PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

Computer Simulation of the Structure Associated with Local Order in Alloys*

P. C. GEHLEN AND J. B. COHEN
Materials Research Center and Department of Materials Science, The Technological Institute, Northwestern University, Evanston, Illinois

(Received 25 January 1965; revised manuscript received 18 March 1965)

Atomic configurations of binary alloys have been generated by a computer using experimentally measured short-range and long-range order parameters and 4000–16 000 atoms. This program did not use energetic considerations; atoms were selected at random and interchanged, if the change in the parameters was toward the experimental values, until computed and experimental values coincided. In systems based on the fcc lattice it is shown that the three first short-range order parameters are sufficient to give a reliable picture of the structure of the real alloy. For Cu_3Au above the critical temperature, small ordered volumes suspended in a random matrix were observed. Below the critical temperature, two-dimensional antiphase domains were found. For $Cu_{72}Au_{28}$ the regions were two-dimensional at low temperatures, but three-dimensional closer to the critical temperature. Some of the excess Au atoms were found in domain boundaries. The rest of them were distributed at random over the matrix. With Cu-14 at.% Al, there were chains of Al second neighbors. The results are discussed in terms of a number of experimental observations and theroetical suggestions.

I. INTRODUCTION

CERTAIN alloys are known to be ordered; that is, each of the atomic species occupies a specific sublattice in the structure. When such an alloy is heated to a given temperature, the long-range order parameter S (which is a direct measure of the fraction of a given atom type on its sublattice) drops from a maximum value to a value characteristic of that temperature. Above a certain critical temperature T_c, one kind of atom no longer has a tendency to be on a specific sublattice ($S=0$) but is found in equal proportions on all of them. Nevertheless, even above T_c, the atoms are generally not arranged at random. There is a tendency to order in shells near any one atom. In some alloys there is only short-range order, but no long-range order at any temperature, and in others there is clustering, i.e., a tendency for like atoms to be neighbors. In order to describe these kinds of "local order," Cowley[1] introduced the Warren short-range order parameters, α_k:

$$\begin{aligned}\alpha_k &= 1-p_{10}^k/m_0 = 1-(1-p_{11}^k)/m_0 \\ &= 1-p_{01}^k/m_1 = 1-(1-p_{00}^k)/m_1. \qquad (1)\end{aligned}$$

p_{10}^k is the probability of finding a 0 atom in the kth shell around a 1 atom and p_{11}^k, p_{00}^k, and p_{01}^k are defined in a similar way; m_0 and m_1 are the atomic fractions of 0 and 1 atoms in the alloy.

In this paper we shall be concerned only with order, not with clustering.

The α_k's can be obtained directly from a Fourier inversion of the diffuse scattering from an alloy[1]; most of the available data have been obtained with x rays. α_k is really a Patterson function, or autocorrelation function, but unlike the situation for a compound, it can vary greatly from unit cell to unit cell in the structure. As a result of this variation, the known techniques for interpreting Patterson functions for periodic structures are not useful; the period is the entire crystal. Furthermore, if measurements are made at a temperature where the atoms can interchange appreciably, the measurement is also an average over a period of time.

Despite this complexity, attempts have been made to describe the microstructure of alloys having a given set of α_k's and S. These attempts can be divided into three categories (and reference will be made only to the work on order). The first approach is based on finding models of very small ordered "particles" that fit the observed shapes of the superstructure peaks[2–5] and the diffuse scattering intensity.[6–10] Another approach is based on interpreting the kinetics of changes in properties associated with changes of S.[2,3,4,11,12] Finally, configurations have been simulated with high-speed computers[13–16] using simple energy models to control atomic interchange. Although the principle of this Monte-Carlo method is well defined, the use of greatly simplified energy calculations leads to uncertainty in the real meaning of the configurations.

The equilibrium value of any given physical property is really a weighted average over all possible microstates, the probability attached to each microconfiguration being proportional to the Boltzmann factor $\exp(-E/kT)$, where E is the internal energy and k and T have their usual meanings. The standard deviation

---

* This research was sponsored by Advanced Research Projects Agency through the Northwestern University Materials Research Center.

[1] J. M. Cowley, J. Appl. Phys. 21, 24 (1950).

[2] C. Sykes and F. W. Jones, Proc. Roy. Soc. (London) **A157**, 213 (1936).

[3] C. Sykes and H. E. Evans, J. Inst. Metals **58**, 225 (1936).

[4] F. W. Jones and C. Sykes, Proc. Roy. Soc. **A166**, 376 (1938).

[5] A. J. C. Wilson, Proc. Roy. Soc. (London) **A181**, 360 (1943).

[6] D. R. Chipman, J. Appl. Phys. **27**, 739 (1956).

[7] S. C. Moss, Sc.D. thesis, Massachusetts Institute of Technology, 1962 (unpublished).

[8] R. Kaplow, Sc.D. thesis, Massachusetts Institute of Technology, 1958 (unpublished).

[9] L. H. Schwartz and J. B. Cohen, J. Appl. Phys. **36**, 598 (1965).

[10] B. Borie and C. J. Sparks, Acta Cryst. **17**, 827 (1964).

[11] F. P. Burns and S. L. Quimby, Phys. Rev. **97**, 1567 (1955).

[12] L. R. Weisberg and S. L. Quimby, Phys. Rev. **110**, 338 (1958).

[13] L. Guttman, J. Chem. Phys. **34**, 1024 (1961).

[14] L. D. Fosdick, Phys. Rev. **116**, 565 (1959).

[15] P. A. Flinn and G. M. McManus, Phys. Rev. **124**, 54 (1961).

[16] J. R. Beeler and J. A. Delaney, Phys. Rev. **130**, 962 (1963).

of the configurational internal energy of the microstructures which have to be considered is equal to the excess specific heat. Hence, far from a critical point, i.e., in a region where the excess specific heat is small, this deviation is small and the energies of the microstructures over which the average is taken do not vary drastically. The α_k's, which are related to the configurational energy[17,18] then do not vary much from one configuration to another. The problem in understanding the meaning of the α_k's, in these cases, reduces to finding arrangements of the atoms such that all the α_k's are satisfied. The α_k's for a given state of an alloy must in fact be related and not independent; the atoms must be arranged in such a way that α_1 is obtained for the first shell around each atom while α_2 results for atoms in the second shell, etc. Clearly each atom is involved in several of these average parameters, because an atom may be a first neighbor to one and, say, a third neighbor to another atom. There may be a unique solution to this problem in a practical sense and it could well be that only the first few α_k's are really important in determining the atomic array. If this is true, one might be able to say that a configuration satisfying for example α_1, α_2, and α_3 can be taken as representative of the actual configuration for the alloy, not just one of many very different configurations. So far this problem has not been developed successfully analytically.

The purpose of this paper is to propose a computer method which generates the microstructures corresponding to a given set of α_k's (the three first α_k's are considered) and S. The basic idea of this approach is purely geometrical; the final configuration must have a number of $1-0$ pairs for each shell such that the resulting α_k's agree with the experimentally determined values. No energetic considerations are made. The alloys considered were: Cu_3Au above and below T_c, $Cu_{72}Au_{28}$ below T_c, Cu-(14.5 at. % Al), and Ag-Zn. These alloys are based on the fcc lattice, except Ag-Zn which is based on the bcc lattice. Models are presented in each case. The configurations for a given set of α_1 to α_3 were generated by starting the computing process with an ordered alloy and then with a random alloy. Except for Ag-Zn, the microstructures came out similar in these two cases and the values of higher order α_k's agreed reasonably well with the measured values. Thus, all of the atomic arrangements do indeed have a definite appearance for a given set of α_k's, and only a small number of these is needed to describe the microstructure in systems based on the fcc lattice.

