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LATTICE PARAMETERS, COEFFICIENTS OF THERMAL EXPANSION,
DENSITIES, AND LATTICE PERFECTION OF THE COPPER-
INDIUM PRIMARY SOLID SOLUTIONS

BY 758
LIN SHENG YU, 1936

A

THESIS

Submitted to the faculty of
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ABSTRACT

Precise measurements of lattice parameters and densities of the alpha-phase Cu-In solid solutions were made at temperatures of 25 °C. The thermal expansion coefficients between 15 and 65 °C, the solid solubility of In in Cu at 650 °C, and the soundness of crystal structure resulting from alloying were determined.

The Cu-In alloys were prepared from high purity (99.999%) Cu and In by melting both metals inside evacuated quartz tubes. The solidified alloys were annealed and then examined by X-ray for homogeneity.

It was found to expand the lattice of Cu up to 10.50 at. % In, which marks the solid solubility limit of the alpha-phase of the Cu-In system at 650 °C in good agreement with the literature. The lattice parameter of Cu ($a_{25} = 3.6149 \text{ \AA}$) increased at a rate of 0.0091 Å per at. % In.

The coefficient of thermal expansion of Cu within the range 15-65 °C increased rapidly with the addition of In up to about 4 at. % In and then remained approximately constant.

The slowly solidified alpha-phase alloys gave densities lower than the theoretical (X-ray) values due to the presence of shrinkage microporosity. This density defect was found to increase with In concentration. The alloys quenched from the molten state, while still exhibiting lower density values, showed no visible porosity. However, upon annealing, voids appeared. It is very possible that the frozen-in vacancies in the quenched alloys coalesced during the prolonged heat treatment to voids visible under the optical microscope.

The pores could be annihilated by plastic deformation (compression or rolling) and then the densities raised up to the theoretical. It is concluded that no structural defects (monovacancies) are formed during the cooling of Cu-In alloys, only microporosity probably due to differential shrinkage of the primary crystallization products as compared with the matrix.

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CHAPTER I

INTRODUCTION

The advances in technology in recent years have resulted in a demand for new and improved materials. Consequently, various alloys have been developed. In the process of alloy formation, it was found that vacant lattice sites in excess of the normal thermal equilibrium concentration were created in the primary solid solutions of many binary systems. Whether this is universally true, however, remains to be proven. Since the formation of the structural vacancy is of great importance with regard to alloy theory, and since this defect in atomic dimensions plays an essential role in many important processes occurring in solids, considerable efforts have been made to evaluate the degree of vacancy concentration in metallic primary solid solutions.

A method for the evaluation of crystal perfection of a solid solution is provided by measuring lattice constants and densities, and calculating the average number of atoms or molecules actually existing in a unit cell of the solid solution. Comparing this number with the theoretical one, or alternatively, the bulk density of the solid solutions with the theoretical X-ray density, conclusions regarding the perfection of structure of the

solutions can be determined. This method requires extreme precision in the determination of bulk densities, lattice parameters, and the thermal expansion coefficients. The bulk density must be measured directly, while the last two are found by the X-ray diffraction.

These techniques were employed to determine if lattice defects exist in the alpha-phase solid solutions of the Cu-In system. As a consequence the limit of solid solubility of In in Cu at a temperature of 650 °C was also redetermined.

CHAPTER II

LITERATURE REVIEW

Since the discovery of In in 1863, many alloy systems of In have been extensively studied. Not much attention has been given, however to the Cu-In alloys. It was not until 1934 that Weibke and Eggers, using thermal, microscopic and X-ray methods, determined the first complete Cu-In phase diagram¹. Then Hume-Rothery, Raynor, and Reynolds in 1940 used classical metallurgical methods to determine the Cu-In phase diagram in the 9-25 atomic % region of indium². In 1949, Owen and Morris published a paper in which the solubility of In in Cu (determined by the X-ray method) at 470-715 °C was given, but without any data on which the figures for the solubility were based³. This information was presented by Owen and Roberts in a later paper⁴ along with the lattice parameters of the alpha Cu-In alloy phase at 18 °C. In their work the alloys made from Cu and In of purities 99.95 and 99.98 % respectively, were prepared by fusing the constituents in evacuated silica tubes. The tubes were vigorously shaken during melting for about 20 minutes and quenched in cold water. The alloys were then lump-annealed at 575 °C for 14 days. X-ray specimens taken from the alloy ingots were annealed overnight at 500-600 °C in small evacuated capsules. X-

ray photographs were taken with a focusing camera and Ni radiation.

Using the same experimental technique, Jones and Owen⁵ in 1953 made X-ray determinations of the alpha-phase boundary of the Cu-In alloys prepared from Cu of 99.999% and In of 99.98% purity.

More recently, Stirling and Raynor⁶ (1955) examined alloys composed of 99.987% O.F.H.C. Cu and "spec. pure" In. The alloys were melted in vacuo, cast, homogenized at a high temperature and then isothermally annealed at the required temperature. Powders for X-ray pictures were stress-relieved at the same temperature and quenched. Powder photographs were taken in a Unicam camera. The lattice spacings were calculated using the extrapolation method of Nelson and Riley. These values, as well as those obtained by others, are listed in Table 1.

The published Cu-In phase diagram⁷ as shown in Figure 1 represents a combination of the results by the last researchers mentioned above. According to this diagram, the maximum solubility of In in Cu is 10.85 atomic % at 575 °C and the solubility at the peritectic temperature is 10.05 atomic % In. These figures are considerably lower than the values of 11.63 at. % and 9.5 at. % In

TABLE I

Published Lattice Parameters of the
Alpha-Phase Cu-In Alloys

(Values in Å, reduced to 18 °C)

At.-% In	W & E	O & R	J & O	S & R
0	3.61529		3.6147	
1.38		3.6274		
2.00	3.6338		3.6343	
2.55		3.6383		
3.10	3.64535			
3.78		3.6501		
4.01			3.6529	
4.60	3.6579			
5.08		3.6624		
5.20	3.6654			
5.83		3.6694		
5.87			3.6698	
6.00				3.6701
7.61			3.6860	
8.00				3.6876
8.20	3.6904			
8.49			3.6949	
9.00			3.6988	
9.12		3.6997		
9.82			3.7067	
10.00				3.7077
10.50			3.7121	
10.80	3.7095			
10.84		3.7147		

