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ORDER-DISORDER IN CU-AU ALLOYS

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WRIGHT AIR DEVELOPMENT CENTER

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United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by F. E. Jaumot, Jr., Instructional Assistant, under the supervision of Foster C. Nix, Professor of Physics and Principal Investigator. This report is in the nature of a final report and summarizes the work on Air Force Contract No. AF 33(038)-11057, under Project No. 51-615A. The work was administered under the direction of the Aeronautical Research Laboratory, Research Division, Wright Air Development Center, with Captain R. B. Sellers acting as project engineer.

The graduate students who performed much of the work described in the individual sections of this report are, Charles H. Sutcliffe, Sections IV, V and VI: and Woodward W. Sanville, Sections II, III and VII. We would also like to express our appreciation for the valuable technical assistance provided by Mr. Fred Witt, Jr. and Mr. Charles Stills.

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ABSTRACT

This report summarizes the result of studies on order-disorder in copper-gold alloys in the composition range from 0 to 35 atomic percent gold. A dilatometric study of the order-disorder transformation in this composition range has been made. The nature of the order-disorder transformation has been studied using x-ray techniques and a two-phase transformation observed for gold-rich compositions. The long-range order present in non-stoichiometric alloys has been studied as a function of temperature. The short-range order present at various temperatures above the critical temperature in a sample containing 23 atomic percent gold has been measured. An experiment designed to study the kinetics of the ordering by x-ray methods is described and some general conclusions are presented.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

LESLIE B. WILLIAMS
Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

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I. INTRODUCTION

General Background.

The principal motivation for studying order-disorder in alloys is the need for a better understanding of the effects of changes in the distribution of atoms in solid solutions and, at present, the phenomena of order provide us with the only means of changing that distribution in anything like a controlled manner. The way in which the various atoms are distributed in a solid solution affects nearly all physical properties of the alloy (e.g. mechanical, magnetic, and thermal properties, resistance to corrosion, etc.). The ultimate goal, of course, is an understanding of the detailed nature of the forces between atoms in alloys and the relationship between these forces and the distribution of the atoms, particularly in the special cases of order-disorder alloys, precipitation systems, and ferromagnetic alloys.

We chose the alloys of copper and gold in the composition range from 0 to 35 atomic percent gold as the system in which to study order-disorder. This particular alloy system was chosen because it is the classical case of an order-disorder alloy on which most theories of the ordering phenomena in A_3B type alloys are based. Further, we chose Cu-Au alloys because we felt that, although much data was present in the literature on this system, there were many gaps in this data which needed to be filled. Finally, a prime reason for choosing this system was the controversy in progress over whether or not the order-disorder transformation in the region near Cu_3Au was a heterogeneous or homogenious transformation.

Briefly, the salient features of the Cu-Au system in the composition range near Cu_3Au are: both ordered and disordered alloys have face-centered cubic structures; at temperatures above a given critical temperature region the alloy is disordered with Cu and Au atoms occupying the lattice sites in a random way; below these temperatures the gold atoms occupy preferentially the cube corners and the copper atoms the face-center positions; the unit cell of the ordered phase is considerably smaller than the unit cell of the disordered phase; there is a severe decrease in the electrical resistivity of these alloys as they pass from an ordered to a disordered condition; ordering is not completed at a single temperature, but increases in degree as the temperature is lowered; x-ray patterns of ordered alloys exhibit superstructure lines, which can be used to detect order and to obtain a quantitative measure of the degree of order present.

We elected to use three principle tools to study the Cu-Au

system: X-rays, electrical measurements, and dilatometric measurements. The particular studies we concentrated on were designed to fill the gaps in the literature in the degree of long-range order present in samples of non-stoichiometric composition, the nature of the order disorder transformation over the entire composition range near Cu_3Au, and the effects of ordering on the thermal expansion of non-stoichiometric alloys. These studies have been described in detail in Progress Reports and publications and only the principal features of each will be summarized in this report.

Preparation of the Samples.

The copper used in preparing the alloys employed in this work was obtained from Johnson, Matthey and Co., and contained 99.998 percent Cu, with traces of Ag, Ni, and Pb. The gold obtained from J. Bishop and Co., was 99.99 percent Au with traces of Pb, Fe, and Ag.

The metals were combined in proper proportions in high purity graphite crucibles and melted with intermittent agitation in a vacuum single crystal furnace similar to that described by Nix (1). After cooling, the ingots were melted and lowered through the heating coil at a rate of about 2.5 inches per hour, with the pressure in the furnace less than 10^{-4} mm of Hg. After removal from the furnace, the single crystals were annealed in evacuated Vycor tubes for 48 hours at temperatures 50°C below their melting points. After annealing, filings from both ends of the crystals were studied by means of x-ray back-reflection photographs to check the homogeneity and the composition of the samples. The desired samples were then cut from the single crystal ingots which were of two sizes; $\frac{1}{4}$ inch in diameter by 1 to $1\frac{1}{2}$ inches long, or $\frac{1}{2}$ inch in diameter by 3/4 inch long. The various compositions used in this work are listed in Table I, which also gives the phase of the study in which the particular compositions were used. Throughout this report, we shall use the nominal composition (Table I) to identify particular samples and shall always mean atomic percent when quoting a given percentage figure.

The wires used in the resistivity studies were drawn to 0.020 inches from the same homogeneous ingots used to prepare the single crystals.

All samples were polished and electrolytically etched in a five percent solution of potassium cyanide before the ordering heat treatment and were etched only lightly thereafter.

The heat treatment given the samples after fabrication was as follows: 48 hours at 875°C, 24 hours at 600°C, 24 hours at 400°C 200 hours at 360°C, 300 hours at 300°C, slowly cooled (2-3°C per hour) to 200°C, 72 hours at 200°C, then slowly cooled to room

TABLE I

Compositions of Cu-Au Alloys

Nominal Composition (percent Au)	Atomic Percent Au	Use*
2	2.0	II, III
5	5.1	II, III
10	10.2	II, III
15	15.5	II, III, IV, V
17.5	17.6	II
19	19.5	II
20	20.25	III, IV, V
22	22.1	II, III
23	23.45	IV, V, VI
25	25.07	VII
28	28.25	II, III, IV, V
30	30.40	III, IV, V
32	32.2	II, III
34	34.2	IV, V

*II Thermal expansion measurements

III Resistivity measurements

IV Nature of the order-disorder transformation measurements

V Long-range order measurements

VI Short-range order measurements

VII Studies of the kinetics of the order-disorder transformation

temperatures. This heat treatment produces what we consider to be well ordered samples. Most of the samples used in repeat runs in the volume expansion work were ordered using the following treatment: 24 hours at 25°C below the ordering temperature, cooled to 250°C at 5°C per hour, 24 hours at 250°C, then cooled to room temperature at 10°C per hour. We do not consider these samples to be perfectly ordered but they were sufficiently ordered to produce reproducible results in the volume expansion studies.

II A DILATOMETRIC STUDY OF THE ORDER-DISORDER TRANSFORMATION

Introduction.

The work discussed in this section has been described in detail in our Progress Report #9 (2). The principle results have been presented before the American Physical Society (3).

When a Cu-Au alloy transforms from a random, or disordered, state to an ordered state, the transformation is accompanied by a decrease in volume which is proportional to the final degree of order attained. This decrease in volume is detectable by an interferometer, even when the degree of ordering is lower than that detectable by the usual x-ray measurements on "super-structure" lines.

The principal difficulty encountered when using dilatometric techniques to study order-disorder is that absolute thermal equilibrium is probably not attained. This difficulty is minimized in the present work by the use of photographic recording of the data, which enables us to use very slow heating rates. One of the many advantages of this method is that the accuracy attainable, apart from equilibrium considerations, is independent of the rate of heating.

Previous work on Cu-Au alloys using the dilatometric method (4) was carried out for alloys containing 22, 25 and 30 atomic percent Au. The present work was done on alloys containing 10, 17.5, 19, 28, and 32 atomic percent Au. Thus the entire ordered region in the neighborhood of Cu_3Au has been investigated by means of volume expansion measurements.

Experimental Technique.

The interferometric-dilatometer used in this work was identical to that described by Nix and MacNair (5). The desired samples were cut from single crystals (See Section I), pointed on one end, and sized so that they would yield three or four fringes when placed in the interferometer. They were then given the ordering treatments previously described.

The rate of heating of the samples in the interferometer was controlled by a Brown program-controller-recorder. The heating program followed was: 15 degrees per hour to 150°C, 20 degrees per hour from 150°C to 270°C, 6 degrees per hour from 270°C to 340°C and 20 degrees per hour thereafter. The fringes exhibited by the interferometer were photographed simultaneously with the fused silica refraction thermometer (5), using the mercury green line (5460 Å) from a mercury arc. Photographs were made once every 30 seconds in the critical region and once every 90 seconds outside the critical region. The exposure time was three seconds.

The data was recorded directly from the film, and the temperature indicated by the refraction thermometer read from a calibration curve. Then the increase in length, Δl, read directly from the film as fringe shifts, was plotted as a function of T. The slopes of the Δl _versus_ T curves give the true coefficients of expansion as a function of temperature.

Results.

Figure 1 gives the curve of the coefficient of expansion as a function of temperature for the 19.5 percent Au alloy. Figure 2 gives a similar curve for a 28 percent Au alloy. If one regards a single peak in the curve as the expected or normal behaviour on going through the order-disorder transformation, then it can be said that the double peak obtained from the 28 percent sample is anomalous. However, multiple peaks were observed for all samples containing more than 25 percent gold and as shown in Figure 3, where we have plotted the coefficient of expansion as a function of temperature in the critical region only, the multiplicity of the peaks is not confined to a two-fold multiplicity. There are three distinct asymmetric peaks in the curve given by the 32 percent Au sample.

Before we discuss these results, it should be pointed out that changes in length equal to 1/8 the wavelength of the mercury green line could be detected quite easily. Also, almost exact reproducibility was obtained for different "runs" on samples of the same composition. At least two "runs" were made in every case.

Discussion of Results.

The data indicate that samples containing less than 17.5 percent Au (specifically samples containing 2, 5, 10 and 15 percent Au) exhibit no detectable ordering. The 17.5 percent sample showed a slightly anomalous rise in the coefficient of expansion in the temperature range between 250°C and 350°C. It is probable that some long-range order is present and its effects would be more marked if absolute thermal equilibrium could be attained.