II. THE COMPUTATIONAL METHOD

The chief aim of the method to be described is to generate an atomic configuration for a given alloy system satisfying an experimental set of values for the first three α_k's and S. This configuration is considered as being characteristic of the given α_k's and S. This does not mean that two configurations satisfying the same such set, but generated along two different paths, could be rigorously superimposed. But on the other hand, as will be shown in a later section, if one defines a suitable set of criteria for "equivalence," such as density of ordered regions (if these exist), volume fraction of ordered material, shape, etc., one finds that the resemblance between two such configurations is quite good. (The configurations to be presented can only be considered as representing equilibrium in so far as this is implied by the imposed values of the α_k's and S.)

Fcc and bcc models with ten unit cells on an edge were used. One fcc system with $20\times20\times10$ unit cells was examined. The programs corresponding to these three models being very similar, we will focus attention on the smaller fcc model. In order to minimize surface effects and to effectively extend the crystal to infinity, periodic boundary conditions were used; a macroscopic crystal was obtained by surrounding each $10\times10\times10$ system by a copy of itself on each side.

The fcc lattice can be decomposed into four interpenetrating simple cubic sublattices which will be designated by α, β, γ, and δ (Fig. 1) and similarly the bcc lattice can be considered as two simple cubic sublattices. A storage location was assigned to each lattice site in the computer. As only binary alloy systems were examined, atoms of one kind were represented by a one, atoms of the other kind by a zero. The indices of each site were x, y, and z, where x ran from 1 to 10, 11 to 20, 21 to 30 and 31 to 40 for the α, β, γ, and δ sublattices, respectively, and y and z from 1 to 10 for each of them. The input data to the computer was as follows: (a) the occupancy of each lattice site, (b) the initial number of 1-atoms in the first, second, and third shells around each atom. (Two initial states were used. For a fully ordered initial state these numbers were the same in each cell and could be readily calculated by inspection of the structure. For a random initial alloy these numbers were computed by examining the surrounding of each atom after producing a random alloy from an ordered one, by imposing $\alpha_1=\alpha_2=\alpha_3=0$, with the program to be described below), (c) the initial and final total numbers of (1,0) pairs [not (0,1) pairs] in each shell, $(1,0)_k{}^i$ and $(1,0)_k{}^f$, $(k=1-3)$. For the initial configuration, these numbers were machine computed from the information in (b) and for the final one, they

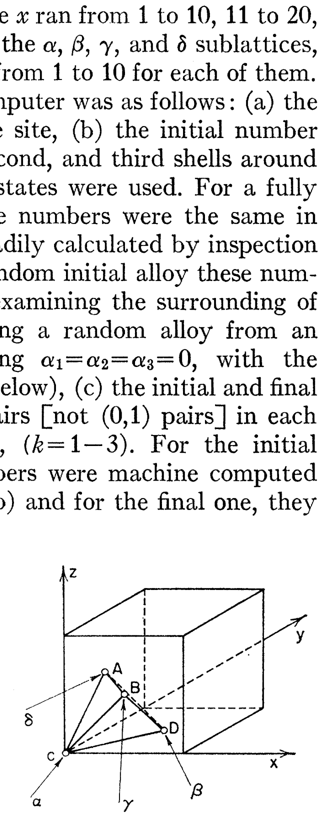

FIG. 1. The four sublattices in a fcc lattice (α, β, γ, and δ). ABC and $ABCD$ are a nearest-neighbor triplet and quadruplet, respectively.

---

[17] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[18] J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

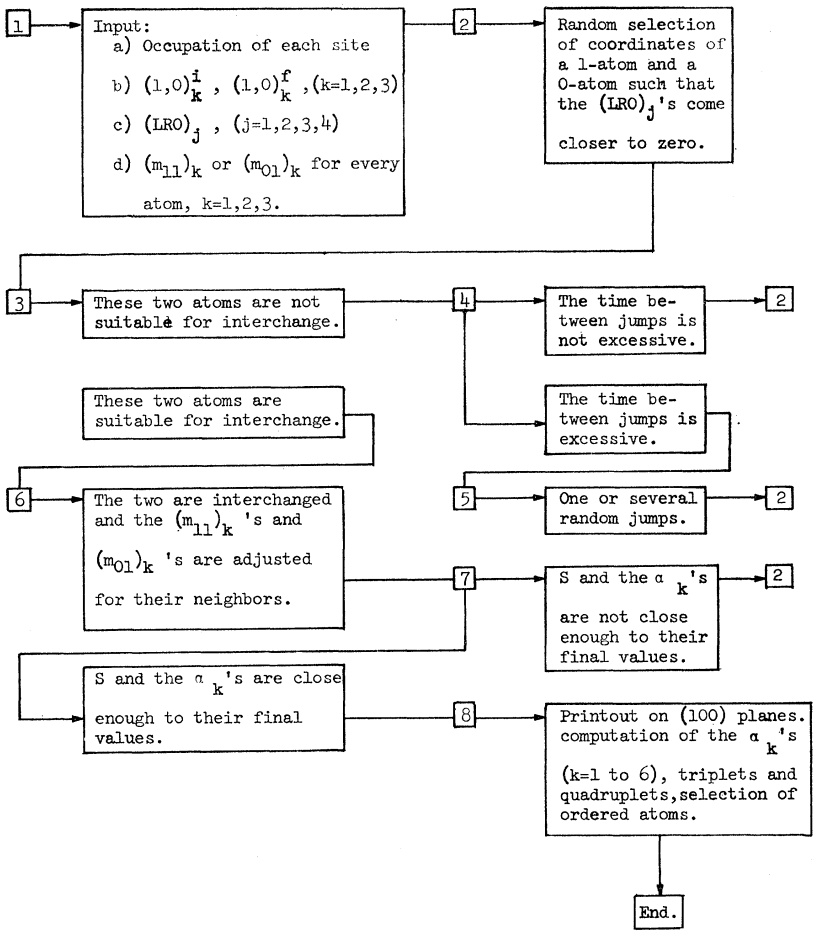

FIG. 2. Flow chart for the computer program.

were obtained from

$$(1,0)_k{}^f=(1-\alpha_k)m_1m_0C_kN\,, \qquad (2)$$

(where C_k is the coordination number of the kth shell and N the total number of atoms in the crystal), (d) the differences $(\mathrm{LRO})_j$ $(j=\alpha,\beta,\gamma,\delta)$ between the initial and final numbers of 1 atoms on each sublattice; the initial number of 1-atoms on each sublattice was found by a direct count, while the final number was deduced, for example, for a structure like $\mathrm{Cu_3Au}$ where the Au atoms (1) occupy primarily the α sublattice and the Cu atoms (0) primarily the β, γ, δ sublattices from

$$S=\tfrac{3}{4}(r_\beta-m_0)/(1-m_0)+\tfrac{1}{4}(r_\alpha-m_1)/(1-m_1)\,, \qquad (3)$$

where r_β and r_α are the fractions of the β- and α-sublattice sites correctly occupied. This equation and a mass balance for 0 and 1 atoms allows the calculation of r_α and r_β, if D is known. [Equation (3) is valid in the case of a stoichiometric or nonstoichiometric alloy and was used with the measurements for $\mathrm{Cu}_{3-x}\mathrm{Au}_{1+x}$ with $S\neq 0$.]

From the definition of $(\mathrm{LRO})_j$, $(\mathrm{LRO})_j=0$ when the experimental value of S is satisfied.

After these data were fed into the computer, the program selected two lattice sites at random,[19] one corresponding to the 1 atom which was to be interchanged, the other to the 0 atom. The generation of random numbers being very time consuming, the three coordinates of one site were derived from a single random number. Suppose a number A, between 0 and 3999 is generated at random, then A can be defined as

$$A=(x-1)\times 100+(y-1)\times 10+(z-1)\,,$$

where x can vary between 1 and 40 and y and z between 1 and 10.

