	$2NV$	1.707	0.854	0	0.854	0.146	2.00	2.21	0.086
	Present	$2NV$	2.00	0.823	0	0.823	0.172	2.42	∞	0.12
	Experiment								5.1	
A_3B alloy Face-centered cubic	$B+W$	$3NV_0/32$	2.19	0.792	66	1.00	0	2.19	2.36	0
	Peierls	$3NV/4$	1.33	0.18	78	0.54	0.46	2.38	—	0.16
	Present	$3NV/4$	2.00	0.308	84	0.748	0.44	2.68	0.43	0.17
	Experiment				63			2.60		

* $E(T_c-)$ = configurational energy just below T_c. $E(T_c+)$ = configurational energy just above T_c. Q = latent heat of ordering at the critical temperature. $E_c(\sigma)$ = energy retained by short-range order just above T_c. $C(T_c-)$ = configurational specific heat just below T_c. $C(T_c+)$ = configurational specific heat just above T_c. E_0 = energy difference between perfect order and complete randomness for N atoms.

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must be written

$$kT\ln\left\{\frac{(3+\alpha_i)[(3m_B^2/m_A^2)+\alpha_i]}{(3m_B/m_A-\alpha_i)^2}\right\}$$

in order to give the correct values of α_i for $T\rightarrow 0$. The change is equivalent to the substitution in this term of $(m_A/3m_B)\alpha_i$ for α_i, so that we put

$$\alpha_{\text{even}}=\frac{16}{3}m_Am_BS^2\cdot\frac{m_A}{3m_B}.$$

For intermediate states of long-range order, it is reasonable to assume that the restriction on r_α introduces a correction to the value of α_{even} which varies with S, or, more probably, S^2. Hence we substitute in the second term of Eq. (1), the relation

$$\alpha_{\text{even}}=\frac{16}{3}m_Am_BS^2\cdot\left\{1-\left(\frac{4m_A}{3}\right)^2\left(1-\frac{m_A}{3m_B}\right)S^2\right\}.$$

For considerations of the critical temperature, the correction to be applied will involve S_c, the value of the long-range order immediately below the critical temperature. This will be zero for the 1:1 composition, but finite for all other compositions. For the case under consideration, we find

$$T_c=\frac{8}{k}\cdot m_Am_B\left(V_1-\frac{3}{2}V_2+\cdots\right)\left[1-\left(\frac{4m_A}{3}\right)^2\left(1-\frac{m_A}{3m_B}\right)S_c^2\right]^{-1}.$$

Similar expressions may be obtained for other composition ranges.

From such expressions the values of T_c were obtained by a series of approximations. The values of S_c first used were those calculated from the simple theory giving a parabolic variation of T_c. The values of T_c so obtained were then used to recalculate S_c, and second approximations for T_c were found. These second approximations were used to give the plot of T_c against composition shown in Fig. 6. For comparison, the experimental phase-diagram determined by Haughton and Payne[14] from electrical resistance measurements is added.

It is seen that the main features of the phase-diagram have been correctly predicted. The theory gives a broad maximum at the 1:1 composition, and a sharper maximum at the 3:1 composition. In the theoretical calculation, the value of T_c for Cu_3Au was assumed, and the assumption that V_1 varies with the inverse sixth power of the average distance between atoms was again employed. This latter assumption rendered the curve unsymmetrical, and depressed the maximum at the 1:3 composition to about 190°C. At temperatures as low as this, the rate of ordering is very low, so that the failure of experimental measurements to reveal a maximum in T_c at the $CuAu_3$ composition is accounted for. The assumption of a more rapid variation of V_1 with interatomic distance would depress this maximum still further.

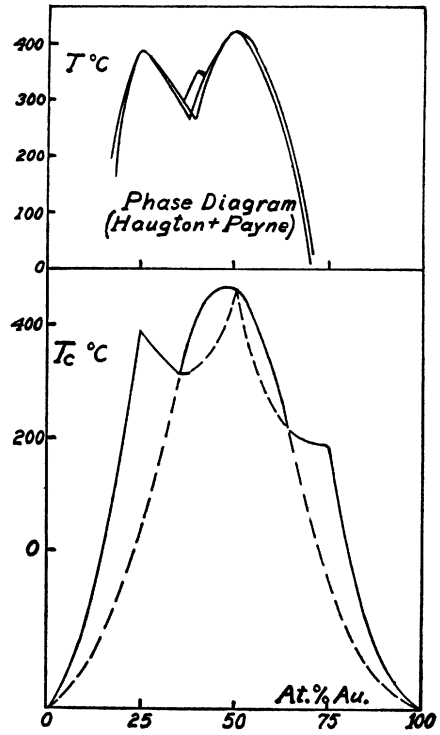

FIG. 6. Theoretical variation of T_c with composition in Cu-Au system, compared with experimental phase-diagram.

No account has been taken of the change in structure from face-centered cubic to tetragonal near the CuAu composition. However, the critical temperature predicted for CuAu is 460°C, in reasonable agreement with the experimental value of 425°C.

It thus appears that the present theory is capable of predicting short-range order parameters with fair accuracy, and long-range order and critical temperature rather more approximately for alloys of arbitrary composition in such a system that of Cu—Au. Similarly it could be applied to a wide range of other alloy systems, showing ordering, and could be extended to the consideration of various related problems without undue difficulty. Where experimental data have been available for comparison, the agreement has in most cases been within the limits of experimental error.

In conclusion I wish to thank Professor B. E. Warren for the interest he has shown in this work, and the Commonwealth Scientific and Industrial Research Organization for a research studentship.

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