W & E: Weibke & Eggers

S & R: Stirling & Raynor

O & R: Owen & Roberts

J & O: Jones & Owen

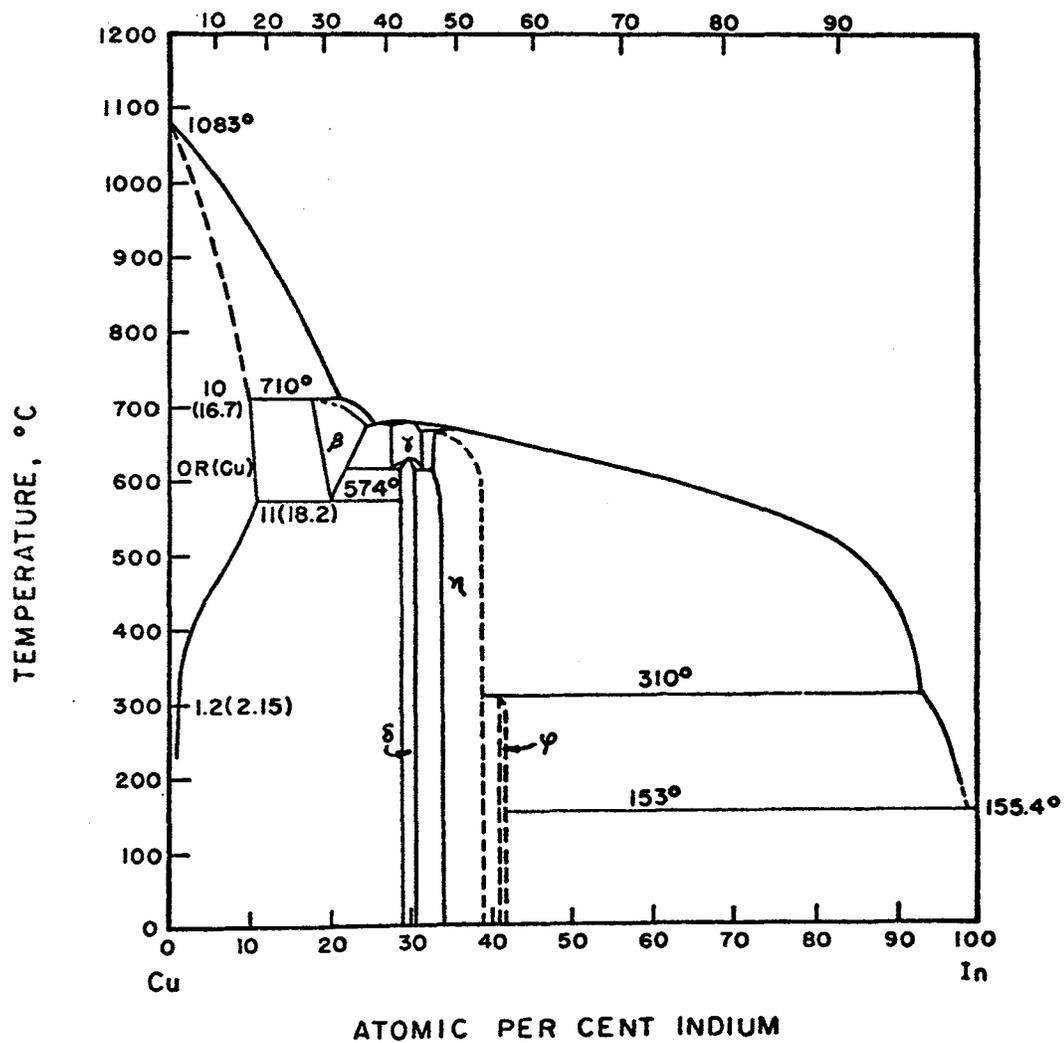


Figure 1. The published Cu-In phase diagram.
(ref. 7)

respectively given by Weibke and Eggers¹. At about 470 °C, the solvus line shows a point of inflection which, according to Jones and Owen, suggests a transformation at this temperature. The solubility of indium in copper decreases rapidly below this temperature, reaching 1.1 at. % at 250 °C.

The articles by Weibke & Eggers, Owen & Roberts, Jones & Owen, and Stirling & Raynor are the only ones giving the lattice parameters of the primary Cu-In solid solutions. No further information on thermal expansion, density and crystal perfection could be found in the literature.

On the other hand, considerable efforts have been made in studying the point defects (vacancies) in many primary solid solutions and intermediate phases of other systems. For example, Ellwood and Bagley found that anomalies in lattice spacing and density existed in the Al-Zn⁸ and Au-Ni⁹ solid solution systems. Similar phenomenon were also observed in the Ag-Zn¹⁰ and Sn-In¹¹ systems. The discrepancies between the measured and the theoretical (X-ray) densities seemed to indicated to these authors that high concentrations of vacancies in the alloys must exist and accordingly, the Brillouin zone concept was applied to explain them. Later investi-

gations of Dodd and his colleagues, however, proved that none of the primary solid solutions contain high vacancy concentrations^{12,13,14,15}. This discovery is of fundamental importance from the view point of alloy theory.

CHAPTER III
EXPERIMENTAL PROCEDURE

A. Source and Preparation of the Alloys

The Cu-In alloys used throughout this investigation were made of high purity (99.999%) metals, supplied by the American Smelting and Refining Company in the form of rods.

The calculated amounts of Cu and In were weighed on a semi-micro balance to make an alloy of about 10 grams of the desired composition. The metals were then placed in a clean, dry quartz tube closed at one end. The tube with its contents was evacuated to a pressure of about 4 millimeters of mercury by means of a mechanical vacuum pump, and then the tube was sealed off.

Melting was done in a vertical tube furnace. The sealed tube was placed on a small cradle of iron wire, which was in turn suspended in the furnace by a thread passing over a pulley coupled to a small clock motor. The sample tube was then positioned in the heating zone and heated to a temperature of 1,150 °C. After melting, the two metals were thoroughly mixed by shaking the tube inside or outside the furnace. The tube with its contents

was returned to the furnace before it could freeze. This operation was repeated several times. In order to minimize the formation of shrinkage voids during freezing as much as possible, and to provide the opportunity for the vacancies introduced to coalesce to larger entities, the homogeneous alloy was passed through the heating zone by lowering the cradle. The solidification occurred at a rate of one centimeter per hour, so that the sample passed the zone from the melting point to about 400 °C in 8 hours.

This rate of solidification, although good for alloys of lower In concentration, was considered insufficient for alloys of higher In content. Therefore, the ingots containing more than 12 wt.-% In were quenched in water from temperatures 50 °C above the liquidus. Thus the metal inside each sealed tube was heated to 1,150 °C and after repeated shaking, was quenched in cold water. Water quenching was necessary to prevent segregation during solidification (see Figure 1).

To insure homogeneity, all the solidified alloy ingots were homogenized at 800 °C for 14 days. They were again water quenched.

Powder samples were taken from both ends of the

ingots and after annealing, were examined by X-ray diffraction for homogeneity. If there was only a small difference in lattice parameters of the two powder samples, the respective alloy was considered homogeneous.

Microscopic examination was also carried out to check for a second phase possibly precipitated and for microporosity. This was done by sectioning a sample from one end of the ingot (in some cases, sections were made at both ends of the ingot), polishing and etching with ferric chloride, and by optical examination at a magnification of 750x.

Since Cu and In were melted under vacuum, their initial weights were taken to represent the chemical composition of the final alloys. Weight losses after annealing amounted to less than 1 part in 4,000 in all alloys.

B. X-Ray Studies

1. Determination of Precise Lattice Parameters

i. Powder Technique

A powder camera of 6.4 cm in diameter was used to obtain diffraction photographs of the powder

samples.

It is possible to calculate the lattice parameters of a cubic substance from each of the powder line after all the lines are properly indexed. However, the parameters calculated from each line are never consistent due to two types of errors: random and systematic.

Random errors arise because of the error in film measurements and non-uniform film shrinkage. These are minimized at high Bragg angles. This results can be shown by differentiating the Bragg equation, which gives $\Delta d/d = -\cot \theta \Delta \theta$. Therefore, as θ approaches 90° , the error in d spacings approaches zero.

Systematic errors arise due to different reasons; namely,

- a. Absorption of X-rays by the specimen
- b. Incorrect camera radius
- c. Non-uniform film shrinkage
- d. Off-centering of specimen
- e. Beam divergence.

The effect of beam divergence and eccentricity are usually minimized by careful design of the camera. Errors due to absorption can be minimized by the use of very thin specimens. The remaining two errors: the radius

error and the error due to non-uniform film shrinkage can be eliminated by the use of asymmetric patterns¹⁶. It can also be shown that all the systematic errors decrease as θ approaches 90° . Thus using the asymmetric patterns and high angle reflections, high precision in lattice parameter measurement can be achieved.

There is one more systematic error known as refraction error. This can neither be eliminated nor minimized but it can be calculated and the correction added to the lattice parameter. This is discussed in detail in a later section.

ii. Preparation of X-Ray Sample Mounts

After the surface layer of the ingot was removed by filing, some further filings were taken from the ingot. The powder, sealed in an evacuated small quartz tube, was annealed at 650°C for 45 minutes to relieve the stress caused by filing. The tube with its contents was quenched from 650°C to prevent the precipitation of a second phase.