In order to adjust S, only random numbers were accepted for which the x value fell on a sublattice with $(\mathrm{LRO})_j>0$ for the 1 atom and on a sublattice with $(\mathrm{LRO})_j<0$ for the 0 atom (i.e., if on a sublattice there were more 1 atoms than there should be in the final configuration, 1 atoms would be removed from this sublattice and put on a sublattice where 1 atoms were missing); see Fig. 2.

The sites selected with these random numbers were not necessarily occupied by 1 and 0 atoms. First consider

---

[19] For the generation of random numbers, see the A. Rotenberg J. Assoc. Computing Mach., **7**, 75 (1960).

the choice of the 1 atom and suppose that the site $(x_1y_1z_1)$ was occupied by a 0 atom. Then the program would scan successively the sites having their coordinates between x_1 and x_s, y_1 and 10, and z_1 and 10 until it found a site occupied by a 1 atom. (x_s was the maximum value x_1 could have on the previously determined sublattice.) A 0 atom was then similarly chosen. Before the interchange was made, the total number of 1–0 pairs for a given vector length r_k was $(1,0)_k^1$, and this same quantity after the jump, $(1,0)_k^2$, would be

$$(1,0)_k^2=(1,0)_k^1+2[(m_{11})_k-(m_{01})_k+\delta], \qquad (4)$$

where $(m_{11})_k$ and $(m_{01})_k$ are, respectively, the numbers of 1 atoms in the kth shell around the 1 and 0 atoms to be interchanged. δ is unity if the sites are kth nearest neighbors and 0 if they are not. These quantities were computed for the three first shells and the interchange was made only if each of the $(1,0)_k^2$'s was not further from the $(1,0)_k^f$'s than were the $(1,0)_k^1$'s. If the selected 0 atom did not satisfy these conditions, the scanning was continued until a more suitable 0 atom was found. If no 0 atom could be found, the procedure was started over again with a new random number.

In certain cases it was found that an appreciable amount of computing time could be saved by selecting the 1 and 0 atoms in two other ways:

(1) Instead of accepting the first 1 atom selected, the scanning was continued until a 1 atom with special $(m_{11})_k$'s was found. These specifications were made in such a way that the chance for interchange was improved. Suppose for example, that $(1,0)_k^f>(1,0)_k^1$. Then $(m_{11})_k>(m_{01})_k$ is required for a jump. But if for example, $(\bar{m}_{01})_k=4$ and $(\bar{m}_{11})_k=0.5$ (where the barred quantities are averages over the whole configuration), very few 1 and 0 atoms will satisfy the conditions for interchange and many selections of random sites must be made before a jump will take place. On the other hand, if a 1 atom is selected only if it has say $(m_{11})_k>2$, then an interchange is more likely to occur. Statistically, the final configuration is the same, because in either procedure the same 1 atoms would have been interchanged (as very few are available). This procedure can only be justified when the average values of $(m_{11})_k$ and $(m_{01})_k$ are extreme. Nevertheless in other cases, it was shown that configurations generated by the two different procedures were equivalent.

(2) Sometimes it happened that even though the special selection procedure discussed above was used, no two atoms suitable for an interchange could be found within a reasonable time interval, say five minutes. (Normally between 60 and 100 jumps were made in a minute in the IBM 709 computer used in this study.) In this case one or several jumps where only the change in S was taken into account were accepted. After this, the program could usually proceed again. Both of these operations were initiated by hand during a run by the operation of sense switches.

After each jump, the $(m_{01})_k$'s and $(m_{11})_k$'s for all the atoms around the two interchanged atoms were adjusted. Finally, it was checked how far S and the α_k's were from the experimental values and the program was stopped, as soon as $(\mathrm{LRO})_j=0$ $(j=\alpha,\beta,\gamma,\delta)$ and

$$\sum_{k=1}^{3}|(1,0)_k^2-(1,0)_k^f|\leq 10.$$

The resulting configurations on (100), (010), and (001) planes were printed out. (Other planes were also used occasionally as a check on the appearance of regions.) The values of α_4, α_5, α_6 and the distributions of 1 and 0 atoms over all the nearest-neighbor triplets and quadruplets (see Fig. 1) were also computed.

It is not certain *a priori* that the configurations generated by this procedure represent the actual microstructure corresponding to the given experimental set of α_k's and S, but instead just one possible one. No mathematical approach could even be found to prove that the three first α_k's were sufficient to characterize a configuration. Nevertheless, experimentally it could be shown that the use of the three first α_k's and S gave results indicating that the configuration *was* representative of the actual atomic arrangement. This could be done by considering data where the excess specific heat was small and by comparing the two final configurations having the same α_k's and S, but generated from two different initial states (say a completely ordered and a completely random initial state). Several aspects of the results were compared from both initial states. (a) The distribution of the two kinds of atoms over all nearest-neighbor triplets and quadruplets was obtained. In a binary alloy, the 1 and 0 atoms can occupy the triplets and quadruplets in nine ways, namely, 1-1-1, 1-1-0, 1-0-0, 0-0-0, 1-1-1-1, 1-1-1-0, $\cdots$, 0-0-0-0. Let N_{111}, N_{110}, $\cdots$ be the numbers of triplets and quadruplets having three 1 atoms, two 1 atoms, and one 0 atom, etc. Seven equations can be written between these nine unknowns, the number of 1-0 pairs in the first shell and the fractions of 1 and 0 atoms. In the case of 4000 atoms and an fcc structure: $N_{000}+N_{001}+N_{011}+N_{111}=$ total number of triplets$=32{,}000$; $N_{0000}+N_{0001}+N_{0011}+N_{0111}+N_{1111}=$ total number of quadruplets$=8{,}000$; $N_{001}+2N_{011}+3N_{111}=$ total number of 1 atoms$\times 24=24\times N_1$; $N_{001}+N_{011}=$ total number of nearest neighbor 1-0 pairs$\times 2=2m_1m_0C_1(1-\alpha_1)=2P_{10}^1$; $4N_{0000}+N_{0001}=N_{000}$; $4N_{1111}+N_{0111}=N_{111}$; $3N_{0001}+2N_{0011}=N_{001}$. (If one introduces higher order α_k's and hence complexes of triplets and quadruplets, the number of unknowns increases faster than the number of new equations.) N_{000}, N_{001}, $\cdots$, N_{0011} can be written as functions of N_{0111} and P_{10}^1. In the systems studied, N_{1111} turned out to be zero. Knowing that all the N's have to be positive, an upper and lower limit can be found for each of them. These intervals are considerable and thus if the numbers of triplets and quadruplets agree for configurations

TABLE I. Results for Cu_3Au at 450°C. Data from Ref. (20).