Samples containing from 17.5 through 25 percent gold (including the data of Nix and MacNair (4)) show marked ordering phenomena,
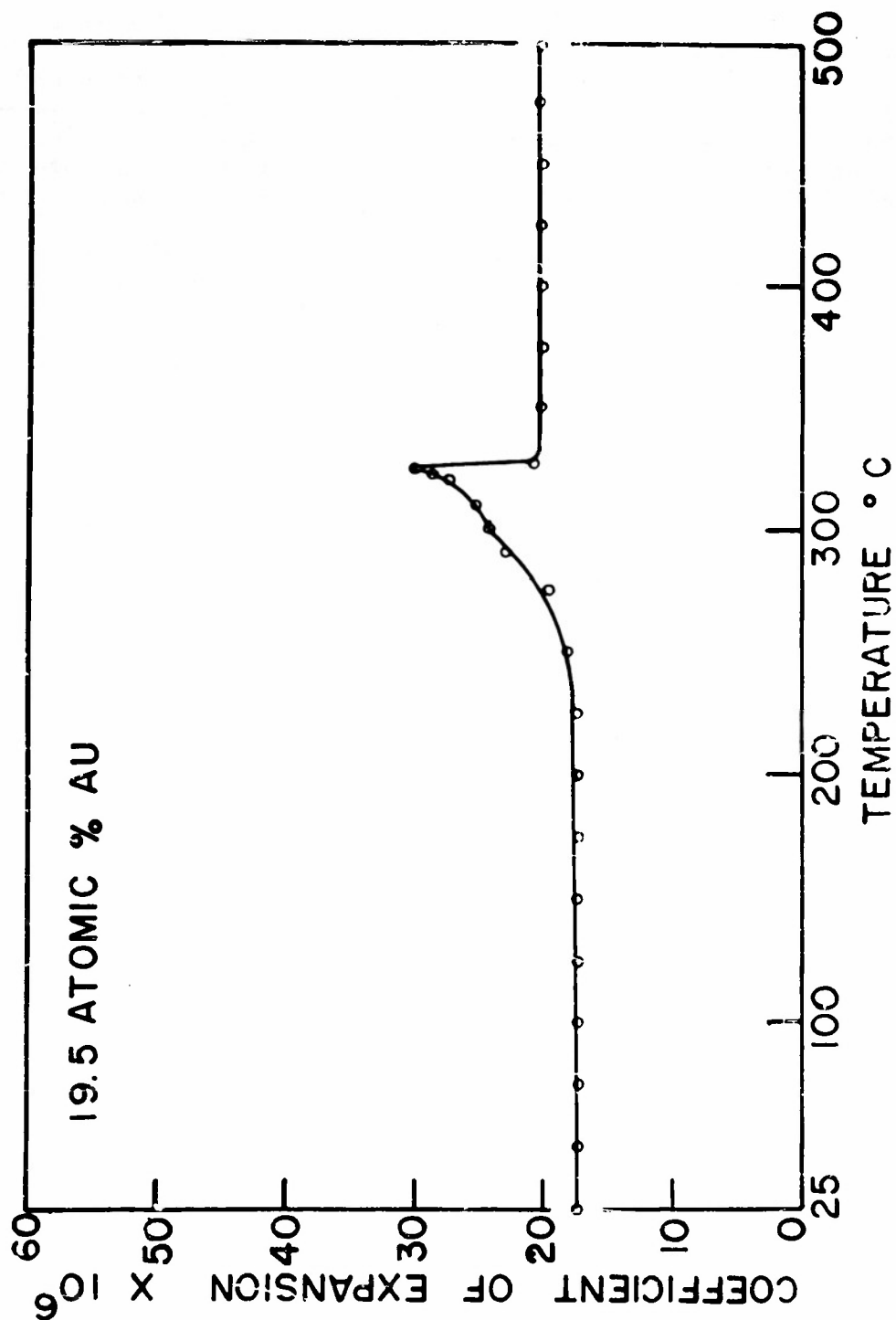
Fig. 1 - Coefficient of Expansion as a Function of Temperature for a Copper-Rich Sample
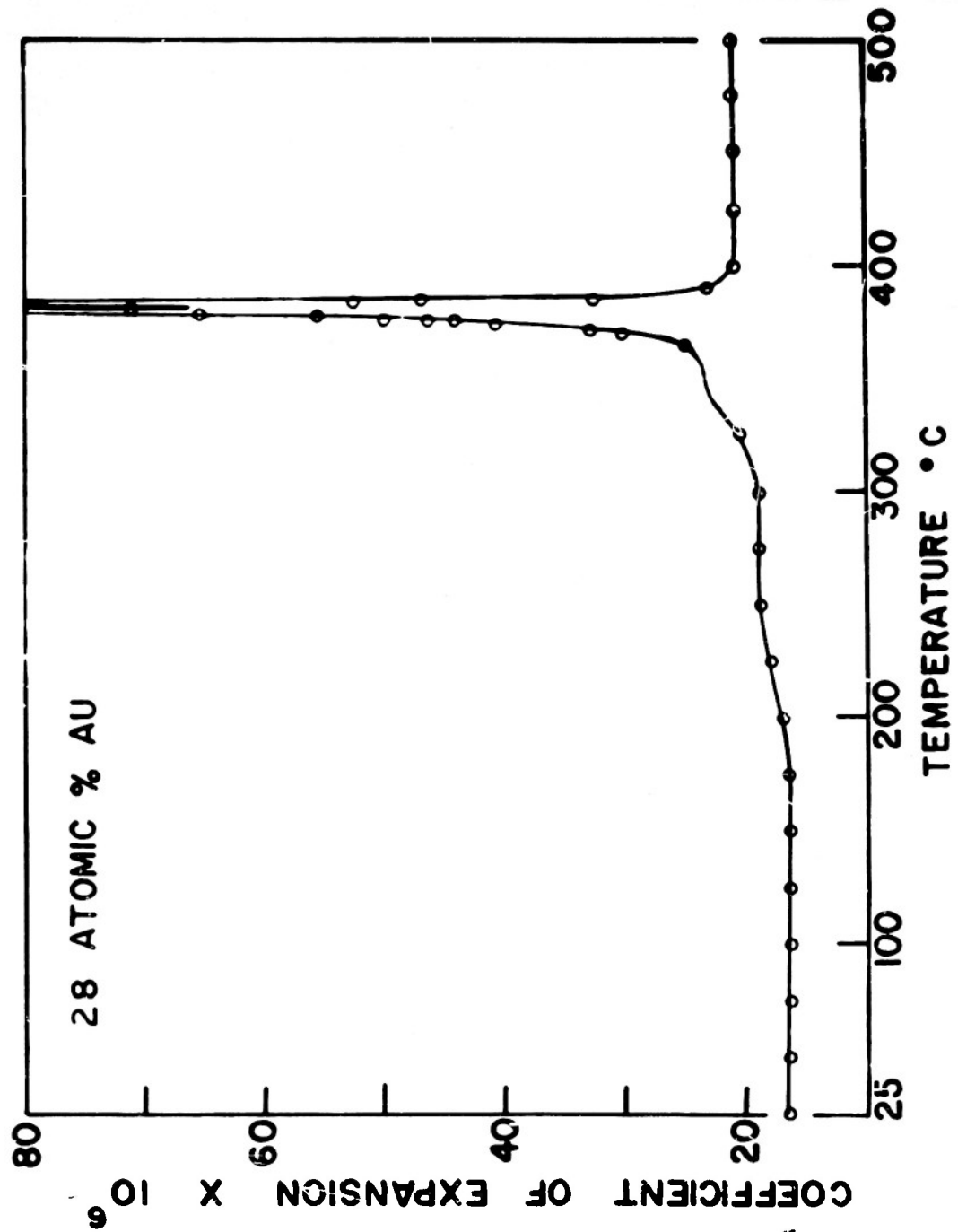
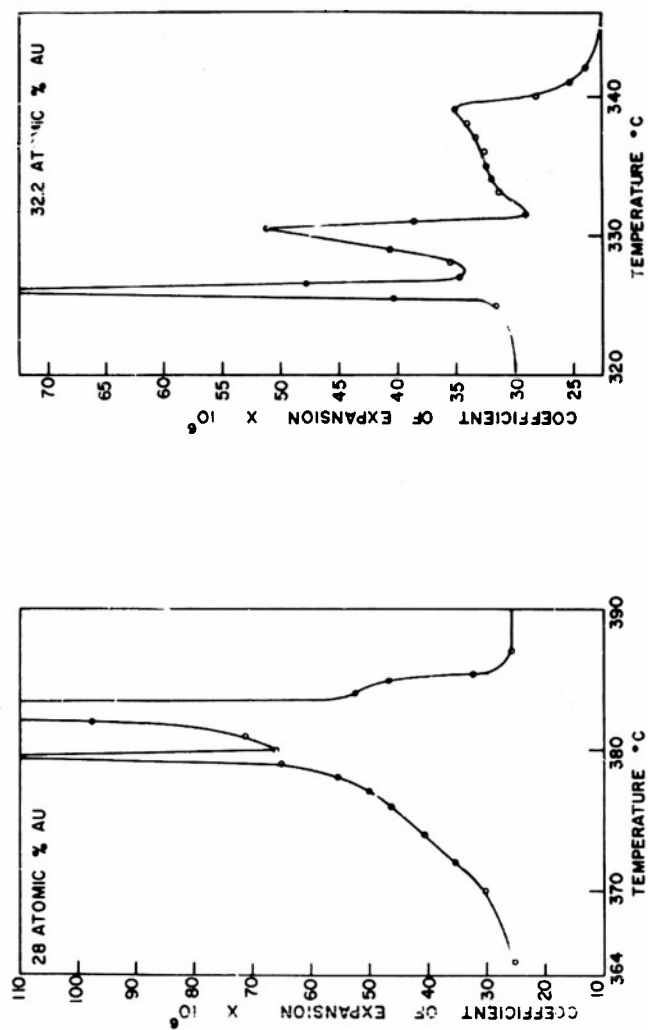Fig. 2 - Coefficient of Expansion as a Function of Temperature for a Gold-Rich Sample

Fig. 3 - Expanded Plot Showing Multiple Peaks in Curve of α versus T in the Critical Region

accompanied by a single anomalous peak of considerable magnitude in the curves of expansion coefficient, α, _versus_ temperature, T. More specifically, for all copper-rich samples, the value of α remains constant from room temperature to about 250°C, at which temperature it begins to rise smoothly reaching a peak at a temperature which agrees well with the accepted "critical" temperature (as given, for example, in the _Handbook of Metals_, 1948 Edition). The values of α then fall to a value associated with the disordered alloy and remain at that value to temperatures in excess of 500°C.

Samples containing more than 25 percent Au (e.g. 28 and 32 percent Au) yield quite different results. Here we observe not only the multiple peaks shown in Figure 3, but we find that the initial rise in the coefficient of expansion is at about 200°C rather than 250°C. The gold-rich samples also exhibit rigorously constant values of α for temperatures above the critical region.

We should like to emphasize that the details of the peaks in the α _versus_ T curves depend upon taking the slopes from the $\Delta \ell$ _versus_ T curves and so cannot be claimed to be exact. However, there is no doubt that peaks similar to those shown are present.

It is not easy to explain why multiple peaks are observed for gold-rich and not for copper-rich samples, nor is it easy to explain the presence of multiple peaks in any composition in terms of a simple phenomenon. The possible causes which one thinks of immediately are: The appearance of a second crystal structure; the coexistance of ordered and disordered phases under rather special conditions; or simply a severe lack of equilibrium. The appearance of a second crystal structure in the 32 percent sample is a remote possibility since it is only a few composition percent away from the boundary of the tetragonal phase. However, this is a very unlikely explanation for the 28 percent sample. An explanation in terms of simple lack of thermal equilibrium does not seem reasonable either, since it is very unlikely that the lack of equilibrium could be so drastic and at the same time make itself evident only for gold-rich samples and also be amenable to entirely reproducible results.

The third possibility, the coexistance of ordered and disordered phases under special conditions, seems to offer some promise of explaining the results. First of all, when we consider the results of Section IV, there is some reason to believe that the difference in behaviour of gold-rich and copper-rich samples is not unreasonable. That is, we discuss in Section IV the probability that, in the case of copper-rich samples, the coexisting ordered and disordered unit cells may be of approximately the same size, notwithstanding the fact that the ordered cell of a given composition is smaller than the disordered cell of the same composition. This same condition could not apply to gold-rich samples(See Section IV for details of this discussion). If this "size-effect" does occur

then we would expect the distortion of the lattice to be greater and more irregular in the gold-rich samples as the temperatures of the two-phase region are reached.

Although the proposed "size-effect" would lead us to expect possibly different results for gold- and copper-rich samples, it does not explain necessarily why we should observe multiple peaks. However, before we continue the discussion along these particular lines let us first return to more general arguments covering the entire ordering range.

In general, there appears to be no particular reason for expecting the existence of a heterogeneous transformation to yield markedly different results for volume expansion measurements than those observed for a homogeneous transformation, as long as one will admit that long-range order could disappear in a manner other than cataclysmically in either case. Thus, whether the transformation be heterogeneous or homogeneous we would expect the coefficient of expansion to increase at an increasing rate as the rate of appearance of the disordered phase (the rate of disordering, in the homogeneous case) increased; then decrease to the value for the disordered alloy as the sample becomes completely disordered.