The powders were sieved through a 325-mesh bolting cloth, using the underscreen for the preparation of the powder mounts. A hair of lithium-boron glass of about 0.08 mm in diameter was glued to the tip of the sample

holder, which was so adjusted that the glass fiber, as viewed under a microscope, rotated within the axis of the X-ray camera. The fiber was then covered with a thin coating of adhesive, and the powder spread evenly over the coated glass fiber. The overall diameter of the mount was never allowed to exceed 0.2 mm in order to prevent broad diffraction lines and to minimize the adsorption effect.

The sample mount was again checked for centering. This was done by observing the rotation of the powder mount in the camera through the collimator with the aid of a magnifying glass. The most appropriate place of the mount to be exposed to the X-ray beam was also chosen during this operation.

iii. Film Loading and Diffraction Patterns

The asymmetric method¹⁶ of film loading was used in the present work. By this method, the circumference of the film and thus the diffraction angles can be determined precisely without the knowledge of the diameter of the camera and the amount of film shrinkage. The method is sufficiently described in the literature.

The loaded film in relation to the incident beam and the film laid out flat after exposure are shown in

Figures 2 and 3.

iv. Temperature Control

It is well known that temperature has a strong effect upon the lattice constant of a crystalline material. A temperature deviation of ± 0.1 °C influences the lattice parameter in the fifth decimal place in a measurable manner, depending upon the magnitude of the expansion coefficient. Close temperature control is thus necessary in precise measurements.

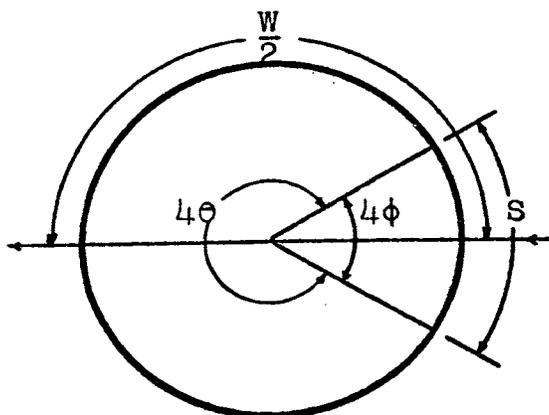


Figure 2. Asymmetric film loading.

To obtain the diffraction patterns at a constant temperature, the loaded camera was placed in a thermostat. By controlling the temperature of the circulating water, the temperature of the camera could be maintained with a precision of ± 0.05 °C. The film was exposed to

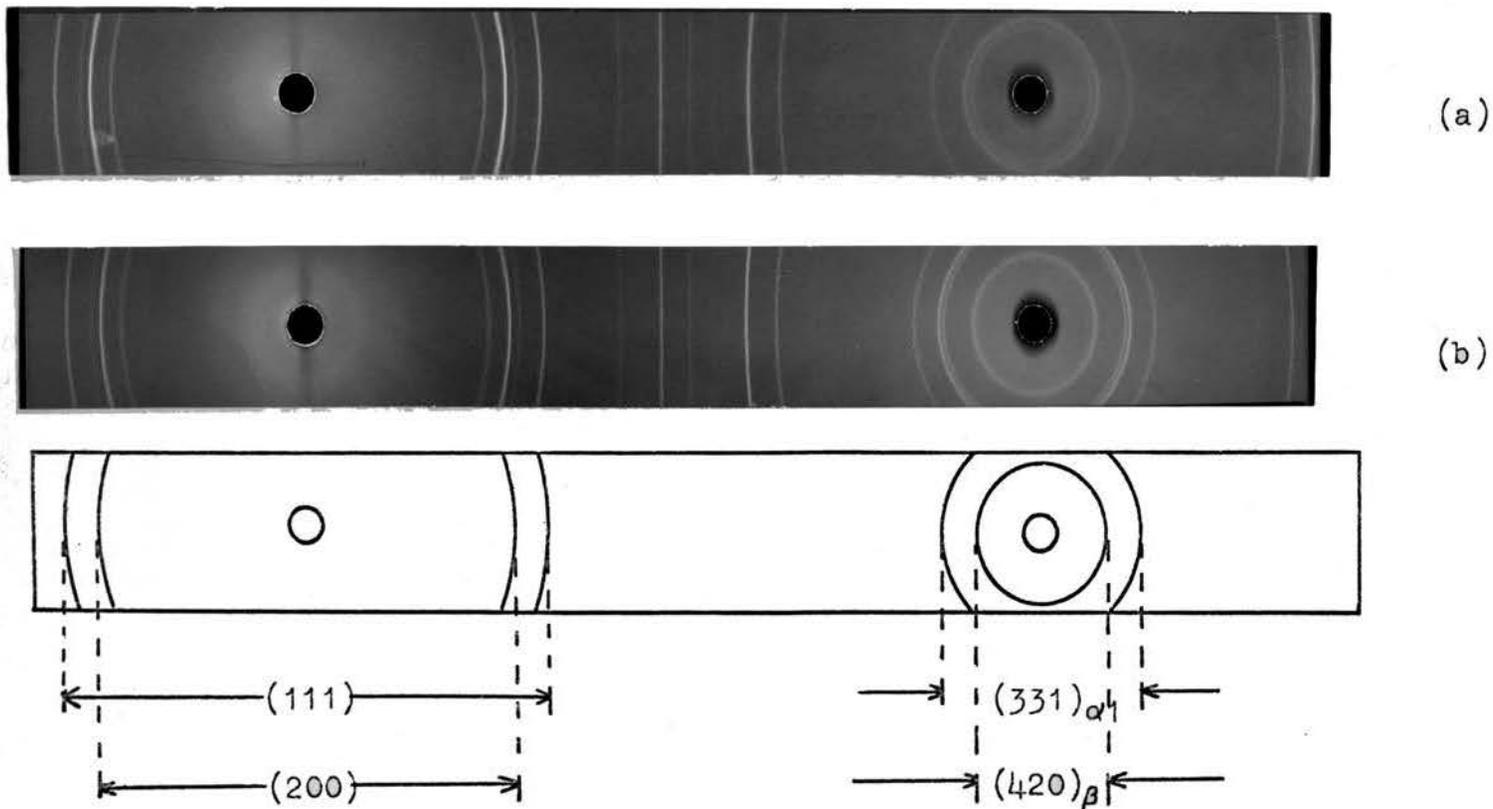


Figure 3. Asymmetric powder pattern of (a) pure copper and (b) Cu-8 wt. % In alloy taken with Co-radiation.

X-rays after keeping the camera at constant temperature for 30 minutes. This resulted in a constant specimen temperature and also prevented any change of length of the X-ray film during exposure.

v. Film Measurement

The diffraction lines on the film were measured using a comparator having a precision of 0.001 mm. The film was clamped between two glass plates and the equator of the diffraction pattern was centered with respect to the cross hairs of the measuring microscope.

Two sets of lines in the front and back reflection regions were measured by superimposing the intersection of the cross hair of the microscope with the maximum intensity of the line. To improve the accuracy, each line was measured several times and the average value was taken. As seen in Figures 2 and 3, the point where the beam entered is half way between the measured positions of the 331_{α_1} lines or of the 420_{β} lines. The point where the transmitted beam left is half way between the lines from the (111) planes or that from the (200) planes. The difference between these two points gives the semi-circumference, $W/2$, and ϕ (see Fig. 2) is found from the equation

$$\frac{4\phi}{360} = \frac{S}{W}$$

where ϕ is $(90 - \theta)$ and S is the diameter of the diffraction ring, and θ is the Bragg angle. Thus from the measured positions of the diffraction lines, the effective film circumference and the back and front reflection Bragg angles can be calculated.

vi. Indexing of the Cu Diffraction Pattern

The Cu diffraction pattern was indexed by a graphical method based on the concept of the reciprocal lattice. This method is simple and convenient for indexing patterns of the cubic system. The proper radiation for a given material can also be selected to give the highest back reflection angles.