	Experimental values	Results obtained with the computer						
		From initially ordered configuration using:			From initially random configuration using:			16 000 atom model[a]
		α_1	α_1, α_2	$\alpha_1, \alpha_2, \alpha_3$	α_1	α_1, α_2	$\alpha_1, \alpha_2, \alpha_3$	
α_1	−0.195	−0.1942	−0.1949	−0.1947	−0.1958	−0.1951	−0.1942	−0.1949
α_2	+0.215	+0.2942	+0.2168	+0.2160	+0.2689	+0.2168	+0.2147	+0.2152
α_3	+0.003	−0.0045	+0.0365	+0.0031	+0.0161	+0.0379	+0.0030	+0.0029
α_4	+0.077	+0.1395	+0.0627	+0.1329	+0.0858	+0.0511	+0.1313	+0.1407
α_5	−0.052	−0.0704	−0.0800	−0.0662	−0.0855	−0.0729	−0.0671	...
α_6	+0.028	+0.0610	−0.0173	+0.0487	−0.0093	−0.0296	+0.0507	+0.0577
Cu-Cu-Cu		10494	10466	10472	10442	10467	10481	10468
Cu-Cu-Au		19022	19094	19080	19150	19087	19061	19088
Cu-Au-Au		2474	2414	2424	2374	2425	2435	2421
Au-Au-Au		10	26	24	34	21	23	23
Cu-Cu-Cu-Cu		1242	1220	1224	1204	1223	1229	1225
Cu-Cu-Cu-Au		5526	5586	5576	5626	5575	5565	5578
Cu-Cu-Au-Au		1222	1168	1176	1136	1181	1183	1177
Cu-Au-Au-Au		10	26	24	34	21	23	22
Au-Au-Au-Au		0	0	0	0	0	0	1
No. of ordered Au atoms		558	473	473	544	461	462	465
No. of ordered Cu atoms		857	915	1102	1045	948	1121	1113
Number of jumps		750	1536	2273	3693	3473	4127	14705

[a] The results have been reduced to a 4000-atom model.

satisfying the same α_k's and S, this is not only by chance, but can be a proof of uniqueness. (b) The higher order α_k's ($k=4$ to 6) which were not adjusted by the program were determined and compared to the experimental values. (c) The total amount of ordered material was obtained. (d) If domains or ordered regions occurred, the density of these (and the average number of atoms they contained) was obtained. (e) The distribution of 1 atoms having a given number of 1 atoms in their kth shell was counted.

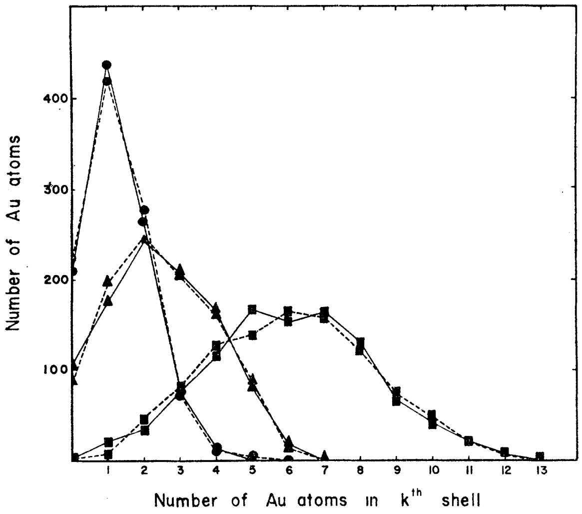

FIG. 3. Distribution of Au atoms in the three first shells around a Au atom. ●-first shell, ▲-second shell, ■-third shell; full line for initially ordered configuration, dashed line for initially random configuration. Cu_3Au at 450°C. Experimental data from Ref. 20.

If these points are satisfactory and in agreement starting from the two initial states, and data are used for a situation with low excess specific heat, the resultant configuration must be truly representative of the actual atomic structure—not just a "picture" of one possible arrangement.

III. RESULTS

(i) Alloys based on the fcc lattice

(*1*) Cu_3Au *above* T_c

The experimental data taken recently by S. Moss[20] at 450°C along with the computed results starting from a fully ordered and from a random configuration, are shown in Table I. Taking into account the experimental error (for the higher order α_k's) one can see that the agreement between the experimental and computed α_k's is quite good. In Fig. 3 the distribution of Au atoms around Au atoms for an initially ordered and an initially random configuration are shown superimposed; the agreement is good. Considering also the fact that at 450°C the excess specific heat of Cu_3Au is about 0.015 cal/g-°C,[2] it can be assumed that the configurations described below are representative of the actual crystal. (Using Moss'[20] value for the first neighbor energy only three near-neighbor bonds would have to be exchanged out of about 11 000 to account for this specific heat and this would not alter the configurations appreciably.)

Note also in Table I the very small changes in

---

[20] S. C. Moss, J. Appl. Phys. 12, 3547 (1964).

triplets and quadruplets when α_2 and α_3 are added to the input and the much larger changes in α_4, α_5, and α_6.

Table I shows the numbers of Au and Cu atoms with ordered surroundings. The definition of "ordered" is somewhat arbitrary and will be specified in each case discussed in this paper. For fully ordered Cu_3Au, Au atoms are at the corners and Cu atoms at the faces of the cubic unit cell. Rigorously then, an Au atom is in an ordered region for Cu_3Au if it has only Cu atoms in its first shell of 12 neighbors, none in its second shell of six neighbors. A Cu atom is in an ordered region if it has four Au atoms in its first shell, zero in its second, etc. (For random alloy, a Au atom has on the average nine Cu first neighbors and 4.5 Cu second neighbors, whereas a Cu atom has three Au first neighbors and 1.5 Au second neighbors.) Using a definition of order based on complete order one would find very few "ordered" atoms (atoms in boundaries of small ordered regions would not be "ordered" for example) and furthermore the ratio of the number of ordered Cu atoms to the number of ordered Au atoms would be far from the value of $m_{\mathrm{Cu}}/m_{\mathrm{Au}}$. This would occur because for a given set of α_k's, the average number of Au atoms around a Cu atom is much closer to the ordered value than for Cu's around an Au atom, i.e., the difference in number of neighbors of each kind between full order and randomness is much larger for a Au atom than for a Cu atom. For these reasons, it was decided to adopt a looser definition of an ordered atom, which would not have the above mentioned disadvantages. The following set of definitions gave satisfactory results: The Au atoms were ordered if there were 0, 1, or 2 Au atoms in the first shell and 3, 4, 5, or 6 Au atoms in the second shell. The Cu atoms were ordered if there were 4 Au atoms in the first shell and 0 or 1 in the second. (For a comparison of the results for a given set of data from two starting states it is only necessary to maintain the same definition.) In addition to a printout of all the atoms, another printout based on these definitions was extracted to help draw any ordered regions. This choice of ordered atoms had another use. The definition of an ordered Au atom being very loose, the total number of ordered Au atoms would be roughly proportional to the total amount of ordered material. On the other hand, the total number of ordered Cu atoms would give an indication of the degree of order inside any domains or of the size of such domains, if they occurred.

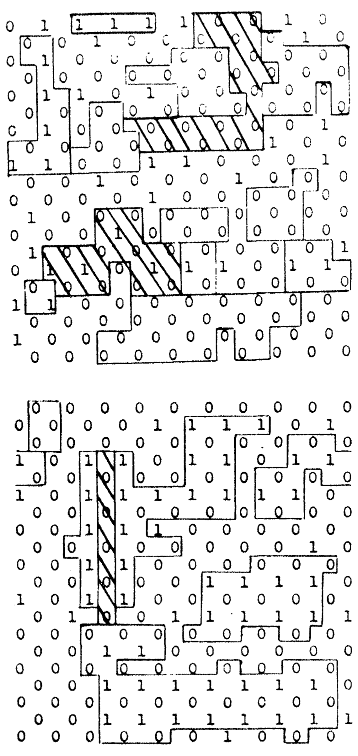

FIG. 4. Cu_3Au at 450°C—Data from Ref. 20. 1=Au, 0=Cu. Two consecutive (100) sections through a crystal having $S=0$, $\alpha_1=-0.1942$, $\alpha_2=+0.2147$, $\alpha_3=+0.003$, $\alpha_4=+0.1313$, $\alpha_5=-0.0671$ and $\alpha_6=+0.0507$. Notice the shaded areas, which are regions which appear to be ordered but which are really not because of wrong neighbors in the planes above or below the ones shown.