Now, what effects might one expect from the "size-effect" mentioned if the transformation be heterogeneous. First, one might expect to detect a change in volume at lower temperatures in the case of the coexisting phases having markedly different sizes, then when they are nearly the same size and consequently produce little overall change in the volume. One does observe changes in α at lower temperatures for the gold-rich samples. Second, one might expect the rate of increase of α with T to be somewhat smoother and less sharp in the case of the copper-rich samples since here one is observing essentially the growth of the stable disordered phase only, without the local inhomogeneities in volume produced by the coexistence of two phases of different sizes. This is also observed. Third, one might expect the maximum value reached by α to be larger in the case of the gold-rich samples (for equivalent composition departures from Cu_3Au) because of the more abrupt effect on the size. This is observed[3] (See Table II) but probably it could be better explained in terms of rates of disordering. Fourth and finally, one might expect that the peak in the curve of α versus T for copper-rich samples might occur at the temperature of the disordus line as given by resistivity measurements, and also that the first peak in the curves for gold-rich samples might occur at the ordus line. We were genuinely surprised to find this to be true when we compared our results (obtained in 1951-52) with those of Rhines and co-workers (6). These data are given in Table II. The agreement is particularly surprising since the present data is not truly equilibrium data.

To return to our previous discussion, it remains that the "size-effect" would in no way guarantee multiple peaks. Thus we

TABLE II

Summary of Expansivity Data

Atomic Percent Au	$T_1{}^a$(°C)	$T_2{}^b$(°C)	$T_3{}^c$(°C)	Coefficient of Expansion at T_1	Reference[d]
2,5,10,15	---	---	---	---	II
17.5	?	293	250	?	II
19.5	325	325	275	30×10^{-6}	II
22.1	378	368	353	65×10^{-6}	I
24.8	393	390	390	120×10^{-6}	I
28.5	379 (383)	385	378	156×10^{-6}	II
30.4	360	371	350	60×10^{-6}	I
32.2	326 (339)	343	310	59×10^{-6}	II

a. T_1 is the temperature of the single peak in the curves for Cu-rich samples and is the temperature for the 1st peak in Au-rich samples. The second temperature, in parentheses, is the temperature of the final peak when multiple peaks occur.

b. The approximate temperature of the disordus line (6).

c. The approximate temperature of the ordus line (6).

d. I, Nix and MacNair (4).

   II, Present work.

were forced to review the experimental set-up. Thermal gradients within a sample could easily give the observed effects, but we had checked the gradient along the axis of the furnace and found it to be completely negligible over distances many times the lengths of the samples. This, coupled with the high thermal conductivity of the samples, completely ruled out verticle gradients. However, we had not investigated horizontal gradients and the samples (3 were used for a given measurement, see references 2, 3, and 4) were placed at varying distance from the axis. Unfortunately, the furnace used was not tested, but several similar furnaces possessed horizontal gradients (from the center out) varying from one to four degrees, at $350^\circ C$. Thus, the multiple peaks could have been caused by a horizontal gradient, which incidentally does not allow one to make use of the high thermal conductivities of the samples to remove it. It is interesting that here again we could expect the more severe effect in the case of two phases differing markedly in size since then the anomalous effect produced by reaching the ordus line at different times in different samples would be greater.

We would like to make it clear that although a horizontal gradient could be the cause of multiple peaks (and probably was present) we are not at all convinced that it was the cause in this case. The temperature spread between the peaks is too great to make a gradient explanation very convincing.

Thus, we conclude from the above arguments (recognizing that those arguments are indirect and cannot be defended strongly) that the existance of multiple peaks in the curves for gold-rich samples lends support to the contention of a two-phase transformation. But more important to us, they apparently lend support to our proposed "size-effect" explanation as to why we were unable to detect two phases in equilibrium in copper-rich samples by x-ray techniques (Section IV).

One of the more outstanding features of the data is the rigorously constant coefficient of expansion exhibited by all samples at temperatures above the critical region, to the highest temperatures attained in the experiments. This phenomenon was observed and discussed previously by Nix and MacNair (4). If the upper portion of the curve were to follow the trend expected on the basis of thermal vibrations, the expansion coefficient would rise. On the other hand, the disappearance of short-range order as predicted by the theories of Bethe and Peierls (7,8,9) and Cowley (10), would cause it to fall over a considerable range of temperatures before "leveling off". At first glance, one might think that the combination of the vibrational component and the disordering component would cancel and yield the observed straight line. This, however, is improbable since the decrease due to short-range order is rapid near T_c with the rate of decrease diminishing with increasing temperature, while the vibrational component increases at an almost constant rate with temperature. Thus, the explanation of a constant coefficient of expansion over such wide ranges of temperatures probably requires introduction of a different component into the process, as first pointed out by Nix and MacNair (4).

III RESISTIVITY MEASUREMENTS

The results of some preliminary resistivity measurements were given in our progress report of August 22, 1951 (Annual Report; Contract AF-33(038)-11057). Mechanical failures of the equipment involved slowed this work considerably, and this, coupled with the knowledge of the extensive work on the resistivities of Cu-Au alloys being done at Carnegie Tech under Dr. Rhines, caused us to divert our major efforts toward other phases of our program.

Thus, we have little to add to the results obtained by Rhines and co-workers on the effects of order on the electrical resistivities of Cu-Au alloys and suggest that those interested in a thorough treatment consult their work (6).

Inasmuch as Rhines and co-workers investigated alloys containing more than 19.5 atomic percent gold, our results on alloys containing 2, 5, 10, and 15 atomic percent gold, while preliminary, may be of some interest. Briefly, they can be described as follows: As in the case of all other parameters studied, resistivity measurements on alloys containing 2, 5, and 10 percent gold exhibited no anomalies. The curves of ρ versus T were linear for the 2 and 5 percent samples, but showed a slight positive deviation from linearity for the 10 percent samples. The 15 percent gold sample proved interesting. Here we observed a decidedly anomalous region extending from about 340°C to 265°C (the thermocouple used was not calibrated so these temperatures may be somewhat in error). In this region, the average decrease in resistivity with temperature was a factor of 2 larger than at temperatures above 340°C or below 265°C. Although a broad, weak superstructure maximum was observed for a 15 percent sample, evidence of ordering in samples of this composition is very difficult to obtain using other parameters. It is a little surprising that resistivity should give such a marked indication since it is generally accepted that short-range order is not detectable by resistivity measurements, and it seems that other parameters would have given stronger evidence of long-range order. However, as we show in other sections of this report, the other parameters we studied are less sensitive in detecting order in compositions containing less than 25 atomic percent gold.

It might be pointed out that the temperature range over which we observe anomalous behaviour in the 15 percent sample does not agree with the phase diagram given by Rhines and co-workers (6) (In fact, they indicate the ordering region does not begin until about 17.5 percent gold), but it does agree reasonably well with the temperature range over which anomalies were observed in x-ray data (See Section IV).

IV THE NATURE OF THE ORDER-DISORDER TRANSFORMATION

Introduction.

The work summarized in this section has been described in detail in our Progress Report No. 10 (11) and has been published in Acta Metallurgica (12).   The principle features of the work have been presented before the American Physical Society (13).

One of the principle aims of these Order-disorder studies was to resolve the controversy over whether the transformation was a homogeneous or heterogeneous one. It was hoped that this could be accomplished in a definitive fashion by using x-ray techniques since it was a well known fact that disordered samples of Cu_3Au have a substantially larger cell size than ordered samples. Consequently, a fundamental x-ray reflection from a sample containing both ordered and disordered phases in equilibrium would appear as a split line.

There were a number of difficulties that could be anticipated (12) and several that could not; in fact, the early x-ray work of Keating and Warren (14) using a 25 percent Au sample, and on this contract (15) using a 23 percent Au sample supported the point of view that the transformation was homogeneous. However, the unusual behaviour observed in the curves of expansion coefficient _versus_ temperature (See Section II), coupled with the resistivity data given by Rhines and Co-workers (6) convinced us that it would be worthwhile to investigate possible line splitting in samples covering the entire composition range.

Experimental Technique.

Single crystal samples containing 15, 20, 25, 28, 30, and 34 percent gold (See Table I) were studied. The angular position of the (4,0,0) fundamental reflection was observed at the temperature of interest (from room temperature to $505°C$) using a fairly elaborate sample holder and temperature controller which enabled us to keep the temperature fluctuations to within $0.05°C$ over long periods of time. The measurements of the peak positions were taken by recording the intensities using a Leeds and Northrup Speedomax Recorder while turning the crystal through the Bragg angle at the rate of $0.1°$ in ϑ per minute. The Geiger counter turned synchronously at a rate of of $0.2°$ in 2ϑ per minute. The line positions were read from the recorder chart with an accuracy of $\pm 0.02°$ in 2ϑ.

The heating program followed was to heat the initially well-ordered sample to a given temperature and allow it to remain at

that temperature until it reached equilibrium. The criterion
used for equilibrium was that the line position should not
change, or the half-width of the line diminish, within a period
of at least 12 hours. Even so, it is probable that absolute
thermal equilibrium was not attained, particularly as regards
agglomeration of fine, widely-disposed nuclii of a second phase.

Results.

Figure 4 gives a typical curve of the (4,0,0) line position
as a function of temperature for samples containing less than
25 percent Au and Figure 5 gives a similar curve for samples
containing more than 25 percent gold. Also listed in the figures
are the half-widths of the lines below, in, and above the crit-
ical temperature region. Figures 6 and 7 show typical line
shapes for the same samples for temperatures below, in, and above
the critical region. These line shapes are direct tracings from
the recorder chart.

The only exception to these typical curves was the result
given by the 15 percent sample. In this case, the data points
(for line position as a function of temperature) can be fitted to
one straight line at low temperatures and to another of slightly
different slope at higher temperatures. These two straight lines
can be joined smoothly by a line with a slight curvature, this
curved region extending from approximatly 290°C to 360°C. Thus,
no marked effect on line position due to ordering was detected
for the 15 percent sample although a weak superstructure maximum
was detected.

Discussion of Results.

For generalization purposes, the data can be divided into
two regions, the gold-rich and the copper-rich. On the gold-
rich side of Cu$_3$Au, we believe the data definitely indicate a
heterogeneous or classical phase transformation. That is, there
is strong evidence of two separate diffraction peaks. The exact
positions of these two peaks is not definite since they are not
clearly resolved throughout the critical region, and for this
reason we show the curve of line position _versus_ temperature as
dotted lines in the critical region, for both the ordered and
disordered phases (See Fig. 5).