Co radiation was chosen to obtain the diffraction photographs of Cu. The graph for the $\text{CoK}_{\alpha 1}$ radiation is shown in Figure 4. The same indexing also applies to the alpha-phase of the Cu-In system since the increase in the In content within the alpha range does not result in an appreciable shifting of the diffraction lines. All lines on the diffraction photographs were measured and the 2θ angles calculated. The 2θ angles were plotted on the reflection circle and the intersections with it

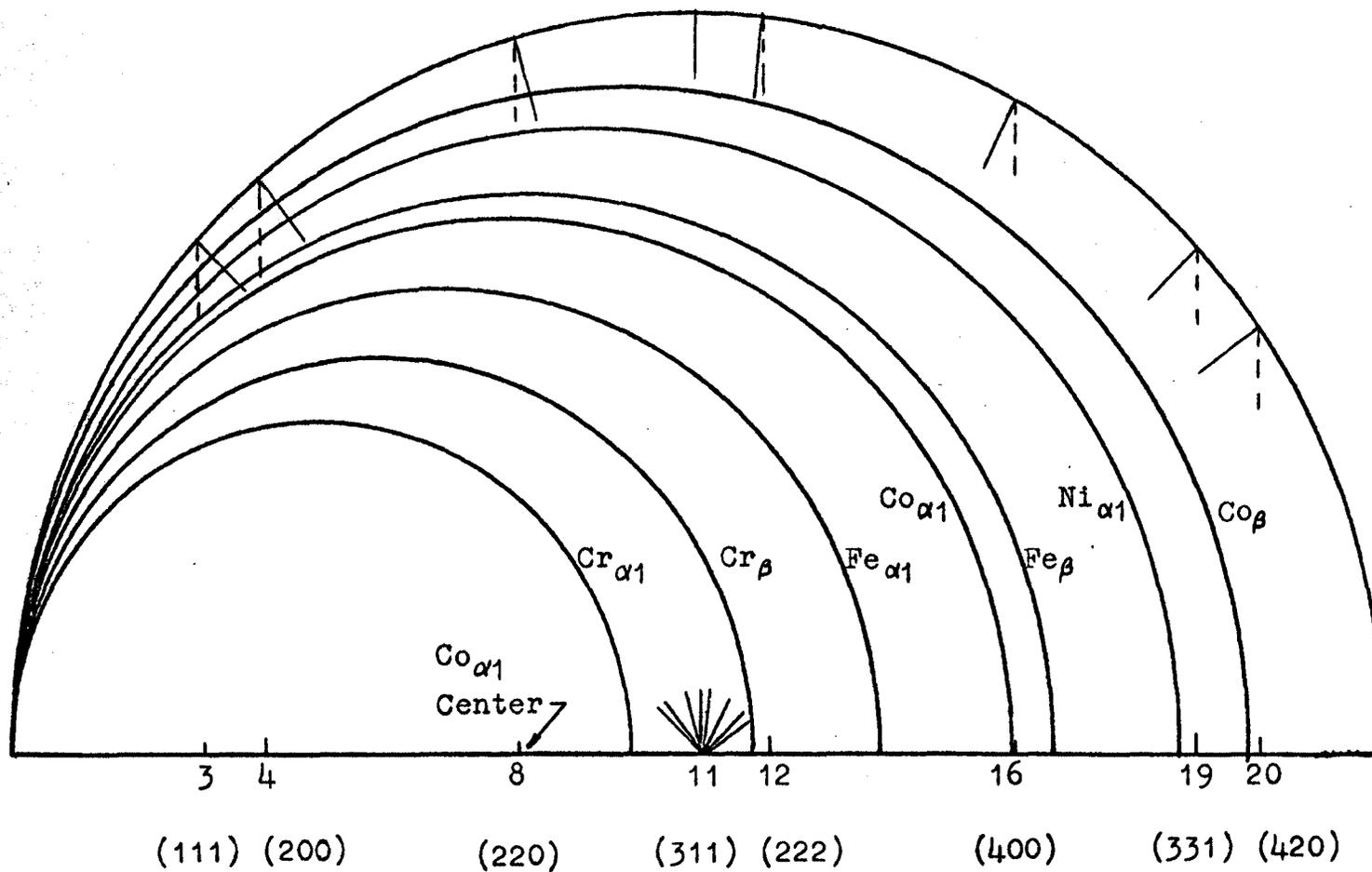


Figure 4. Graphical indexing of a powder pattern of pure copper.

were projected onto the horizontal diameter of the circle. The indices were read from divisions on the diameter.

vii. Calculation of Lattice Parameters

The lattice parameters of the alpha-phase Cu-In alloys were calculated from the Bragg equation in the form:

$$a = K_0 / \sin \theta \quad (1)$$

where the values of K_0 is shown below.

In the present work, $\text{Co}_{\alpha 1}$ radiation, $\lambda = 1.78529 \text{ kX}$, and the (331) plane were used for calculating the lattice parameters of Cu-In alloys containing less than 4 wt.-% In. For alloys containing 4 wt.-% In and above, the 420 diffraction line showed up clear enough to be read on the comparator. Using these wavelengths and the Miller indices, the following constants of K_0 were obtained:

Alloy	Radiation	Wavelength in kX	(h,k,l)	K_0
<4 wt.-% In	$\text{CoK}_{\alpha 1}$	1.78529	(331)	3.57058
>4 wt.-% In	CoK_{β}	1.61744	(420)	3.61671

viii. Refraction Correction

The wavelengths of the X-rays are altered

when they pass from one medium to another. This phenomenon causes a deviation from Bragg's law, leading to slightly lower lattice constants. The corrected Bragg equation may be rewritten as follows:

$$n\lambda = 2s \left(1 - 5.40 \frac{ds^2}{n} \cdot 10^{-6} \right) \sin \theta \quad (2)$$

where n is the order of diffraction, λ is the wavelength of the X-ray used, s is the interplanar spacing, d is the density of the crystal, and θ is the Bragg angle.

Substituting the interplanar spacing, s , of cubic substances into equation (2) and equating equation (1), the following convenient form for the refraction correction is obtained:

$$a_{\text{corr}} = a + \frac{5.40 da^3 10^{-6}}{h^2 + k^2 + l^2} \quad (3)$$

where a_{corr} is the lattice parameter a corrected for refraction.

Substituting the appropriate values for a , d , etc. in equation (3), the value for refraction correction of the Cu and Cu-In alloys was found to be 0.00014 Å.

ix. Error Calculation

In order to evaluate the precision of the

lattice constant determination, error calculations are necessary. The values of the lattice constants measured at different temperatures were reduced to 25 °C, using the following equation:

$$a_{25} = a_t (1 + \alpha (25 - t)) \quad (4)$$

where α is the coefficient of thermal expansion and a_t is the lattice constant at t °C.

The average values of these reduced constants were found and the deviations from this average value were calculated. The standard deviation and the probable error are given by equations (5) and (6) respectively:

$$S = \sqrt{\sum(dx)^2 / (n - 1)} \quad (5)$$

where S is the standard deviation, $\sum(dx)^2$ is the sum of the squares of the deviations and n is the number of measurements or degrees of freedom.