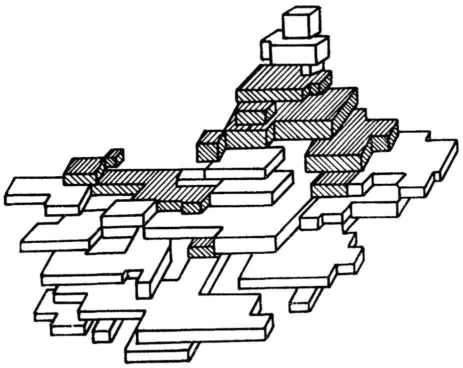

FIG. 5. Cu_3Au at 450°C—data from Ref. 20: Three-dimensional model of an ordered domain. The shaded regions have their Au atoms on a different sublattice from that of the white regions.

Figure 4 shows two consecutive (100) sections through the configuration, corresponding to Moss' data at 450°C. The whole configuration can be described as a random matrix in which ordered regions are suspended. (The shaded areas in the figure are regions which might appear to be ordered in this section, but which in fact are not, because of wrong neighbors in the planes above or below the section shown.) The ordered regions are composed of successive (100) layers whose shapes vary considerably from one plane to the next one, so that very irregular volumes result. The dimensions of these domains vary between 1 and 7 or 8 unit cells in the ⟨100⟩ directions. Some of these domains are connected through an antiphase boundary. Several interconnected domains are shown in Fig. 5. (The general shape of these regions was not affected by the

TABLE II. Results for Cu_3Au and $Cu_{72}Au_{28}$ below T_c. Experimental data from Ref. 9.

	Cu_3Au $S=0.80$					$Cu_{72}Au_{28}$ $S=0.71$		$Cu_{72}Au_{28}$ $S=0.83$	
		Results obtained with the computer							
	Experimental results	α_1 from random	α_1, α_2 from random	$\alpha_1, \alpha_2, \alpha_3$ from random	$\alpha_1, \alpha_2, \alpha_3$ from order	Experimental results	Computed results $\alpha_1, \alpha_2, \alpha_3$ from random	Experimental results	Computed results $\alpha_1, \alpha_2, \alpha_3$ from random
α_1	−0.265	−0.2642	−0.2642	−0.2651	−0.2644	−0.238	−0.2382	−0.280	−0.2790
α_2	+0.715	+0.7271	+0.7155	+0.7146	+0.7151	+0.620	+0.6209	+0.804	+0.8041
α_3	−0.209	−0.2212	−0.2223	−0.2091	−0.2092	−0.176	−0.1760	−0.250	−0.2499
α_4	+0.636	+0.6851	+0.6866	+0.6651	+0.6637	+0.540	+0.5706	+0.734	+0.7671
α_5	−0.223	−0.2305	−0.2275	−0.2323	−0.2349	−0.197	−0.2000	−0.253	−0.2549
α_6	+0.643	+0.6723	+0.6690	+0.6446	+0.6400	+0.544	+0.5579	+0.750	+0.7542
No. of Cu atoms in ordered matrix		2817	2810	2824	2830		2669		2806
No. of Au atoms in ordered matrix		857	854	851	859		872		950
No. of isolated Au atoms		13	11	21	30		82		68
Ratio of total No. of misplaced Cu at. to total No. of misplaced Au at.		1.28	1.30	1.18	1.20		0.76		0.34
Number of jumps		1047	1009	1401	1554		1164		6108

initial configuration or by the definition of an ordered atom.)

Raether[21] observed sharp superstructure peaks, using electron diffraction, even above T_c, where such peaks might be expected to disappear. Because of the small wave length in electron diffraction the tiny regions in Figs. 4 and 5 would give such sharp peaks and in fact if the more diffuse x-ray scattering due to local order is treated as due to small ordered particles the resulting dimension of these particles (about 12 Å) agrees well with the average dimension of the domains in Figs. 4 and 5.

One model with 16 000 atoms was made for Moss' data at 450°C starting from an ordered configuration. The results which have been reduced to a model of 4000 atoms are shown in the last column of Table I. Although here the history of the configuration was quite different from the one for a 4000 atom model, the results are in good agreement; the amount of ordered material is the same (i.e., the number of ordered Au atoms) and the degree of order inside the domains is also similar. Nevertheless, it should be pointed out that the configuration was not merely a superposition of four 4000-atom models. In the 16 000-atom model there was more freedom to arrange the domains. The random regions between two ordered regions changed their dimensions considerably. Suppose, for instance, that there are two ordered regions at least two unit cells apart. Then they can be shifted farther apart over any distance without changing the seven first α_k's appreciably.

Only the results for the most recent experimental data on Cu_3Au are presented here. Nevertheless, runs were made using several other sets of experimental data.[1,7,22] The results were as satisfactory in all cases and also quite similar regions were obtained.

Table I shows also the results for configurations where α_1 alone and α_1 and α_2 alone were adjusted. α_1 alone seemed to determine the distributions of Au and Cu atoms over the triplets and quadruplets (more com-

TABLE III. Experimental and computed φ_i's for Cu_3Au and $Cu_{72}Au_{28}$ below T_c (experimental values from Ref. 9).

	Cu_3Au $S=0.80$						$Cu_{72}Au_{28}$ $S=0.71$		$Cu_{72}Au_{28}$ $S=0.83$	
		Results obtained with the computer								
	Experimental results	α_1 from random	α_1, α_2 from random	$\alpha_1, \alpha_2, \alpha_3$ from random	$\alpha_1, \alpha_2, \alpha_3$ from order	After adjusting results in column 6 (see text)	Experimental results	Computed results; $\alpha_1, \alpha_2, \alpha_3$ from random	Experimental results	Computed results; $\alpha_1, \alpha_2, \alpha_3$ from random
φ_1	−0.052	−0.051	−0.051	−0.052	−0.051	−0.047	−0.057	−0.057	−0.032	−0.031
φ_2	+0.075	+0.087	+0.075	+0.075	+0.075	+0.076	+0.076	+0.076	+0.060	+0.060
φ_3	+0.004	−0.008	−0.009	+0.004	+0.004	+0.004	+0.005	+0.005	−0.002	−0.002
φ_4	−0.004	+0.045	+0.047	+0.025	+0.024	+0.004	−0.004	+0.026	−0.010	+0.023
φ_5	−0.010	−0.017	−0.014	−0.019	−0.022	−0.014	−0.016	−0.019	−0.005	−0.007
φ_6	+0.003	+0.032	+0.029	+0.005	+0.000	+0.000	+0.0005	+0.014	+0.006	+0.010

---

[21] H. Raether, Z. Angew. Phys. 4, 53 (1952).

[22] S. C. Moss, International Union of Crystallography, Sixth International Congress and Symposium, Rome, 1963, p. A 100 (unpublished).

pletely than was to be expected from the equations presented in the previous section) but not the total amount of ordered material. The adjustment of α_2 on the other hand determined the number of ordered atoms (i.e., the number of ordered Au atoms), but not the order inside the domains (given by the ordered Cu atoms).

The small experimental value of α_3[1,20] makes it difficult even to be sure of its sign in experimental determinations. For this reason the effect of variations in α_3 was studied while α_1 and α_2 were kept constant. The small changes required to maintain the magnitude of the measured value but change its sign have a negligible effect on the structure.

The general configuration at 405°C is similar to that for 450°C, but the total amount of ordered material is increased by about 20% at the lower temperature.

Beeler and Delaney[16] used a Monte Carlo approach with only a first-neighbor energy to allow a vacancy to move around in the alloy below T_c. The initial stages of ordering were observed and the regions that developed were quite similar to those presented here.