The manner in which the second phase became evident can be
seen in Figure 7. (It is, of course, much more striking when
one sees 15 or 20 recorder charts in this region). First, an
asymmetry appears in the low angle side of the line and increases
with increasing temperature in such a way that it can be regarded
only as another peak. At still higher temperatures, the line
becomes quite level and relatively flat at the peak (See Fig. 7),
and finally, the asymmetry appears on the high-angle side of the
line. We believe this behaviour can be interpreted only in
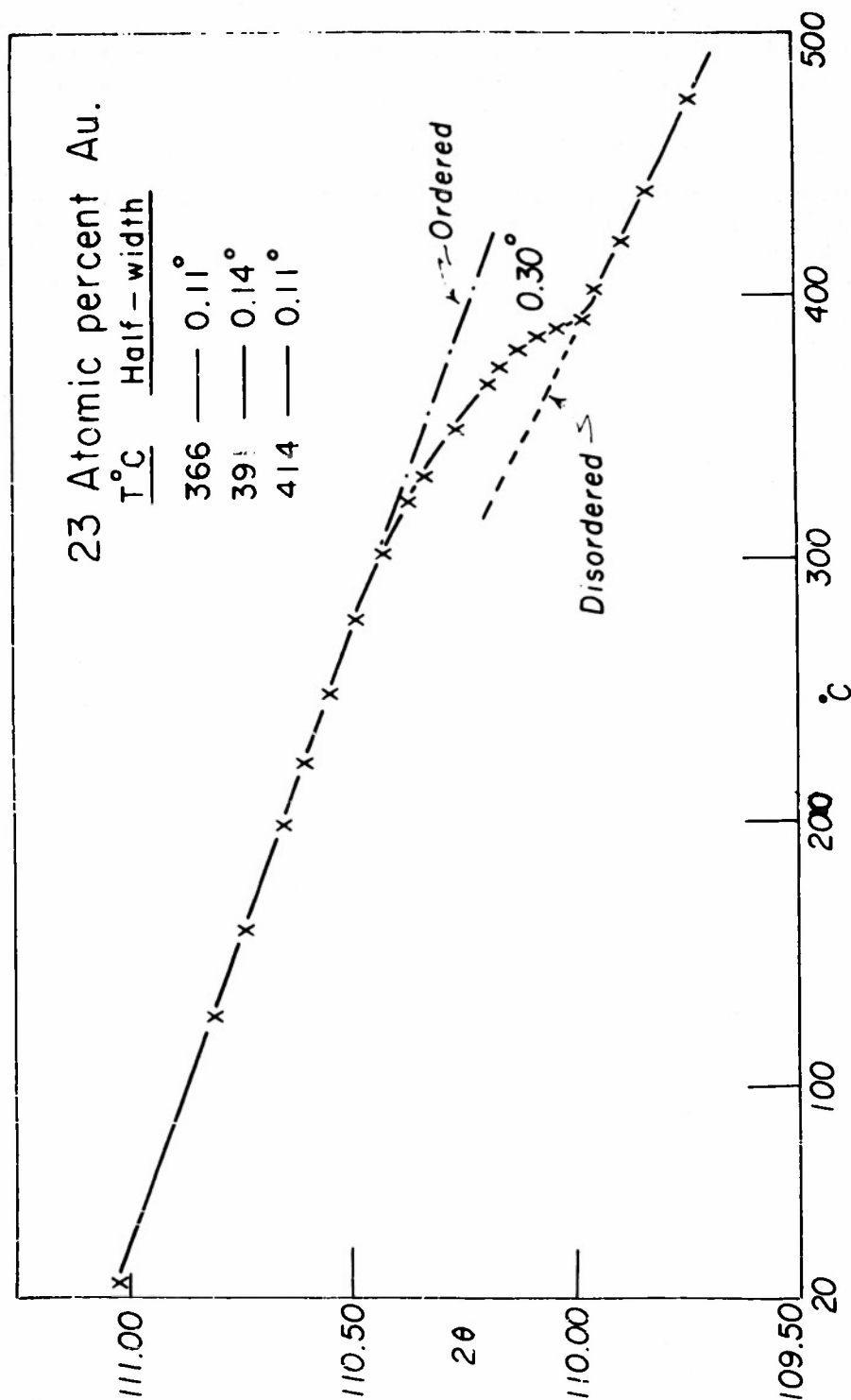terms of a two-phase transformation.

Fig. 4 — (4,0,0) Line Position as a Function of Temperature for a 23 Atomic Percent Gold Sample
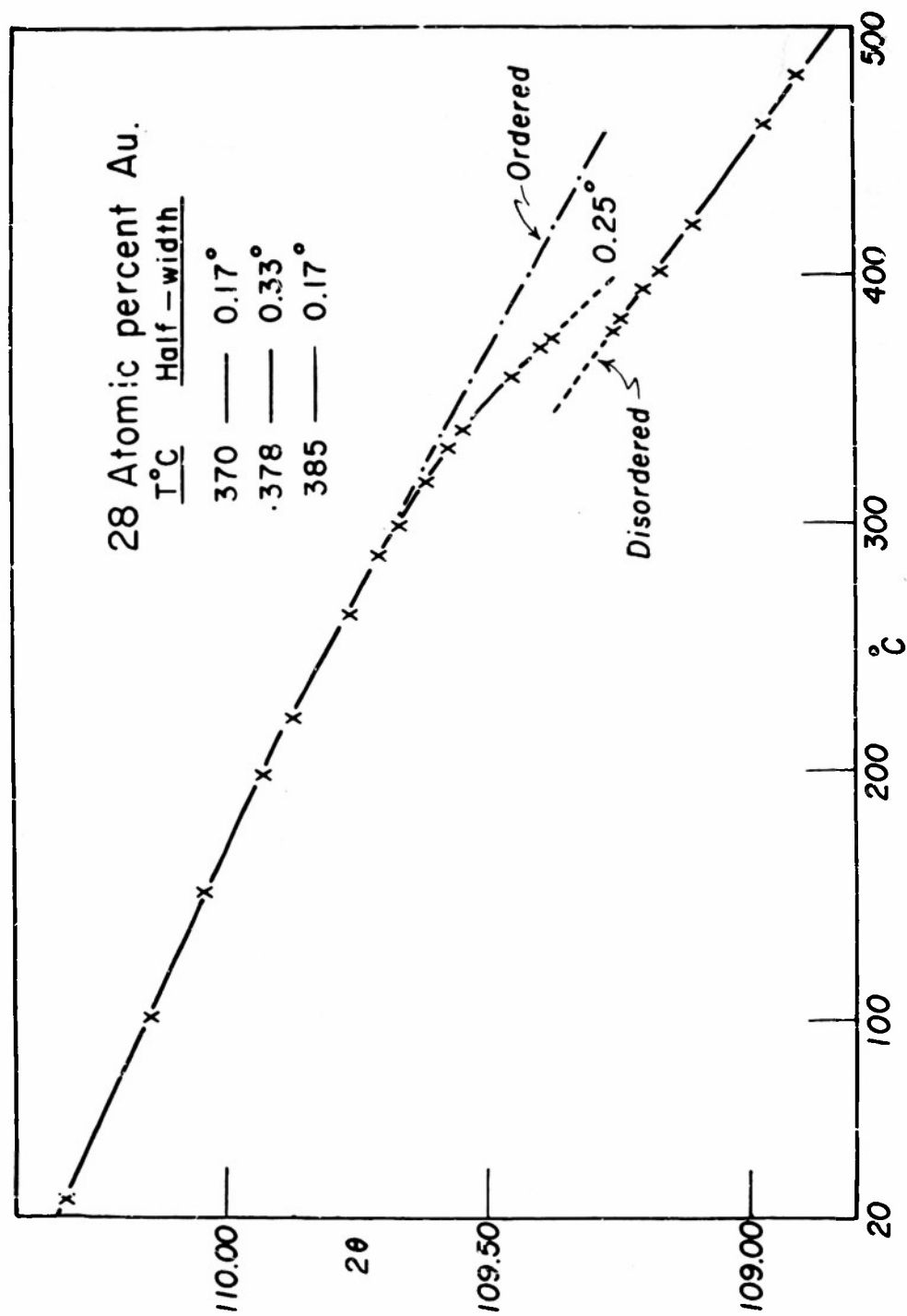
Fig. 5 — (4,0,0) Line Position as a Function of Temperature for a 28 Atomic Percent Gold Sample
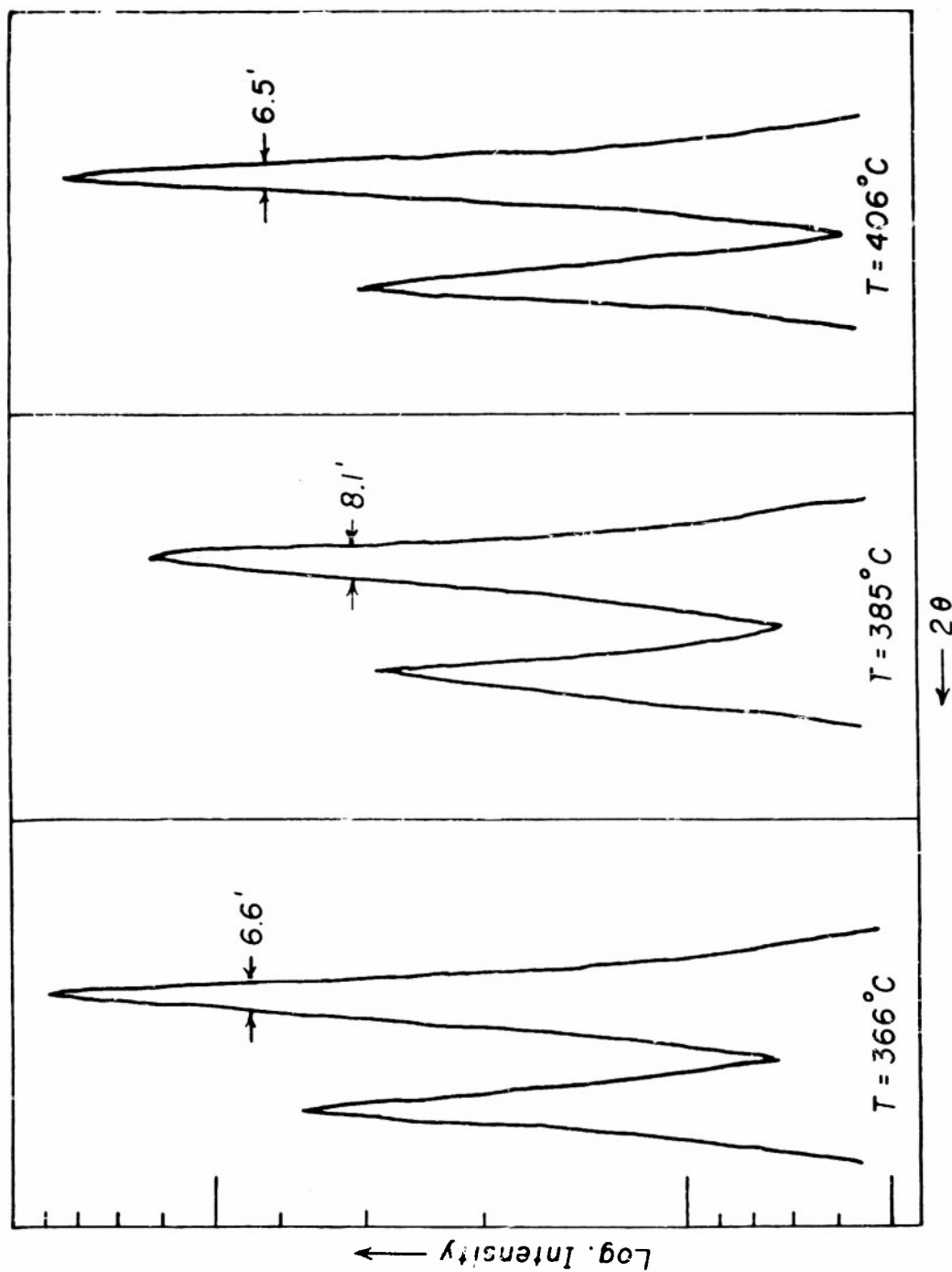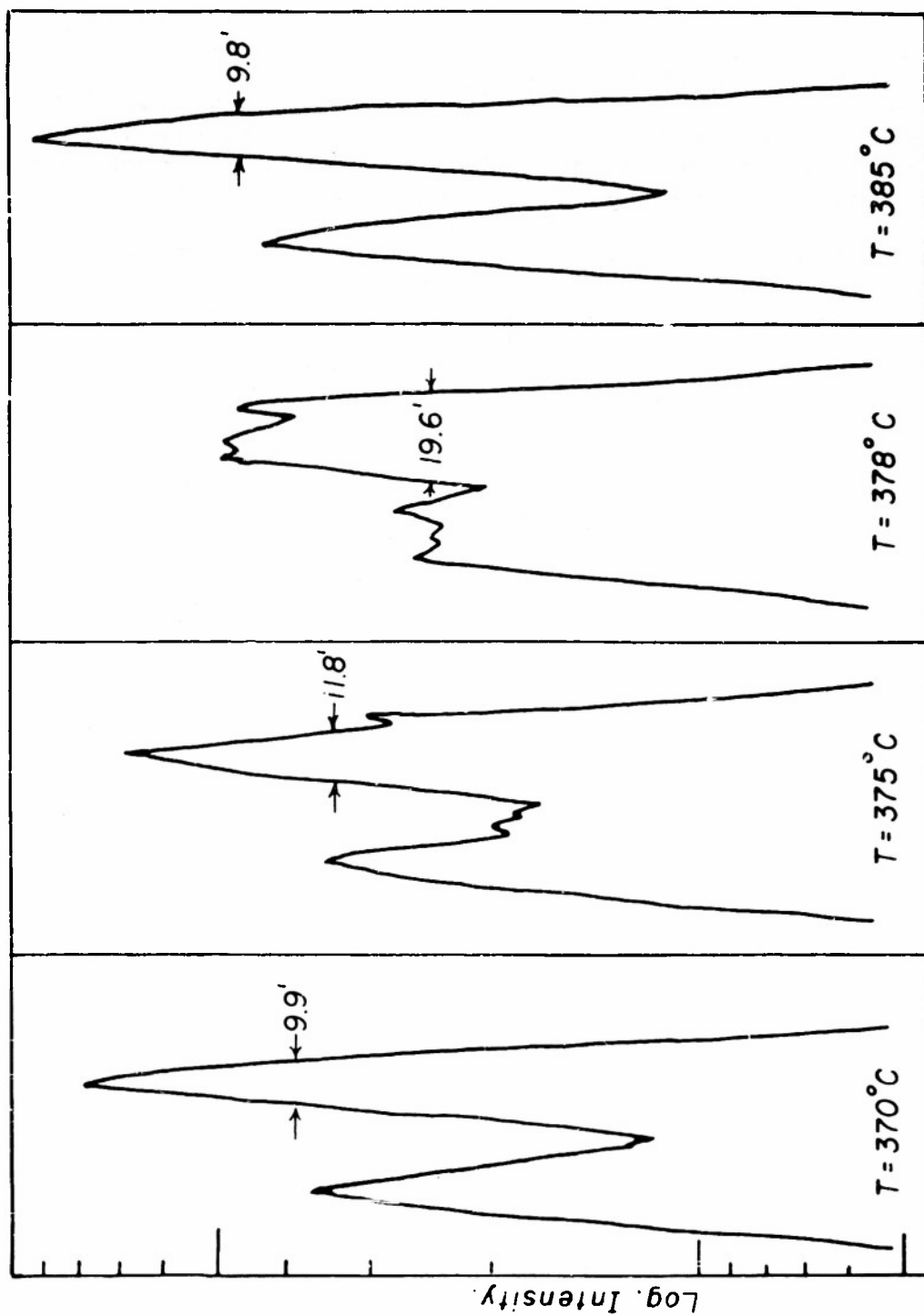
Fig. 6 - Line Shapes of 23 Percent Sample