Multiplying S by 0.675, the probable error, S' , is obtained at a 50% confident limit:

$$S' = 0.675 S \quad (6)$$

2. Coefficients of Thermal Expansion

The coefficients of thermal expansion of the

Cu-In solid solutions were determined from the lattice parameters at six different temperatures ranging from 15-65 °C. Two films of each sample were taken at each temperature, and the average lattice parameter was plotted against the temperature. In all cases, the relationship was essentially linear. The linear thermal expansion coefficients were calculated using the following equation:

$$\alpha = (a_t - a_{25})/a_{25}(t - 25)$$

or, $\alpha = \Delta a/a_{25}\Delta t$ (7)

where a_t is the lattice parameter at t °C, and a_{25} is the lattice parameter at 25 °C.

In the above equation, $\Delta a/\Delta t$ is the linear thermal expansivity of the unit cell in angstrom per degree C and is represented by the slope of the straight line in the plot of the lattice parameter versus temperature. The coefficients of thermal expansion were determined from these values and the lattice parameters at 25 °C.

C. Density Measurements

Density determination is important in many instances. A precise density determination is a requisite in distinguishing the type of a solid solution or of an alloy and

evaluating the perfection of a crystal structure by establishing the number of atoms or molecules per unit cell.

The densities of Cu and Cu-In alloys were measured by hydrostatic weighing which is based on the displacement principle of Archimedes. The method involves weighing the sample in air and in a liquid of known density. To obtain maximum accuracy, the whole surface of the specimen must be covered with the liquid and the change in temperature due to evaporation must be kept to a minimum. Thus the liquid must have a low surface tension and a low vapor pressure. Xylene $C_6H_4(CH_3)_2$ possesses these properties and was chosen for the measurements.

1. Determination of the Density of Xylene

"Natural Histological Xylene", supplied by Fisher Scientific Company, was used for the immersion liquid. The density of this liquid was determined at 25 °C, using a thermostatically controlled pycnometer and triply distilled water.

A Fisher pycnometer was cleaned, dried, and weighed in air. It was then filled with deaerated triply distilled water, and placed in a thermostated water bath, (± 0.02 °C). The pycnometer was immersed in the circu-

lating water of the bath for about one hour to thermal equilibrium.

The water level in the pycnometer was adjusted to the mark on the pycnometer neck by removing the excess liquid with a strip of clean filter paper. The pycnometer was then checked for the absence of air bubbles, removed from the water bath, dried on the outside, allowed to attain room temperature and finally weighed.

The difference in the weight of the pycnometer before and after filling it with water gave the net weight of the distilled water being used to fill the marked volume of the pycnometer at the particular temperature of the water bath. This weight was then corrected for buoyant effect of the air using the following equation:

$$m = w - wd_a(1/d_m - 1/d_b) \quad (8)$$

where m is the mass of the distilled water, w its weight in air, d_a the density of air at the time of weighing, d_m the density of water, and d_b the density of the brass weights.

The volume of the pycnometer at 25 °C was calculated from the mass of the distilled water, using the densities

of water as listed in the International Critical Tables at specific temperatures.

The pycnometer was then emptied, cleaned, dried and filled with xylene. The mass of xylene which occupied the same volume as the water at the same temperature was determined similarly. The density of xylene, reduced to vacuum, at this temperature was calculated by dividing the mass of xylene by the volume found.

The densities of Cu and its alloys were then determined at 25 °C.

2. Preparation of Samples for Density Determination

Two or more samples of pure Cu and Cu-In alloys up to 8 wt-% In were prepared in the manner as described in Chapter III, page 9. Since they were originally slowly cooled from the liquidus temperatures, the resulting ingots consisted of a few large crystallites. Microscopic examination showed, however, that shrinkage porosity still existed with the exception of pure Cu. On the other hand, it was evident that water quenching after homogenization at 800 °C had prevented the precipitation of a second phase.

Two sets of density values were obtained: first

with samples subjected only to homogenization treatment, and then with the same samples cold rolled to reduce shrinkage voids. The samples were annealed at 550 °C for 24 hours to remove the stress. Before measuring the density, the surface layer and the shrinkage pits were removed from each of the samples by filing and then they were etched in dilute nitric acid (one part HNO₃ to four parts H₂O) for removal of the stressed surface layers, washed with distilled water, and dried in vacuum.

3. Method of Measuring the Bulk Density

The specimen, suspended on a thin tungsten wire of known weight, was first weighed in air. It was then immersed in a beaker containing xylene. To improve the accuracy of the density measurement, the gases adsorbed on the surfaces of the specimens were removed by placing the beaker in a desiccator and subjecting it to mechanical vibration under reduced air pressure.

The specimen was then suspended in xylene at 25±0.01 °C for one hour before weighing. The weight of the specimen in xylene was not corrected for the effect of surface tension, because it affected only the circumference of the thin W wire (0.08 mm in diameter).

The density of the specimens, corrected for the

buoyancy of air, was calculated from the following equation:

$$d_{25,\text{vac}} = (d_1 - d_a) \frac{W_a}{\Delta W} - d_a \quad (9)$$

where $d_{25,\text{vac}}$ is the density of the sample in vacuum, d_1 is the density of xylene, d_a is the density of air, W_a is the weight of the sample in air and ΔW the weight loss of sample in xylene, all at 25 °C.

This method was checked by determining the density of two single crystals of Ag as described later. A value of 10.4973 was obtained, comparing favorably within the limits of error with the calculated X-ray density of 10.4978 g cm⁻³.

CHAPTER IV
EXPERIMENTAL RESULTS

A. Lattice Parameters of Cu-In Alloys at 18 °C

The powder from eight homogenized alloy ingots containing 0.25, 0.50, 1.00, 2.00, 3.00, 4.00, 8.00 and 12.00 weight % of In was prepared as previously described (page 13). From each of these alloys, two photographs each were taken at six constant temperatures ranging from 15 to 65 °C. The exposure time was one hour for temperatures lower than 45 °C and 75 minutes for temperatures above this.

The average lattice parameter of two determinations at each temperature is plotted against the temperature as shown in Figure 5. The lattice parameters of the alpha-phase solid solutions reduced to 18 °C, are plotted versus In content in Figure 6 for the purpose of comparison with the measurements of other authors.

B. Solid Solubility of Indium in Copper at 650 °C

In determining the solid solubility of In in Cu, or of the alpha-phase boundary at 650 °C, three addi-