(*2*) Cu$_3$Au *below* T_c

The experimental data used in this section were taken from Schwartz and Cohen[9] for $S=0.80$. In this case the excess specific heat is of the order of 0.15 cal/g-°C$^{(2)}$, i.e., still quite low.

As shown in Table II, the computed results are in good agreement with the experimental values. Nevertheless it should be noted that the method of analysis used by Schwartz and Cohen did not yield the α_k's directly but the quantities φ_k:

$$\varphi_k=\alpha_k-\alpha_k^0S^2\,,$$

where α_k^0 represents the limiting value of α_k when the atoms on wrong sites are randomly distributed ($\alpha_k^0=bm_0m_1$ with $b=16/3$ for k even and $b=-16/9$ for k odd). The results are compared with the experimental φ_k's in Table III; the experimental errors for the φ_k's given by these authors were ±10% for k odd, ±30% for φ_2, ±200% for φ_4 and φ_6. The agreement between the experimental and computed φ_4 and φ_5 is then only fair, and the reasons for this will be discussed after more of the results are presented.

The most interesting sampling procedure for atoms was found in this case to be a count by eye of all the Cu and Au atoms which were not in the ordered matrix. First consider the case where the three first α_k's have been adjusted simultaneously, [see Fig. 6(a)]. In this case, starting from an ordered configuration, it was found that the alloy was composed essentially of an ordered matrix in which 10.5×10^{20} antiphase domains per cc were suspended. On the average each such domain contained 5.2 atoms, i.e., about seven percent of the atoms were in domains. In the case where a random alloy was used as the initial configuration, these numbers were found to be 11.2×10^{20} and 5.1, respectively. The domains were two-dimensional, lying on {100} planes, and were mostly rectangular, the sides lying along ⟨100⟩ directions. (A few domains were observed containing two or three layers stacked over each other.)

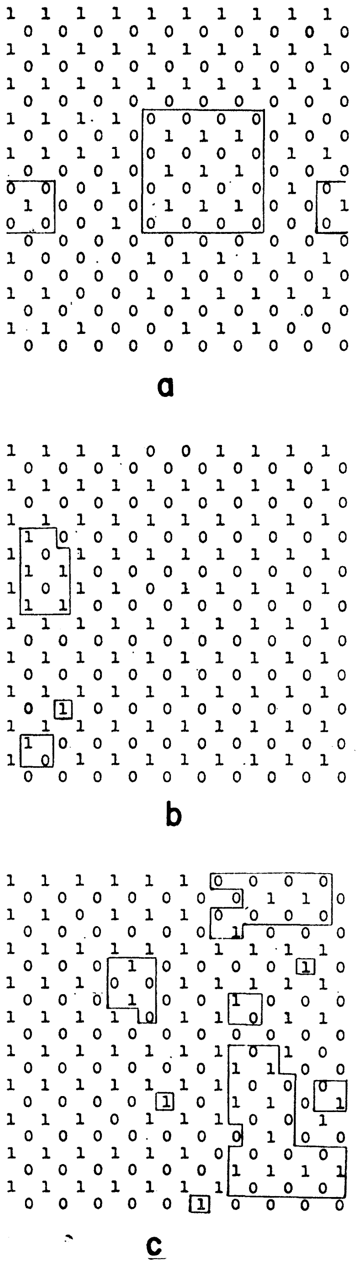

FIG. 6. (a) Cu$_3$Au below T_c: (100) section through the crystal. $S=0.80$, $\alpha_1=-0.2644$, $\alpha_2=0.7151$, $\alpha_3=-0.2092$, $\alpha_4=+0.6637$, $\alpha_5=-0.2349$, and $\alpha_6=0.6400$. (b) Cu$_{72}$Au$_{28}$ below T_c: (100) section through the crystal. $S=0.83$, $\alpha_1=-0.2790$, $\alpha_2=+0.8041$, $\alpha_3=-0.2499$, $\alpha_4=+0.7671$, $\alpha_5=-0.2549$, and $\alpha_6=+0.7542$. (c) Cu$_{72}$Au$_{28}$ below T_c: (100) section through the configuration. $S=0.71$, $\alpha_1=-0.2382$, $\alpha_2=+0.6209$, $\alpha_3=-0.1760$, $\alpha_4=+0.5706$, $\alpha_5=-0.2000$, and $\alpha_6=+0.5579$. Data from Ref. (9)—1=Au, 0=Cu.

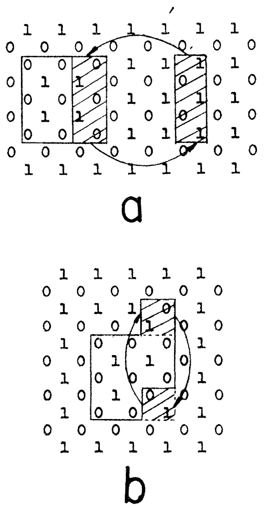

FIG. 7. Models for altering the antiphase domains of Fig. 6 to bring φ_i's within their experimental limits. 1 = Au, 0 = Cu.

Chipman[6] suggested this kind of region, but in attempting quantitative comparisons to the local order from his x-ray measurements he assumed that the composition of the domains did not change from one domain to another. The computer results reported here show that this assumption was not valid and this probably accounts for the poor agreement found by Chipman and also Schwartz and Cohen between measured α_k's and values calculated from such a model of tiny domains.

If α_1 alone was adjusted, the structure was quite similar and the total number of atoms in domains was not very much affected. The only difference was that the domain plates had a tendency to overlap. The effect of α_2 was to split the domains on $\{100\}$ planes. The overlapping in the third direction was still present.

As mentioned earlier, the values of φ_4 and φ_5 were not within the experimental error. Many attempts were made to slightly rearrange the antiphase domains in such a way that these two values would fall within the experimental accuracy without changing the values of any of the other φ_i's. All but one of these failed, so that the effect of φ_4 on the structure must be practically unique.

First consider Fig. 7(a) and suppose that the antiphase domain on the left is split into two parts and the two shaded areas interchanged. The changes in Au-Cu pairs will be, using Eq. (4), -8, $+10$, 0, $+12$, -20, and 0 for the first six shells. From the computer results for the initially ordered configuration, the number of Cu-Au pairs in the fourth shell is 3026 while from the experimental data this number must be at least 3204, even allowing for the experimental error. Hence 178 additional bonds must be created, or 14.8 domains like that in Fig. 7(a) must be split (less than 30% of the total number of domains). The changes in Cu-Au pairs in shells 1–6 then would be -118, $+148$, 0, $+178$, -296, and 0.

Now, considering the first-nearest-neighbor shell, the generated configuration contained 11 380 Cu-Au pairs, but there were 11 262 after the 14.8 domains had been split, while the minimum value compatible with the experimental data would be 11 338. Hence 76 additional bonds must be found.

Consider Fig. 7(b). If the two shaded areas are interchanged, the following changes in Cu-Au bonds are found for shells 1–6, respectively; $+2$, -4, 0, 0, $+4$, 0. Therefore 38 such changes are required to adjust α_1 again and the changes of the Au-Cu pairs in each shell would then be 76, -152, 0, 0, $+152$, and 0; and the over-all changes would be -42, -4, 0, $+178$, -144, and 0. The resulting values of the φ_i's are shown in Table III and are in excellent agreement with the experimental values; although no effort was made to bring φ_5 closer to its experimental value, it is in excellent agreement. Note that the changes discussed here are minor in terms of the appearance and percentage changes in the bond numbers. It appears that the adjustment of higher order φ_i's would produce a splitting of some of the domains and that their shape would become more regular.