Fig. 7 — Line Shapes of 28 Percent Sample

The half-widths of the lines provide equally strong evidence for the existence of two phases. We see in Figure 7 the anomalous broadening of the $(4,0,0)$ line of the 28 percent sample. (It is important to note that the intensity scale is logarthmic in order to get a proper prospective of the half-intensity measurements. These are given in minutes in 2ϑ in Figures 6 and 7). Even for the highest composition sample, 34 percent Au, the broadening was considerable. The half-width was 7.2' in 2ϑ at room temperature and only 7.8' at 352°C. However, in the critical region the maximum half-width exceeded 13' in 2ϑ.

The valley between the $K\alpha_1$ and $K\alpha_2$ peaks provides the most striking indication of the critical region when one is actually observing the transformation in progress. At temperatures below and above the critical region, this valley is deep and symmetric, but in the critical region it becomes very shallow and takes on an asymmetry compatable with that of the $K\alpha_1$ peak.

Samples containing less than 25 percent gold present an altogether different picture. As illustrated in Figure 6, none of the points mentioned above as being evidence for a two-phase field are clearly observed for copper-rich samples. There is a slight broadening of the diffraction peaks in the critical region with the lines having their maximum half-widths there. However, the broadening is so slight that it can hardly be considered anomalous. No definite asymmetry was observed in the peak of any copper-rich sample, and the peak positions were relatively definite throughout (as contrasted to the wide irregular peaks of the gold-rich samples). The curve of peak position _versus_ temperature in the critical region can be drawn as a smooth curve joining the more or less linear portions of the ordered and disordered phases. Thus, the data for copper-rich samples do not lend support to the contention of a heterogeneous transformation.

It is probable that the transformation on the copper-rich side of Cu_3Au is a heterogeneous one with the failure to detect the two phases possibly being due to the difference in size of the two atoms. The combination of circumstances which make the detection of two phases difficult in this region can be seen more clearly by referring to Figure 8.

Consider the disordered composition D, which when cooled to a certain temperature separates into the two-phases D' and D". D', the disordered phase, is relatively poorer in gold and thus has a smaller cell size than composition D. D", although ordered and consequently reduced in cell size from a disordered alloy of the same composition, is rich in gold compared to D and thus is relatively larger. It is possible that these conditions combine to cause a superposition of the peaks so that two phases,
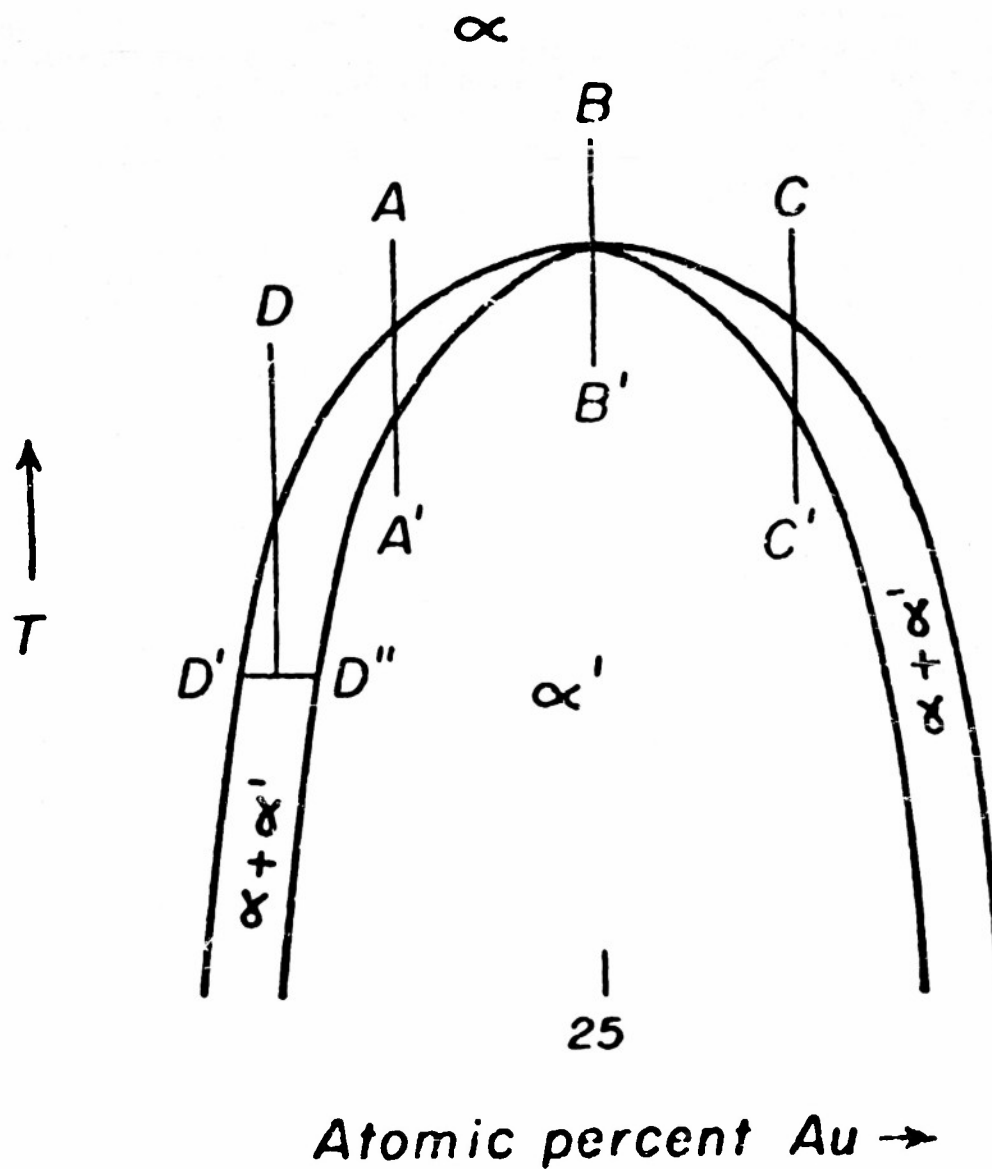
Fig. 8
Idealized Heterogeneous Phase Transformation

if present, cannot be detected by the present method.

A sort of "reverse" reasoning applies on the gold-rich side of Cu₃Au so that there the condition is more favorable for detection of two phases than might be expected if both atoms were of the same size.

However, we can say that if the transformation on the copper-rich side took place over an extended range of temperatures or of compositions it should have been detected. Thus we can conclude that if the transformation be a heterogeneous one on the copper-rich side of Cu₃Au, the two-phase region must span a narrow composition range.

Inasmuch as we cannot state that an equilibrium process has been demonstrated if the desired temperature has been reached from one direction only, we repeated the experiment on the 28 percent sample by cooling a disordered sample. Fortunately, the results obtained in heating an ordered sample were reproduced (12).

We should like to emphasize that although we have used the word "equilibrium" in our discussion we do not claim (or believe) that we attained an absolute thermal equilibrium in all cases. However, we do believe that we have approached equilibrium to the degree that the conclusions presented are valid.

Figure 9 gives a qualitative picture of the transformation as determined from our data. There is no claim made for accuracy since the individual points have a possible error of at least ±5°C. The points on the gold-rich side were taken as the lowest temperatures at which definite asymmetry was first visible on the low angle side of the line and the highest temperature at which it was seen on the high angle side of the line. The points on the copper-rich side were taken at the temperature at which the slope of the line position _versus_ temperature were steepest. The dashed line then represents what would be the critical temperature for a homogeneous transformation.

V LONG-RANGE ORDER IN CU-AU ALLOYS OF NON-STOICHIOMETRIC COMPOSITIONS

Introduction.

The work summarized in this section has been described in detail in our Progress Report No. 10 (11) and has been published in Acta Metallurgica (12). The principle features of the work have been presented before the American Physical Society (13).