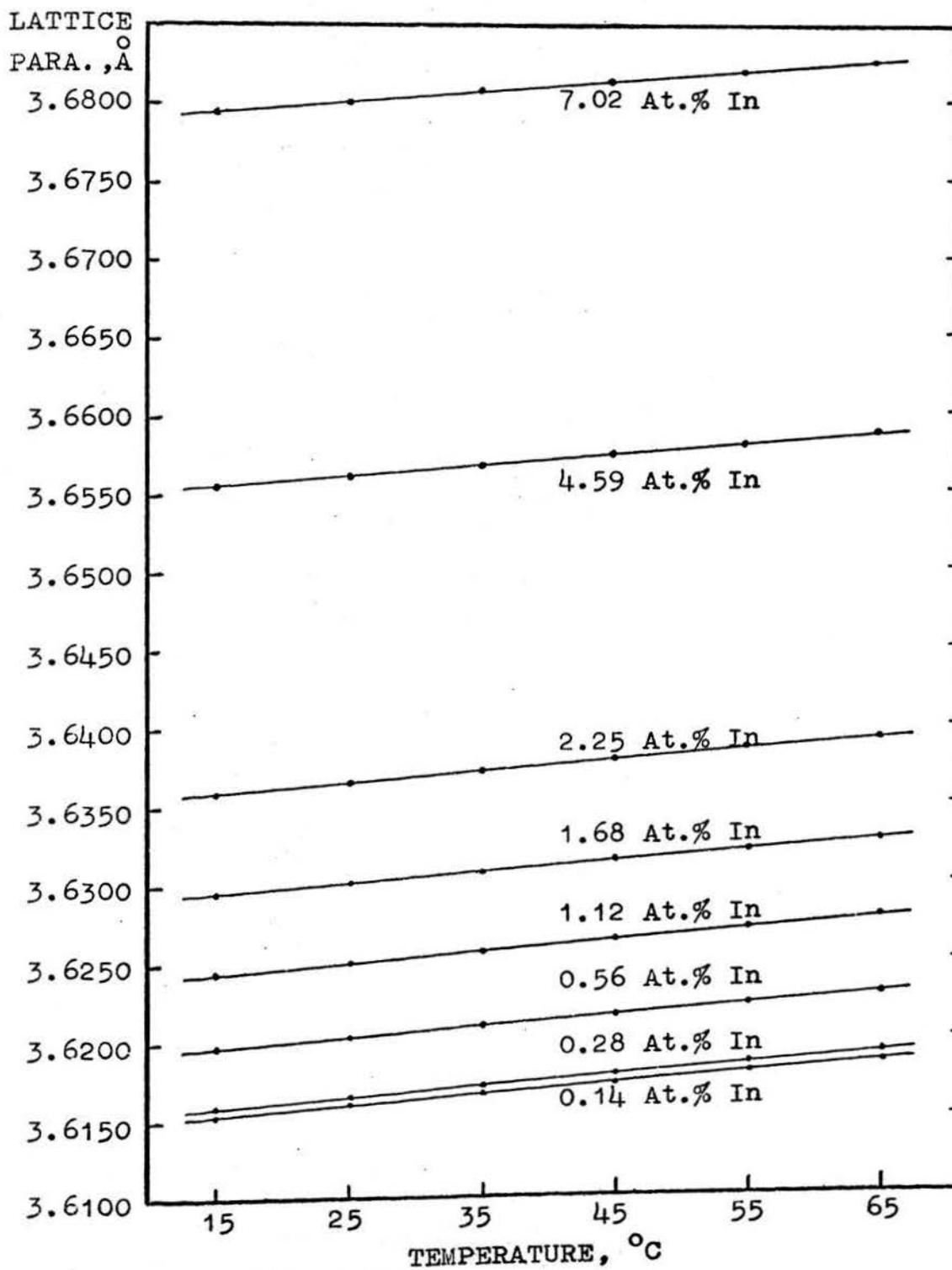


Figure 5. Lattice parameters of the alpha-phase Cu-In alloys as a function of temperature.

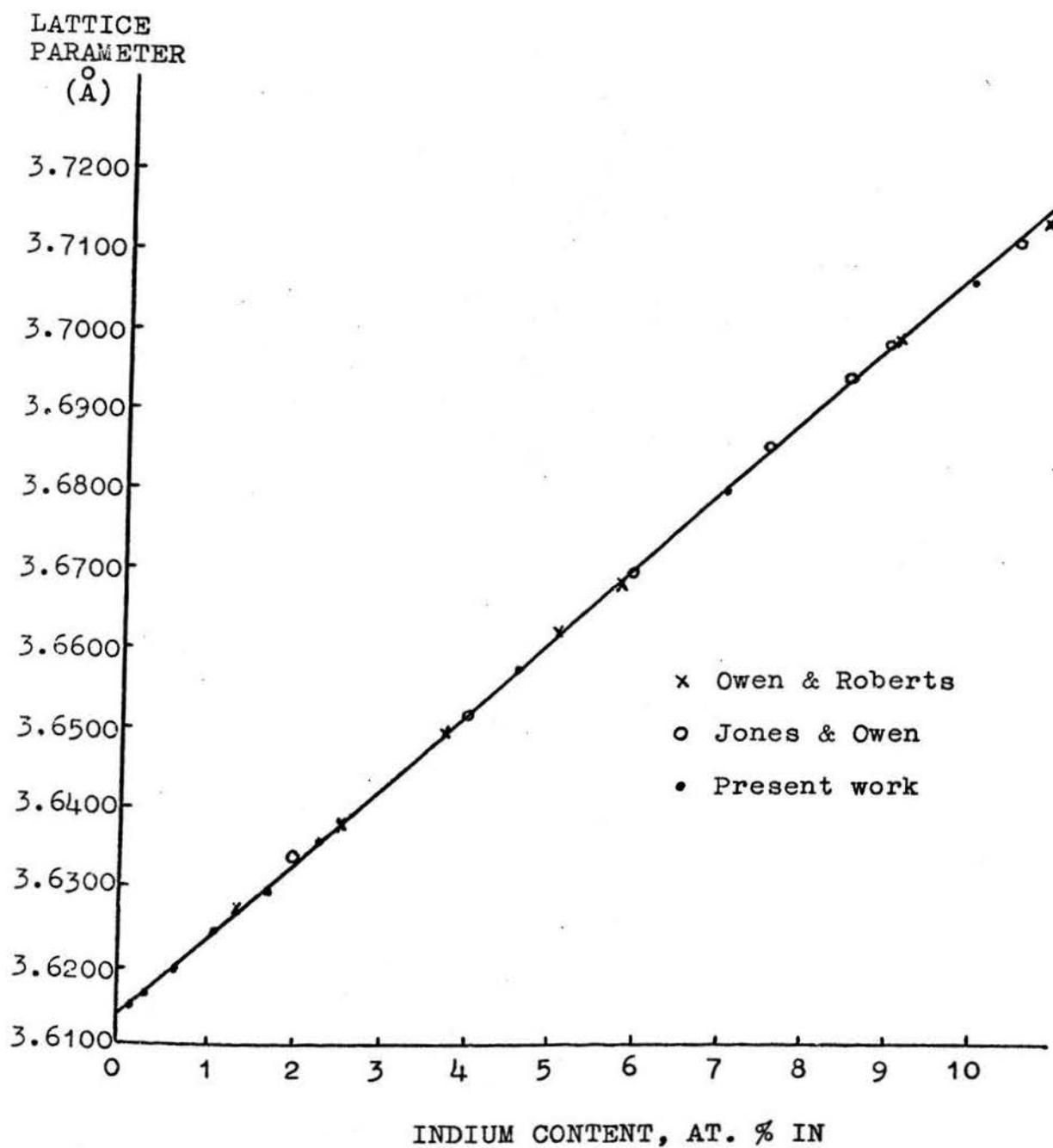


Figure 6. Alpha-phase lattice parameters of copper-indium alloys at 18 °C

tional alloys of composition 17.00, 20.00 and 23.00 weight % In were prepared as described previously; the last two alloys are in the two-phase region at temperatures above the eutectoid temperature (Fig. 1). The X-ray samples were heat-treated in the same way, i.e., annealed for 30 minutes at 650 °C followed by quenching in cold water. Powder patterns were taken at 25 °C. The lattice parameters of these, together with the other eight alloys, are listed in Table 2, and plotted against composition in Figure 7. Since all the alloys were quenched from 650 °C, the values represent the lattice parameters of the alpha-phase solid solutions of a composition at that temperature. From Figure 7, the maximum solubility at 650 °C is found to be 10.50 atomic % In.

C. Coefficients of Thermal Expansion

From the plots of lattice parameter vs. temperature (Figure 5), it is seen that the lattice of the alloys expands linearly with temperature in the range 15 - 65 °C. The thermal expansion coefficients for the respective alloys are calculated from the slopes of these lines using equation (7). The results are given in Table 3 and plotted in Figure 8. A curve approaching a limiting value with increasing In content results.