(3) $Cu_{72}Au_{28}$ *below* T_c

The experimental data taken by Schwartz and Cohen[9] and the computed results are presented in Table II. Figures 6(b) and 6(c) show (100) sections through the crystals with $S=0.83$ and $S=0.71$, respectively. This set of data was run in order to determine how the nonstoichiometric Au atoms were distributed; the results here should be compared with those of the previous section. The maximum order in this alloy is $S=0.88$. $Cu_{72}Au_{28}$ $S=0.71$, corresponds to a state a few degrees below T_c, similar to Cu_3Au $S=0.80$. (A) The ratio of the number of Cu atoms in domains to the number of Au atoms in domains dropped from 1.5 for Cu_3Au $S=0.8$ to 1.1 for $Cu_{72}Au_{28}$ with $S=0.71$ and to 0.5 for $Cu_{72}Qu_{28}$ $S=0.83$, i.e., the number of Au atoms in domains was increased as compared to the stoichiometric case.[23] This increase as shown in Fig. 6 was due to the

TABLE IV. Results for Cu -14.5 at. % Al. (Experimental data from Ref. 27.)

		α_1 α_2, α_3	
	Experimental	From Order	From Random
α_1	-0.137	-0.1369	-0.1369
α_2	$+0.124$	$+0.1228$	$+0.1215$
α_3	$+0.096$	$+0.0957$	$+0.0959$
α_4	-0.041	-0.0328	-0.0381
α_5	$+0.011$	-0.0456	-0.0466
α_6	-0.184	-0.0909	-0.0879
Number of jumps		10 288	1527

---

[23] From the measured value of S and a mass balance one can calculate r_α and r_β and show without the computer that there are more wrongly occupied Au sites for $Cu_{72}Au_{28}$ than for Cu_3Au. However, the ratios reported here refer only to the domains and cannot be inferred from S. [See Eq. (3)].

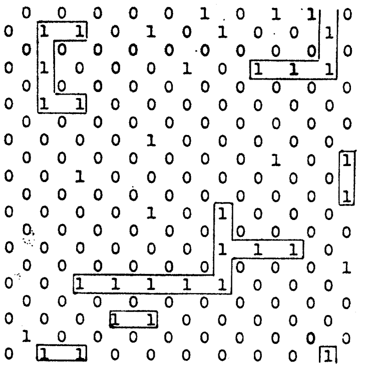

FIG. 8. Cu-14.5 at. % Al—data from Ref. (27): (100) section through a configuration with $S=0$, $\alpha_1=-0.1369$, $\alpha_2=+0.1215$, $\alpha_3=+0.0959$, $\alpha_4=-0.0381$, $\alpha_5=-0.0466$, and $\alpha_6=-0.0879$. 1 = Al, 0 = Cu.

presence of Au atoms in the boundaries of the domains. Cahn and Kikuchi[24] suggested that this could occur, as based on first-neighbor energies there is no difference in having the extra Au's in $Cu_{72}Au_{28}$ randomly distributed or in the boundaries. Their appearance in the boundaries in fact suggests that the second-neighbor energy has the same sign as the first, because there are more wrong (Au-Cu) second-neighbor bonds with the extra Au atoms in domain boundaries than if they are randomly distributed. Conflicting opinions have been expressed previously concerning the sign of this energy,[17,18,25,26] but this result supports the latest estimate.[7,20] (B) The number of isolated Au atoms was increased, as compared to Cu_3Au, from 5.7×10^{20} per cc to 13×10^{20} for $S=0.83$ and to 15.6×10^{20} for $S=0.71$ (i.e., about 2% of the total number of atoms). Thus the Au atoms do not seem to avoid each other as has often been suggested[5]; in the boundaries of the domains or as random wrong Au atoms they have many Au neighbors that could be avoided if they were inside the domains.

For $S=0.83$ all the domains were one layer thick. The density of plates was 6.3×10^{20} per cc. Each plate contained 5.3 atoms on the average. For $S=0.71$ the density of {100} plates was found to be 17×10^{20} per cc. Only 30% of these were not clustered. The rest of them formed domains several layers thick suspended in an ordered matrix. The shapes of these plates were no longer rectangular but were more like the ones found in Cu_3Au above T_c (Fig. 5). Thus, just below T_c the nonstoichiometric alloy has a very different structure from that for Cu_3Au.

(4) Cu-14.5 at.% Al

The experimental data[27] along with the computed α_k's are presented in Table IV. A (100) section through the crystal is shown in Fig. 8. The microstructure can be pictured as a Cu matrix in which are suspended Al rods, one atom thick. Each Al atom is linked to the next one in a rod by a second-nearest-neighbor bond. These rods were not always straight lines but were often composed of segments, each of which lay along one of the ⟨100⟩ directions. Several rods intersected or ran parallel to each other one lattice distance apart, so that in some cases, little plate-like domains appeared. It is interesting that although the local-order parameters are characteristic of an alloy containing short-range order, the configuration can better be pictured as a Cu matrix in which little Al clusters are suspended. The atoms in these clusters are linked together by second-nearest-neighbor bonds and the local order comes from the Cu first neighbors to these rods.

In this particular case, the computer could easily count the numbers of atoms in each domain. Two Al atoms are considered to be in a domain if and only if they have a common second-nearest-neighbor bond. Table V shows the distribution of the Al atoms among these domains. Although the numbers of jumps between the initial and final configurations were quite different (10 288 jumps from the ordered configuration and 1527 from the random one), the agreement between the two configurations is excellent. First- and third-nearest neighbor Al-Al bonds could be adjusted independent of the number of second-neighbor bonds by placing the rods in a suitable way with respect to each other. Any place two rods are only one nearest-neighbor distance apart first-nearest neighbor Al-Al bonds are created, and each place two lines run perpendicular to each other on planes one lattice distance apart third-nearest neighbor Al-Al bonds are created.

Recently, Borie, and Sparks[10] proposed a model for the distribution of the Al atoms in the Cu matrix for this alloy system. In their experiments [on Cu-16 at. %

TABLE V. Distribution of Al atoms in domains in Cu-14.5 at. % Al[a].

	Numbers of domains containing between 1 and 5 atoms	5 and 10 atoms	10 and 15 atoms	15 and 20 atoms	20 and 25 atoms	25 and 31 atoms	Total number of domains
From Order	163	10	7	3	2	2	187[b]
From Random	162	11	7	4	0	2	186

[a] The numbers are related to a 4000-atom model.
[b] This corresponds to 3.88×10^{21} domains/cc.

---

[24] J. W. Cahn and R. Kikuchi, J. Phys. Chem. Solids 20, 94 (1961).

[25] G. Fournet, Compt. Rend. Reunion Ann. Avec. Comm. Thermodynam. Union Intern. Phys. (Paris, 1952), p. 199.

[26] C. H. Sutcliffe and F. E. Jaumot, Jr., Acta Met. 1, 725 (1953).

[27] C. R. Houska and B. L. Averbach, J. Appl. Phys. 30, 1525 (1959).

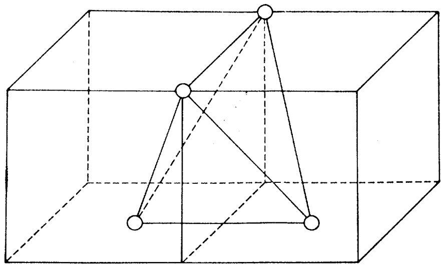

FIG. 9. Two face-centered cubic unit cells containing a tetrahedron as used by Borie and Sparks[10] to represent local order in Cu-16 at. % Al. (The Al atoms are represented by open circles.)