The degree of long-range order present in a particular alloy (which we will designate by the parameter S) can be interpreted
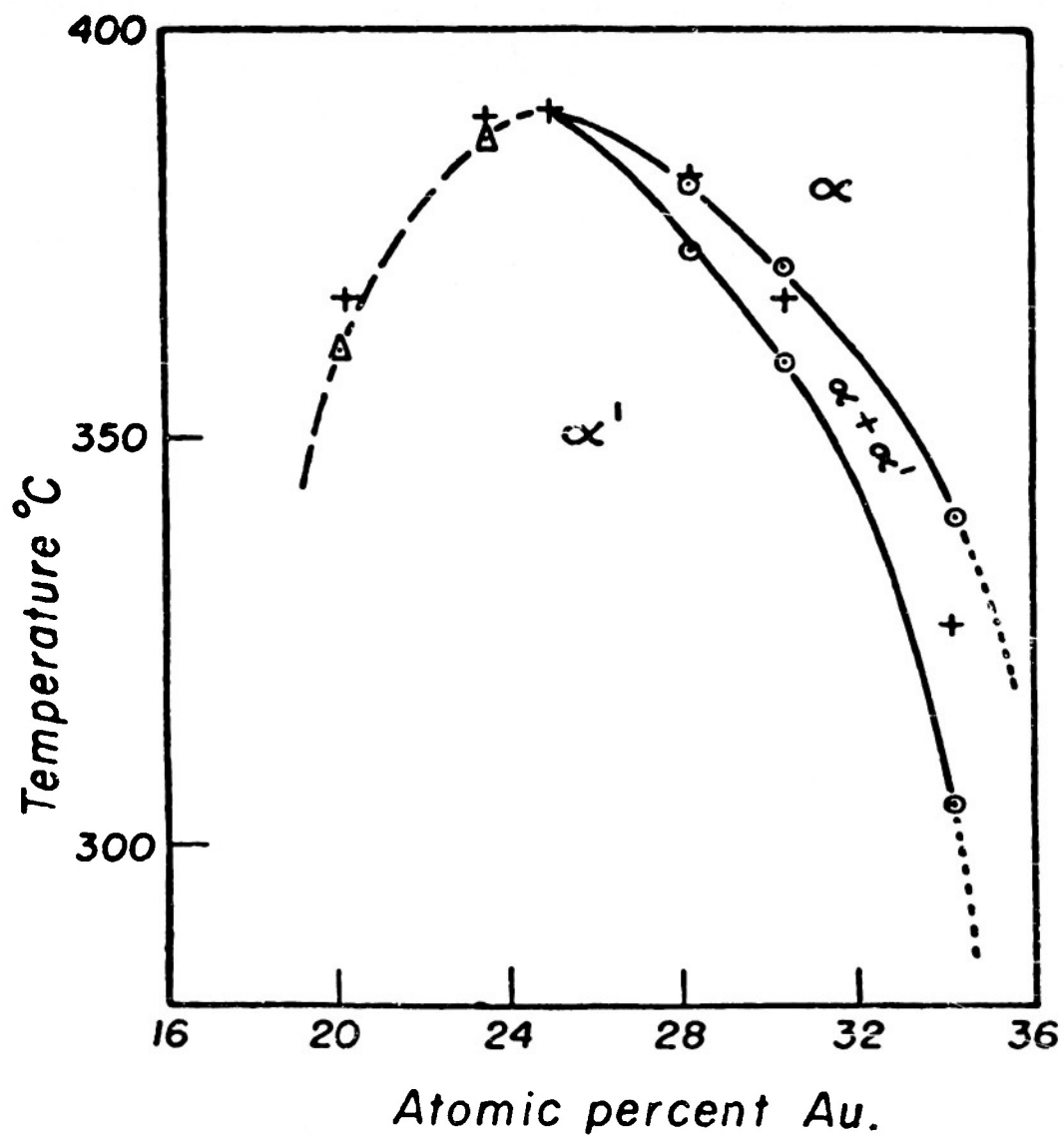
Fig. 9

Phase Boundaries of Ordered Region as Determined from X-ray Diffraction Study

in two ways. The first interpretation arises when it is established that there is only one phase present in the alloy at any given temperature. In this case, S is to be interpreted in the manner of Bragg-Williams as a parameter indicating to what degree the lattice sites are occupied by the correct atoms. On the other hand, if the transformation is a classical phase transformation so that ordered and disordered phases are present in equilibrium, then the square of the parameter S gives a measure of the material in the ordered state. Thus, regardless of the nature of the transformation, values of the parameter S are of interest.

To date, too little work has been done on the determination of the long-range order parameter by x-ray means (16,17,14) and this has been done for stoichiometric compositions. Hence, it was decided to measure this parameter for non-stoichiometric alloys since the samples were available under the proper conditions in the course of the preliminary work on the nature of the order transformation. It must be admitted that the use of single crystals is not particularly desirable in studying long-range order. However, the nature of the transformation work requires single crystals and it was regarded as relatively more important in the choice of samples.

A value of S can be obtained experimentally at the desired temperature by comparing the x-ray integrated intensity of superstructure reflections to the integrated intensity of principle reflections. It has been shown (14) that if the long-range order parameter is S_o at room temperature, at some elevated temperature it can be obtained from

$$S = S_o \left[\left(\frac{P_T}{P_o} \right)_{sup} \left(\frac{P_o}{P_T} \right)^{\gamma}_{fund} \right]^{\frac{1}{2}}$$

where
$$\gamma = (h^2 + k^2 + l^2)_{sup} \Big/ (h^2 + k^2 + l^2)_{fund}$$

$\left(\frac{P_T}{P_o} \right)_{sup}$ = ratio of elevated and room temperature intensities of a superstructure reflection

$\left(\frac{P_o}{P_T} \right)_{fund}$ = ratio of room and elevated intensities of a fundamental reflection

The value of S_o can be obtained from detailed comparison with a fundamental line, if extinction can be ignored. This has not been done, since in the present work single crystals were used and no reliable method has been devised to correct accurately for extinction in single crystals (18). Instead, perfect order

for the given composition has been assumed at room temperature and the calculated value of S_o used. In the present case S_o has been calculated (assuming maximum possible order) from the expression:

$$S = r_\alpha + r_\beta - 1$$

where r_α and r_β are the fractions of α and β sites properly occupied. This expression for S has been chosen from a consideration of the x-ray structure factors. It is important to recognise that if any different value for S_o were the correct one, the only result would be to multiply the given values by a constant factor.

Experimental Technique.

The same crystals were used for this work as were used for the work described in Section IV, and were given the same initial "ordering" treatment. The samples were mounted in a specially constructed furnace which allowed us to observe six samples simultaneously. The furnace is described in detail elsewhere (11, 12).

Monochromatic CuK_α radiation and the following technique were used to obtain the integrated intensities of the lines. The beam slits limited the monochromatic beam to a divergence of less than one-half a degree, illuminating an area of 0.044 inch by 0.20 inch of the approximately $\frac{1}{4}$ inch diameter samples. The reflected radiation passed through a counter slit wide enough (2.2° in 2ϑ) to allow all the radiation from a diffraction peak to enter the counter chamber. The diffuse background was taken on both sides of the peaks with the same slit arrangement, and one-half the sum subtracted from the peak intensity.

Results.

Values of S were obtained for temperatures from room temperature to temperatures above the critical temperatures (11,12). A typical curve of S _versus_ T is shown in Figure 10. Since the transformation is probably heterogeneous we have also included the values of S^2. We were unable to obtain quantitative values of the long-range order parameter for the 15 percent sample. However, for temperatures below about 350°C, some order is present as evidenced by an extremely broad maximum in the region of the expected superstructure peak.

Discussion of Results.

Since the transformation through the region investigated is probably a two-phase one, the "tail" of the plot of S _versus_ temperature may not be as much a result of experimental
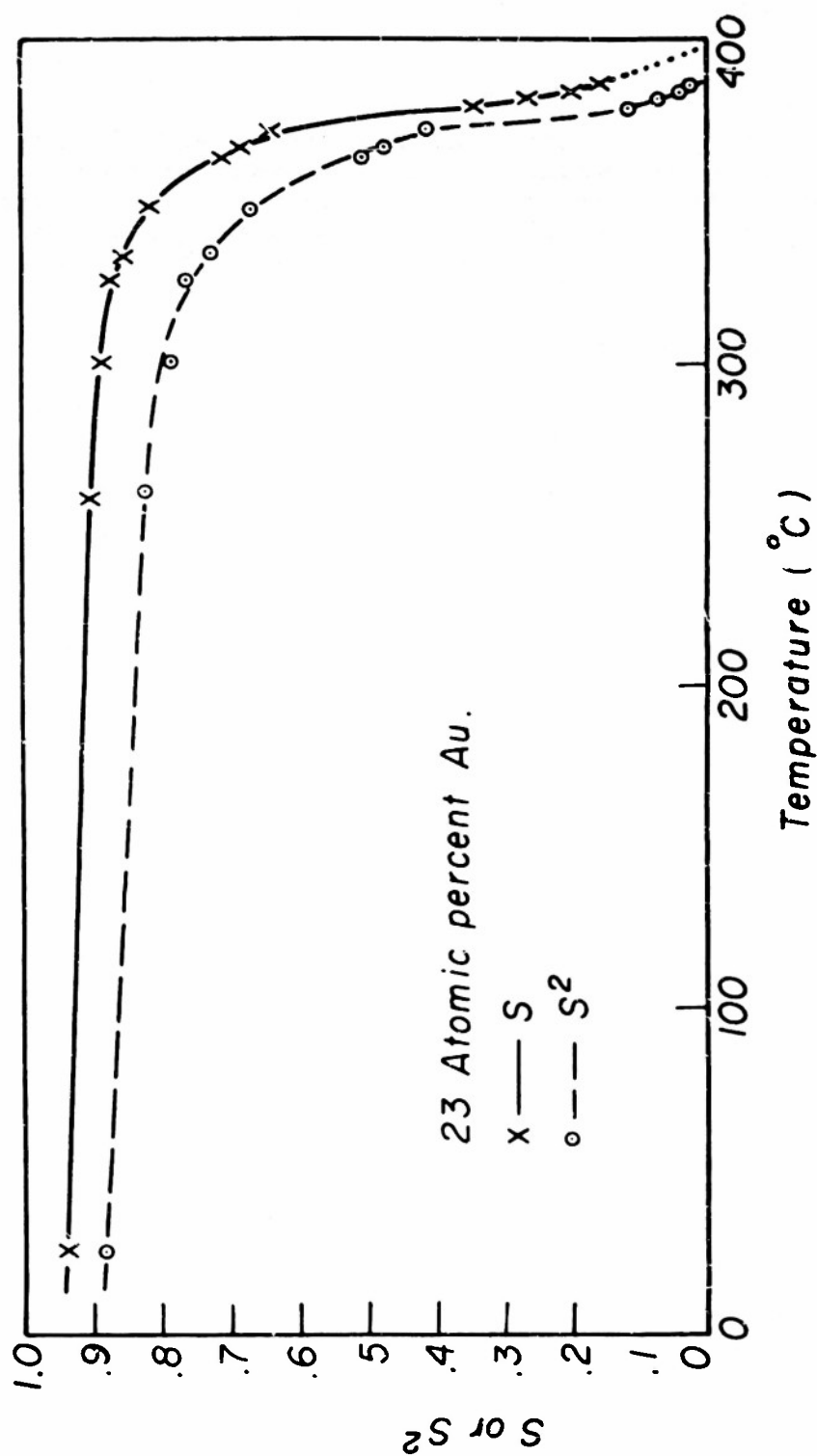
Fig. 10 - Typical Curve of Long-Range Order Parameter as a Function of Temperature

limitations as originally thought.   That is, one would expect
the dimunition of the ordered phase to occur slowly initially,
becoming more rapid until nearly all the material is in the
disordered state, followed by a "tailing-off".

     The meaning of a critical temperature is at best uncertain
in view of a two-phase transformation.   However, since a critical
temperature can always be defined from the results of long-range
order studies, we have included in Figure 9, Section IV, the
"critical" temperatures taken from the plots of S _versus_ temper-
ature. We have defined the critical temperature in the present
work by a extrapolation of the relatively precipitous portion of
the curves of S _versus_ T. On the gold-rich side of Cu_3Au, the
points so defined fall generally within the two-phase region.
On the copper-rich side, the points are all above the points
determined from line position as a function of temperature. No
particular significance is attached to this, other than experi-
mental uncertainty.

VI SHORT-RANGE ORDER IN AN ALLOY CONTAINING 23 ATOMIC PERCENT GOLD

Introduction.

     The work summarized in this section has been described in
detail in our Progress Report No. 9 (2) and has been published
in Acta Metallurgica (19).   The principal features of the work
have been presented before the American Physical Society (20).

     X-ray measurements of short-range order in the alloy Cu_3Au
have been made previously, using powder samples and film
techniques (16) and Geiger counter spectrameter techniques (17).
A recent theory of short-range order (10) predicts that the
short-range order parameters defined have maximum values at the
50-50 atomic percent composition. Thus, considerable interest
is attached to measurement of this short-range order parameter
for compositions other than the stoichiometric. As as integral
part of the study of order-disorder in alloys, we have measured
the short-range order present at temperatures above the critical
temperature, in a single crystal of Cu-Au alloy containing 23
atomic percent Au.

Experimental Techniques.

     The short-range order parameter is defined by:

$$\alpha_{lmn} = 1 - P_{lmn}/m_A$$

$$= K \sum_{h_1} \sum_{h_2} \sum_{h_3} I_D' \cos 2\pi (lh_1 + mh_2 + nh_3)$$

Here, P_{lmn} is the probability that an atom with coordinates l,m,n with respect to a B-atom is an A atom; m_A is the fraction of A atoms; h_1, h_2, h_3 are continuous coordinates in reciprocal space; and I_D' is the diffuse x-ray intensity due to short-range order.