TABLE II

Lattice Parameters of the Alpha-Phase
Cu-In Alloys Reduced to 25 °C

Composition		Lattice Parameter
Wt.% In	At.% In	at 25 °C, Å
0.00	0.00	3.61490 ±0.00003
0.25	0.14	3.61610 ±0.00001
0.50	0.28	3.61669 ±0.00003
1.00	0.56	3.62044 ±0.00001
2.00	1.12	3.62522 ±0.00002
3.00	1.68	3.63020 ±0.00002
4.00	2.25	3.63675 ±0.00002
8.00	4.59	3.65626 ±0.00001
12.00	7.02	3.68001 ±0.00003
17.00	10.18	3.70745 ±0.00004
20.00	12.15	3.71037 ±0.00004
23.00	14.18	3.71045 ±0.00004

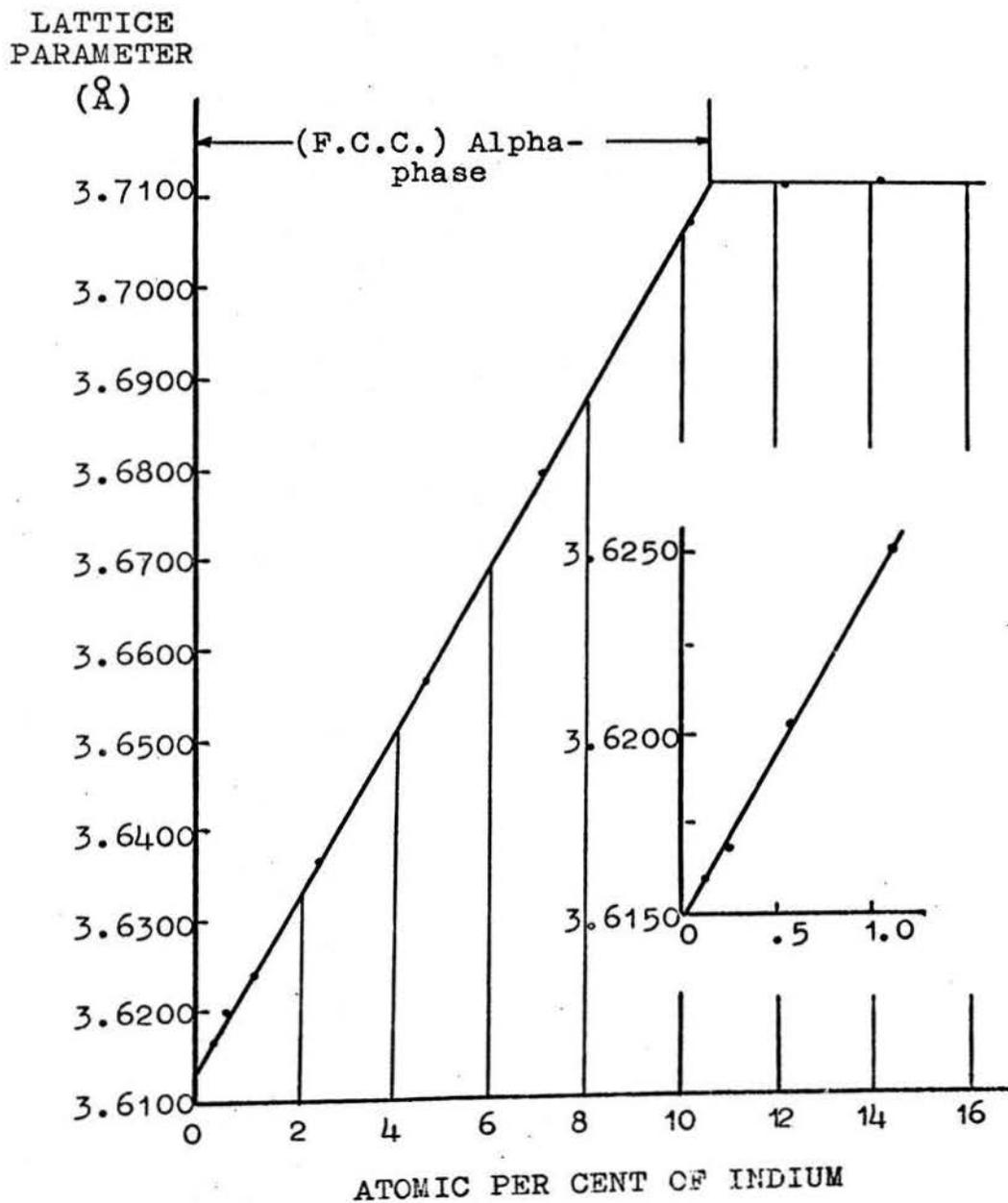


Figure 7. Lattice parameters of the alpha-phase at 25 °C. Alloy powders quenched from 650 °C.

TABLE III

Linear Thermal Expansion Coefficients of
the Alpha-Phase Cu-In Solid Solutions

Composition		Coefficient of Thermal Expansion, $\times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Wt.% In	At.% In	
0.25	0.14	16.43
0.50	0.28	16.48
1.00	0.56	16.57
2.00	1.12	16.72
3.00	1.68	16.84
4.00	2.25	16.94
8.00	4.59	17.17
12.00	7.02	17.20

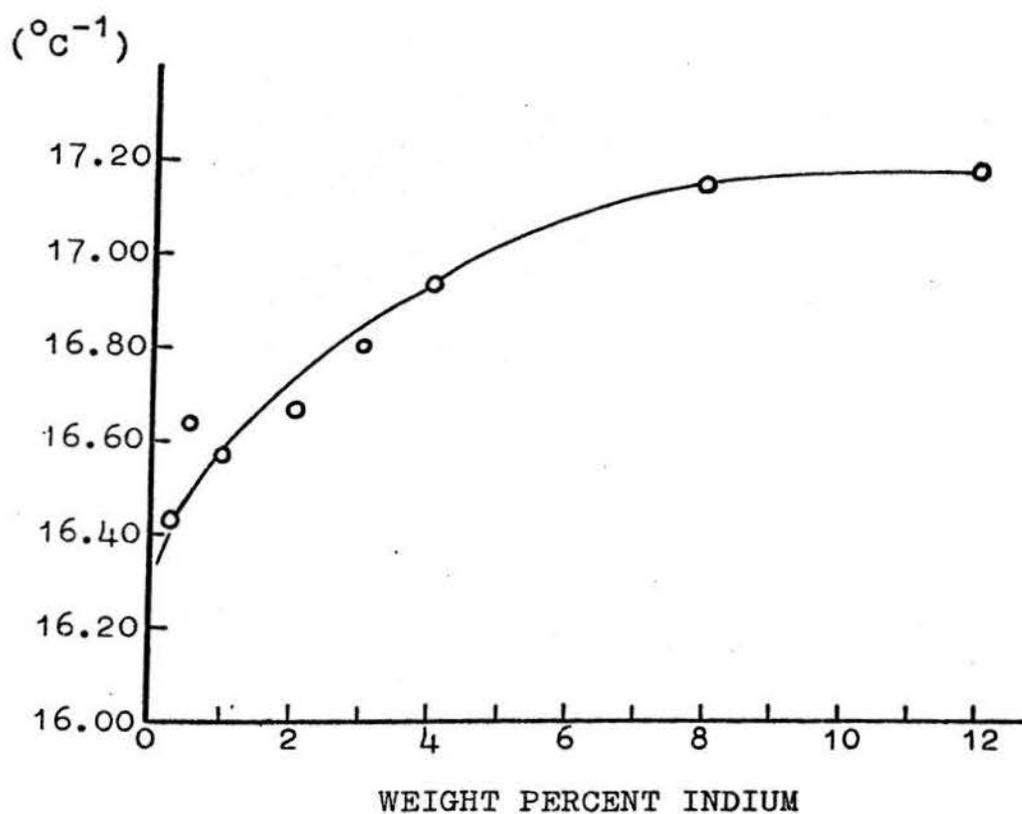


Figure 8. Thermal expansion coefficients of Cu-In solid solutions within the range 15 - 65 $^{\circ}\text{C}$

D. Densities Obtained

1. Densities of Copper, Silver, and of Copper-Indium Alloys

Although the alloy samples for density measurements were carefully cooled from the liquid temperature, solidification microporosity still existed, and in the case of 8 wt-% In alloy, the shrinkage voids could be seen with a magnifying glass. Surface pits were also present in the ingots.