Al], they did not actually determine the α_k's but quantities involving complex sums of these, which could not be solved uniquely for the α_k's; all possible solutions showed that α_1 was its minimum, i.e., there were no Al-Al first-nearest-neighbor bonds. They assumed that the Al atoms were placed on the corners of a tetrahedron as depicted in Fig. 9 and then assumed a distribution of such tetrahedra in the crystal in such a way that no first-nearest-neighbor Al-Al bonds were created and that yielded values for these complex sums that were close to their experimental values. A simple calculation shows that for Borie's and Spark's data, or the data in Ref. 27 for Cu-14.5 at. % Al, such a distribution would be quite complex; the tetrahedra must, in fact, be linked together in big clusters. If the tetrahedra were isolated there would be 145 of them in a 4000 atom crystal of 14.5 at. % Al, and as each one has two and four Al-Al pairs involving second and third neighbors a total of 290 and 580 second- and third-nearest neighbor Al-Al pairs, respectively, would be created as compared to 437 and 1580 calculated from α_2 and α_3 reported in Ref. 27. In order to make up for the missing pairs, big clusters have to be assumed and the tetrahedra would no longer be recognizable. In the printout not even one complete isolated tetrahedron could be found. Clusters were not the predominant feature anyway. Between 85 and 90% of the Al atoms were in rods. The remainder of them were in little two-dimensional plates.

(ii) Alloys Based on the bcc Lattice

Alloys based on the bcc lattice provide another interesting opportunity to examine the effect of the α_k's on the structure of an alloy. α_2 and α_3 involve atoms on the same sublattice whereas, this is true only for α_2 in structures based on the fcc lattice. For the fcc structure each atom has twelve first-, six second-, and twenty-four third-nearest neighbors, while for the bcc structure these numbers are, respectively, eight, six, and twelve; therefore, not only is the relation between sublattices more poorly defined, but also the relation between individual atoms. Unfortunately, accurate α_k's are not really available for the bcc case. Two systems that involve only local order, Ti-Mo[28] and Li-Mg,[29] have been studied using powder specimens, and in obtaining the α_k's by a Fourier transformation of suitable intensity data, there was too much overlap between the first and second shells to separate α_1 and α_2 in a straightforward manner. β-Ag-Zn has been examined at a temperature above T_c[30] using a single crystal, but the thermal-diffuse scattering was so large that after correcting for it, the α_k's obtained were not very accurate. There was an indication that the α_k's fell off rapidly and were close to the random values by the fifth shell. An attempt was made to use this set of data, with the computer program reported here. The fcc program could be easily adapted; the only change was that only two sublattices were involved.

The results were not as satisfactory as in the fcc case. Even when α_4 was added to include a value, besides α_1, involving the two sublattices, this did not seem to be sufficient to determine the structure uniquely. The total amount of ordered material varied by about 25% for runs from the two different initial states and the distribution of the atoms over the ordered regions varied drastically from one run to the other. Attempts starting from an ordered configuration had to be rejected because too few jumps were required to adjust the α_k's and hence the influence of the initial configuration was too important; there was one very large ordered region.

That two configurations having almost the same α_k's can have quite different aspects was not observed for the fcc case. It is not clear whether this difference is due to the data or to the different geometries of the two types of structures. More conclusive analysis of the meaning of local order in alloys based on the bcc lattice must await more precise data.

IV. CONCLUSIONS

It has been shown that the computer can be used to generate the microstructure of a binary alloy by using the experimentally determined short-range order and long-range order parameters (α_k and S). Definite ordered regions were found above T_c which were different in shape in different systems.

At least for alloys based on the fcc lattice the first three short-range order parameters give essentially the same structure starting from different initial states, and good agreement with the experimentally observed higher order α_k's (which are not used by the computer). A qualitatively correct picture can be obtained in some cases with only α_1.

If α_1 alone is used, the distribution of the atoms over the triplets and quadruplets is determined. In some cases even the amount of ordered material is determined (Cu_3Au below T_c) while in the case of Cu_3Au above T_c,

---

[28] J. M. Dupouy and B. L. Averbach, Acta Met. 9, 755 (1961).
[29] F. H. Herbstein and B. L. Averbach, Acta Met. 4, 414 (1956).
[30] E. Suoninen and B. E. Warren, Acta Met. 6, 172 (1958).

α_2 is required to determine this amount. α_3 and α_2 determine the distribution and size of the ordered domains.

Though it could not be shown analytically that the first three α_k's were sufficient to practically determine the structure of an fcc alloy, from the computer results it could be seen that higher order α_k's would not add much to the appearance of the structure. Higher order α_k's may be required however for bcc structures.

The computer program used here is written in such a way that the configuration corresponding to any given composition in a binary alloy or degree of order can be generated. It could prove useful in a study of kinetics of ordering, by measuring the changes in the α_k's with time and following the changes in the shapes and sizes of the ordered regions by starting each computation with the final configuration for the previous time.

It could also be helpful in pursuing the problem of determining alloy structure analytically. This type of program might also be applied to other problems, such as the distribution of magnetic spins, using results of studies of the diffuse magnetic scattering of neutrons; and it could also be altered to use the experimental data on pair densities in liquids.

ACKNOWLEDGMENTS

The authors wish to thank the Northwestern University Computing Center (and the National Science Foundation whose funds helped establish the Center) for the extensive use of the computer. One of the authors, (P.C.G.) is indebted to A. L. Morris and W. R. Decker for invaluable advice on the computer programs. Our thanks go also to Mrs. A. Gehlen who helped draw many of the models.

PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

Higher Order Corrections to the Molecular-Field Theory of the Magnetic State

G. Dresselhaus
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

(Received 9 March 1965)

A generalized Weiss molecular-field calculation is presented for the solution to the Heisenberg Hamiltonian. Thermodynamic perturbation theory is used to define a series of approximations for the magnetic state. In particular, the equations for the ferromagnetic state are expanded near the transition temperature T_c, in order to examine the temperature dependence of χ. Numerical results suggest that 6th-order perturbation theory gives the susceptibility accurately in the temperature range above $1.5T_c$.

I. INTRODUCTION

THE Heisenberg Hamiltonian which describes the behavior of some magnetic insulators has been solved previously in the low-temperature limit ($T \ll T_c$) and in the high-temperature limit ($T \gg T_c$), where T_c is the critical temperature at which a phase transition takes place. The region around the transition, $T \approx T_c$, is intriguingly simple experimentally[1]; nevertheless, no really satisfactory theory yet exists for this temperature region.

The theory developed in the present paper, though applicable to the magnetic state, is closely related to the high-temperature expansion, which if carried to high order gives information about the transition region. The scheme is based on thermodynamic perturbation theory[2] which is not valid at low temperatures. The high-temperature expansion for the magnetic susceptibility derived in this work is suggestive of the Padé approximant scheme discussed extensively by Baker and others.[3] Whereas the Padé approximant scheme is a mathematical extension of an expansion of the susceptibility, the present perturbation theory approach is a physical extension of the Weiss molecular-field solution to the Heisenberg Hamiltonian.

Section II contains the mathematical development of the approximation scheme. In Sec. III the calculation is specialized to ferromagnetic nearest-neighbor interactions. An expansion of the magnetization is then made near the transition temperature T_c which allows a calculation of both the high-temperature susceptibility (paramagnetic state) and the temperature dependence of the magnetization at the transition (ferromagnetic state). In Sec. IV the results of the ferromagnetic calculation are discussed with regard to fitting the susceptibility and magnetization to a simple power law.

---

* Operated with support from the U. S. Air Force.

[1] P. Heller and G. Benedek, Phys. Rev. Letters **14**, 71 (1965); 8, 428 (1962).

[2] L. D. Landau and E. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1958), p. 93.

[3] G. A. Baker, Jr., Phys. Rev. **124**, 768 (1961); J. W. Essam and M. E. Fisher, J. Chem. Phys. 38, 802 (1963); J. Gammel, W. Marshall, and L. Morgan, Proc. Roy. Soc. (London) **A275**, 257 (1963).