The coefficients, α_{lmn}, provides us with convenient short-range order parameters as has been discussed in detail by Cowley (10,17).

The details of the experimental set-up and techniques are described elsewhere (2,19). A single crystal $\frac{1}{4}$ inch in diameter was used, and the diffuse intensities were measured as 900 points contained within 1/32 of a unit cell. The entire unit cell was built up from these intensities by use of the center of symmetry and the planes of symmetry in the unit cell of a face-centered cubic material. The final result was a cubic net of intensity values containing 8000 points, with cube axes h_1, h_2, and h_3.

The measured diffuse intensities were corrected for intensities due to several causes (2,19) and the short-range order parameters calculated from the above equations.

Results.

The distribution of the intensities, I_D', was found to be similar to that reported by Cowley (17). The disc-like character of the diffuse maxima reported by Cowley for a 25 percent sample was clearly observed in the 23 percent sample.

One would expect that the distribution of I_D' would be symmetrical throughout the unit cell with respect to h_1, h_2, h_3. However, it turned out that this symmetry was not realized. That is, values of α_{lmn} for various permutations of the l, m and n were not equal. This asymmetry probably arose from experimental errors, but it could have been due to the difference in size of the atoms. If the latter were the case, a weighted average of values of α_{lmn} for various permutations of l, m, and n would correct for it. In any case, such an average would tend to reduce the error and has been made for all α_{lmn}. The absolute differences in the α_{lmn} were small but for the higher values of l, m, n the percentage differences became as high as 20 percent.

Table III gives the values for the α_i for values of i from one to ten, for the temperatures 404°C, 450°C, and 525°C. Here i is the number of the shell of atoms surrounding the origin atom. Also included in the table are the coordination numbers C_i, the values of α_i for the case of perfect order, and the coordinates of representative points in the ith shell, referred to half of the length of the face-centered cubic cell as unit distance.

TABLE III

Short-Range Order Parameters for Cu-Au Alloy Containing 23 At. % Au.

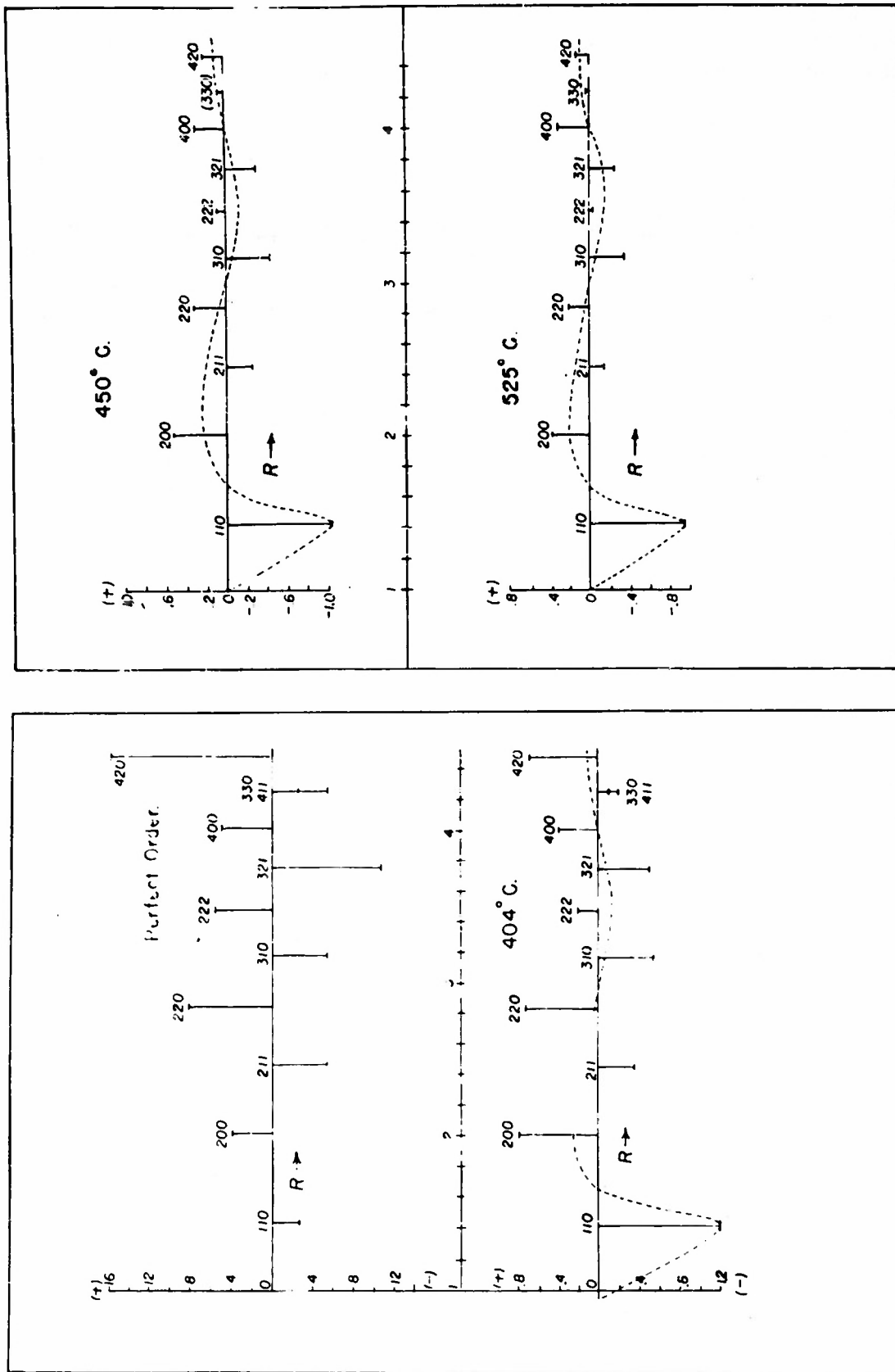| i	C_i	Coords.	i			
			Perfect Order	404°C.	450°C.	525°C.
1	12	110	−0.299	−0.137	−0.115	−0.104
2	6	200	+0.896	+0.179	+0.118	+0.089
3	24	211	−0.299	−0.019	−0.012	−0.007
4	12	220	+0.896	+0.074	+0.037	+0.022
5	24	310	−0.299	−0.041	−0.023	−0.018
6	8	222	+0.896	+0.036	+0.014	−0.002
7	48	321	−0.299	−0.014	−0.008	−0.006
8	6	400	+0.896	+0.093	+0.070	+0.072
9	12	330	−0.299	−0.020	−0.002	−0.001
	24	411		−0.005	−0.000	+.0003
10	24	420	+0.896	+0.039	+0.012	+0.008

Discussion of Results.

The short-range order parameters decrease with temperature in all cases, as expected. Also, in general, the tendency is for α to decrease with increasing distance from the origin. Further, in all cases except the 6th and 9th shells at the higher temperature, all have the same sign as for the case of perfect order. The departures from expected behaviour will be discussed presently.

The absolute values of the α_i are less for the 23 atomic percent Au alloy than for the 25 percent Au alloy (23) as predicted by the theory (24).

Errors in this work are potentially large and somewhat uncertain. Certainly, the major source of error was the corrections for scattering due to factors other than short-range order--in particular, the correction for temperature-diffuse scattering. A rough estimate of the error involved, based partly on the asymmetry of the α_i and on the calculable error in the experimental procedure, leads us to believe that the error in the α_i probably does not exceed 10 percent for the inner shells, and possibly 30 percent for the more distant shells, which have smaller values of α_i.

It was mentioned above that, although the general tendency is for the α to behave as if order were the predominating mechanism, there are deviations from this behaviour. For example, α_8 is larger than α_6, and for i odd, α_5 is larger than α_3. Furthermore, while the α_i have, for the most part, the same sign at the experimental temperatures as for perfect order, we have α_6 and α_9 with reversed signs at 525°C. Both types of deviations were explained by Cowley (17) in terms of a "liquid-like" arrangement of atoms about the origin atom. By plotting the radial distribution of atoms in a monatomic liquid on the same plot as the defect of copper atoms in a given shell, he was able to show comparatively good agreement with his experimental data on a 25 percent Au alloy. The data we obtained for a 23 atomic percent Au alloy do not show the effect nearly so strongly as Cowley's. This is evident in Figures 11 and 12 where we have plotted the copper atoms in defect in a given shell as a function of the distance from the origin (D_{Cu} = 0.77 $C_1 \alpha_1$). We have also included (dotted curve) the radial distribution function fitted at the first shell. There is some tendency to a "liquid-like" behaviour, particularly at the higher temperatures. However, compared with the data on a sample of stoichiometric composition (17), the 23 percent Au sample shows a tendency toward what one would expect if what might be called "medium-range" order were present.

Figs. 11 & 12 - Defect of Copper Atoms About a Gold Atom as a Function of the Distance from the Au Atom

Cowley (10) has related the α_i and the interaction energy, V_{IJ}, between an atom in the Ith shell and one in the Jth shell, through the expression:

$$2 \sum_J V_{IJ} \alpha_J$$

(1)

$$+ kT \ln \left(\frac{m_A}{m_B} + \alpha_i\right)\left(\frac{m_B}{m_A} + \alpha_i\right) \Big/ (1 - \alpha_i)^2 = 0.$$

T is the absolute temperature, k, is Boltzmann's constant, m_A and m_B are the fractions of A and B atoms present.

Thus, knowing the α_i, the V_{IJ} can be calculated. If we choose a given atom (say a gold atom) as origin atom, we can put $V_{IJ} \rightarrow V_i$, where i is the number of the shell in which the Jth atom appears. The interaction energies have been calculated for the first three shells, assuming that only V_1, V_2, and V_3 are appreciable. The values obtained are $V_1 = 394k$, $V_2 = 43k$, and $V_3 = 65k$, in units of energy per atom.

The value of V_3 should be considered more uncertain than V_1 or V_2, since its magnitude is very sensitive to the values of α_i, and the coefficient of V_3 in equation (1) contains a predominance of α_i with i large, and it is these α_i which probably have the greatest error.

The magnitudes and signs of the V_i are of some interest. In general, a positive sign would indicate a tendency to unlike pairs of atoms and a negative sign would indicate segregation of like atoms.

$$\left(V_{IJ} = \frac{V_{AA,IJ} + V_{BB,IJ}}{2} - V_{AB,IJ}\right)$$

However, when one considers shells beyond the first nearest neighbors, the relative values of the interaction energies of like pairs (V_{AA}, V_{BB}), as well as unlike pairs (V_{AB}), must be considered. Also the variation of the interactions with distance becomes important. Thus, it is not obvious that one should expect a particular sign for V_2 in spite of the fact that a tendency to order leads to the first shell about an Au atom at the origin being Cu-rich, the second Au-rich, and the third Cu-rich. Certainly, one would expect V_1 to be positive and large compared to V_2 and V_3. At the same time, lacking detailed information on the individual interactions, a positive value for V_2 is not unreasonable, nor is the fact that V_3 apparently has a larger magnitude than V_2.

The average number of copper atoms in a given shell about an origin atom can be calculated from $n_i = m_{Cu}C_i(1 - \alpha_i)$. The value of n_i for the first six shells are given in Table IV for the cases of disorder, perfect order, 404°C, and 525°C. Also included are the number of copper atoms in defect at perfect order, 404°C and 525°C. The last two columns, labeled percentage of perfect order, are simply the percentage ratios of the copper atoms in defect at the temperatures given, to the defect at perfect order.

It is obvious from the table that there is considerable tendency to short-range order even at the higher temperature. Also, we see evidence of a tendency to a "liquid-like" distribution. That is, shell 3 shows an inconsistently small amount of order, while shell 5 shows an abnormally large amount. Shell 6 at 525°C actually shows the liquid-like tendency to such an extent it exhibits less than zero order, or a negative order. It should be repeated, however, that this tendency is less than that found in a 25 atomic percent Au sample (17).

For more specific comparison with the results on the 25 percent alloy, we have reproduced Cowley's data in Table V (17). Notice in particular that although the difference in magnitudes of the α_3 for the 23 and 25 atomic percent Au samples is not large, there is a change of sign.

From the data in Table V, Cowley (10) computed values of the V_i and found $V_1 = 358k$, $V_2 = -34k$ and $V_3 = -19k$. Although we have relative agreement in magnitude, V_2 and V_3 are of opposite sign from that found in the present work.

Cowley (10) relates the V_i to the critical temperature, T_c, for the stoichiometric alloy through the relation

$$T_c = \frac{3}{2k} (V_1 - \frac{3}{2} V_2 + 2V_3 - \ldots).$$

Using this relation, we have calculated T_c using values of the V_i obtained from Cowley's data and the present data. We find $T_c = 284°C$ and $417°C$ respectively. The experimental value is generally given as 390°C to 396°C. Using a somewhat different formula for T_c for the case of Cu-rich alloys (10), we find for the 23 percent alloy: $T_c = 149°C$ from Cowley's data and $311°C$ from the present data. The experimental value appears to be approximately 386°C (12).

VII KINETICS OF THE ORDER-DISORDER TRANSFORMATION

The experiment to be described in this section was begun very shortly before the expiration date of the present contract and had

TABLE IV

Comparison of The Number of Cu Atoms, and The Number of Cu Atoms in Defect in A Given Shell About An Au Atom

i	c_i Disorder	n_i			Copper Atoms in Defect			Percentage of Perfect Order	
		Perfect order	404°C	525°C	Perfect order	404°C	525°C	404°C	525°C
1	12	9.24	12	10.50	10.20	-2.76	-1.34	-0.96	48.5%	34.8%
2	6	4.62	0.48	3.79	4.21	+4.14	+0.83	+0.41	20.0	9.9
3	24	18.48	24	18.83	18.61	-5.52	-0.35	-0.13	6.3	2.4
4	12	9.24	0.96	8.56	9.04	+8.28	+0.68	+0.20	8.2	2.4
5	24	18.48	24	19.24	18.81	-5.52	-0.76	-0.33	13.8	6
6	8	6.16	0.64	5.94	6.17	+5.52	+0.22	-0.01	4	0

TABLE V

Experimental Values of Short-Range Order Parameters for Cu_3Au at Temperatures above The Critical Temperature*

1	C_1	Coordinates	Perfect order	405°C	460°C	550°C
1	12	1,1,0	-0.333	-0.152	-0.148	-0.131
2	6	2,0,0	1.00	0.186	0.172	0.105
3	24	2,1,1	-0.333	0.009	0.019	0.026
4	12	2,2,0	1.00	0.095	0.068	0.045
5	24	3,1,0	-0.333	-0.053	-0.049	-0.032
6	8	2,2,2	1.00	0.025	0.007	-0.009
7	48	3,2,1	-0.333	-0.016	-0.008	-0.003
8	6	4,0,0	1.00	0.048	0.042	0.019
9	12	3,3,0	-0.333	-0.026	-0.022	-0.011
	24	4,1,1	-0.333	0.011	0.020	0.007
10	24	4,2,0	1.00	0.026	0.025	0.007

* Permission has been obtained from The Journal of Applied Physics to reproduce this table.

barely left the planning stage when sponsorship was moved to another agency. However, since it is an integral part of our order-disorder program, we feel that a description of the experiment is properly included here.

One of the most important and least well-known features of the order-disorder phenomena is the nature of the ordering force. It would seem that the best way to attack the problem is through the activation energies, or experimentally through isothermal anneals data.

The activation energy we obtain depends on what parameter we follow during the isothermal anneal. For example, published work to date has been done using resistivity as the parameter and this gives us an activation energy for the entire process of ordering. However, it is entirely possible and even probable that two or more processes occur simultaneously in the growth of ordering. Specifically they may be lattice strain recovery and growth of the ordered domains which may not necessarily coincide with each other. Fortunately, we now have x-ray techniques for detecting strain and crystallite size and separating their effects on the diffraction intensities. We are attempting to use these techniques to obtain some specific data on the kinetics of the order-disorder transformation.

When a Cu_3Au alloy, which has been quenched from a high temperature, is annealed at temperatures below the critical temperature for ordering, superstructure lines appear in the x-ray pattern, first as very broad, very weak lines which become narrower and stronger with continued annealing until they reach an equilibrium value. From Fourier analyses of the details of the superstructure line profiles for different orders of the reflection we can compute the lattice strain and the domain size of the ordered regions. Then from plots of strain versus anneal times and domain size versus anneal times for different temperatures we can get equal property curves and consequently separate activation energies for recovery and domain growth-providing they both occur, of course. From these results and similar results from resistivity data we hope to be able to say something of the role strain plays in order, and perhaps even say something of the mechanism of ordering.

We are also recording line profiles of fundamental lines so that we will be able to compute the long-range order parameter as a function of annealing time. Since we are recording the profile of several orders of several different lines we may, in this case, be able to do something (experimentally) about

extinction (See Section V).

In addition, we are following the entire process by means of powder techniques, employing a 19 cm camera with a very fine pinhole collimater which coupled with other experimental precautions should allow us to obtain lattice parameters (and relative shifts in line positions) to about one part in 50,000.

It is important to realize that the experiment we have described is concerned with only part of the ordering process; that part of the ordering which occurs after the initial appearance of a super-structure line and which could be considered the "completion" of the ordering process. The "initiation" of the ordering process which involves what we may call the nucleation of the ordered phase and the agglomeration or growth of these nucleii to a size which will produce ordered domains (about 18 atoms on an edge according to Sykes and Jones (21)) is also very important. However, it does not lend itself so readily to x-ray studies. It could be studied by observing changes in lattice parameters but this not only requires very precise measurement of the lattice parameter; but also the change in lattice parameter due to short-range order must be corrected for. The latter statement is not meant to imply that short-range and long-range order are different phenomena and we do not have the space to note all the arguments here, but there seems to be a discontinuity in lattice parameters (and lattice parameter change) as we pass through the "disordus" temperature. At the same time there is an anomolous change in lattice parameter above this temperature which is attributed to short-range order.

In any event, there is much to be learned of the details of the ordering process by studying both phases, and we are presently trying to overcome the experimental difficulties involved in studying the "initiation" of the ordering process by resistivity and thermoelectric power techniques.

VIII GENERAL DISCUSSION

It appears fairly well established from x-ray evidence (this report), resistivity data (6) and galvanic cell measurements (22) that the order-disorder transformation in the neighborhood of Cu_3Au is a classical phase transformation. Since the transformation temperatures are quite low, the nucleation rate is high and the growth rate low so that the equilibrium problem is a severe one and detection of the two phases in equilibrium difficult. The same statement will apply to many order-disorder transformations and in some cases, even if two phases coexist, they may defy detection. For example, in the Cu-Pd system near Cu_3Pd the volumes of the ordered and disordered unit cells are

are equal so that the x-ray techniques described in this report could not be used. In other systems such as Fe-Pt, the resistance changes on ordering are negligible. It is entirely probable that all order-disorder transformations are heterogeneous, but however attractive this probability may be it definitely cannot be assumed, but will have to be determined for each system.

Rhines and Newkirk (6) have discussed in detail the approach to equilibrium in Cu-Au alloys which exhibit order. Their discussion is based on resistivity measurement made in the course of what amounts to isothermal anneals. They attribute the long times required for equilibrium to different reasons for different cases. Where a long induction period is required to initiate parameter changes nucleation is considered to be the time controlling factor and where there is only a short induction period but a very gradual change of parameter the time controlling process is the growth of the domain (the diffusion process). Further, Rhines and co-workers found that the induction period was much longer when the temperature was raised (instead of lowered) so as to cause the alloy to change from an ordered state to a two-phase or disordered situation. From this, they concluded that the nucleation rate is slower and the required nucleii larger in the disordered state. In this latter respect, our observations are at considerable variance with theirs. Although we believe that the nucleation rate is lower at the (higher) temperatures required for disordering, we found no long induction periods on heating our samples, but we found very long induction periods in cooling ($\sim$10 days). We admit that we did not have the degree of equilibrium described by Rhine and co-workers and it is possible that these induction periods existed but were missed in the copper-rich samples. However, we held copper-rich samples at temperatures in the critical region for as long as two weeks and furthermore in the gold-rich region the appearance of a second phase was always observable within a few hours ($\sim$4) of the time of this initial temperature change. It is possible that there is a difference in the effects produced by order-disorder in resistivity and lattice structure which can explain the discrepancy, but it is not obvious.

We found, as did Rhines and co-workers, that the transformation rates were slower for compositions considerably removed from stoichiometric. However, it is not clear whether this is due to the lower temperatures of transformation or to the fact that the ordered phase is less perfect and consequently differs less in energy content from the disordered phase.

Let us return a moment to the difference in results on heating ordered samples or cooling disordered ones to obtain a given condition. When one cools a sample while studying the

x-ray diffraction lines produced, satellite lines appear near the diffraction lines when the critical temperature region is approached. (The appearance of these lines was first pointed out to us by Professor Warren of M.I.T.). We have obtained as many as four satellites on one side of a given line for 34 percent gold samples. These satellites, which appear within about 1 or 1.5 degrees in 2ϑ of the principle line, appear only on cooling and were never observed on heating. (This observation was also made by Professor Warren). Their presence is difficult to explain, but perhaps it is due to the fact that certain mosaic blocks are ordered before others and the difference in size of the ordered and disordered phases causes a tilting of some of the mosaic blocks. This is strictly a suggestion and the feeling here is that it would be difficult to defend.

The data of Section VI have indicated that the short-range order parameters as defined by Cowley (3) are definitely smaller for copper-rich samples than for Cu_3Au. In order to check the theory further, there is real need for work on short-range order on gold-rich samples for which the α are predicted to be larger (10). At the same time, our results have indicated that there is a stronger tendency toward what might be called "medium-range" order in the 23 percent Au sample than in the 25 percent sample. That is, the "liquid-like" distribution found by Cowley (17) is not as predominant in the non-stoichiometric samples. It is easy to interpret this effect as less tendency for proper next nearest neighbors and probably this is actually the case. However, more data on other non-stoichiometric composition samples are needed (particularly gold-rich samples) before we can rule out less obvious, but perhaps more fundamental possibilities (assuming, of course, that we cannot attribute the whole effect to experimental error).

It appears that the overall behaviour of the long-range order parameter does not differ greatly for the various compositions, apart from a slight decrease in the rate of disappearance of S with temperature as we depart from the stoichiometric composition. The existance of the two phases is not detectable from a measurement of S as a function of temperature when the measurements are no more detailed than those reported here. However, some interesting results have been obtained in Fe-Pd alloys near $FePd_3$ by measuring S as a function of time at a given anneal temperature (22). Thus, it is hoped that similar measurements now being made on Cu_3Au (Section VII) will be more fruitful from the interpretation point of view. The results of long-range order studies reported here are primarily of academic interest since such studies (on non-stoichiometric alloys) had not been made and

were needed not only for completeness, but to determine the over-all value of such studies and for comparison with theory.

It is hoped that considerable information on the size of the ordered domains will be obtained from the experiment described in Section VII. The domain size is of interest and importance in mechanical and magnetic property measurements and their correlation with the order phenomenon. The size of the ordered domains under various conditions has been measured previously by Sykes and Jones (21) who calculated it from the total broadening of x-ray diffraction lines. However, lattice strain, if present, contributes to line broadening, and this is one of the points we hope to clear up with the experiment described.

There is still considerable work to be done on order-disorder and specifically on Cu-Au alloys. Detailed measurements of the effects of order on the temperature coefficient of resistivity, the diamagnetic susceptibility and thermoelectric power should prove interesting (we are presently studying these quantities elsewhere). A great deal of work is needed on the annealing kinetics; the type and number of experiments which come under this general topic are practically innumerable. More work is needed on the effects of radiation and cold-work, and the relative behaviour on annealing of irradiated, cold-worked, and quenched samples.

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