The shrinkage voids were closed after severe plastic deformation as shown in Figure 9. The density values obtained from these samples before and after deformation are given in Table 4 and plotted in Figure 10. The figures represent the highest densities obtained after solidification and mechanical treatment of the samples as described in Chapter III.

Several density measurements were made on Cu at different cold working stages. The results of these determinations are given in Table 5. The density of Ag, determined as a check on the method of density measurement, is shown in Table 6 along with other published results.

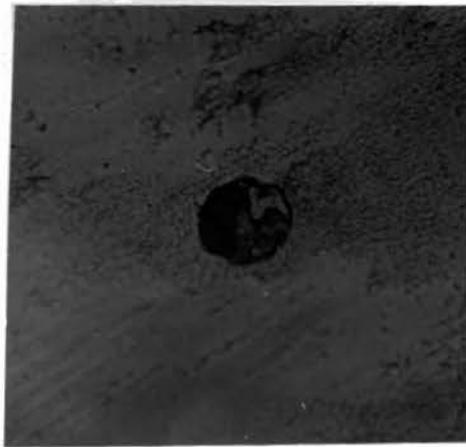


Figure 9. A micropore in 8 wt.-% In alloy after 70% cold reduction. 750x

TABLE IV

Densities at 25 °C of Primary Cu-In Solid
Solutions Water Quenched from 800 °C

At. % In	Sample Weight g	Density before Deformation* g/cm ³	Density after Deformation** g/cm ³
0.00***	12.91	8.9333 ±0.0002	8.9316 ±0.0001
0.14	4.47	8.9284 ±0.0002	—————
0.28	9.23	8.9258 ±0.0002	8.9322 ±0.0004
0.56	5.45	8.9238 ±0.0004	8.9344 ±0.0004
1.12	6.10	8.9123 ±0.0003	8.9364 ±0.0002
1.68	6.50	8.9187 ±0.0005	8.9382 ±0.0001
2.25	7.28	8.9175 ±0.0004	8.9404 ±0.0003
4.59	6.34	8.8200 ±0.0001	8.9492 ±0.0004

* Figure represents the highest value obtained.

** Annealed at 550 °C after deformation.

*** 99.999+ % Cu, ASARCO.

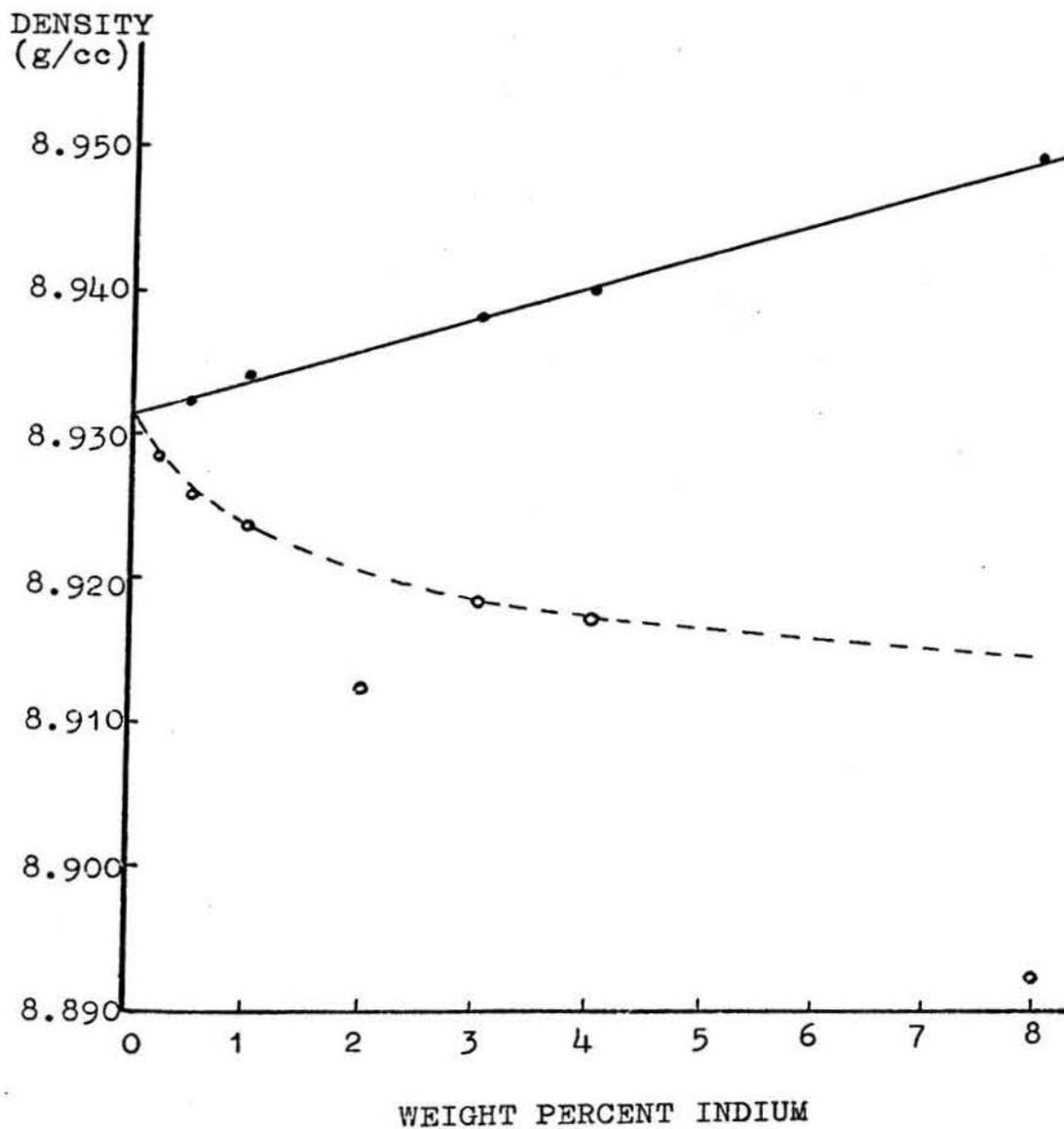


Figure 10. Densities of Cu-In alloys within the composition of the alpha-phase.

- X-ray densities.
- Experimental densities of cold-worked and annealed sample.
- Densities of slowly cooled alloys.

TABLE V

Density of Pure Copper at 25 °C

Sample	Sample Weight (g)	Density (g/cm ³)
Single Crystal*	12.809	8.9332 ±0.0001
Polycrystal,* Annealed	17.287	8.9334 ±0.0002
Polycrystal,* Cold-Worked	9.804	8.9316 ±0.0001
Zone-Refined**	7.947	8.9314 ±0.0001

* ASARCO copper, 99.999+ pure

** German copper

TABLE VI

Density of Silver at 25 °C

Reference	Year	Density (g/cm ³)	Remark
Present Work	1968	10.4973 ±0.0001	Single Crystal
International Critical Table	1926	10.4914	Electrolytic
Riad	1964	10.4904	Polycrystal
Shodham	1965	10.4936	Single Crystal
Patel	1967	10.4951	Single Crystal
Theoretical (X-Ray)	1968	10.4978	

2. The Number of Atoms or Molecules per Unit Cell
and the X-Ray Density of the Solid Solutions

i. Pure Cu and Ag

In establishing the number of atoms present in a unit cell in copper and silver, the lattice parameter of Cu at 25 °C was used ($a = 3.6149 \text{ \AA}$), and that of Ag was obtained from the thesis of Riad (4.0861 \AA)¹⁷.

The number of atoms per unit cell was calculated from the measured bulk density, D , and the atomic mass for each atom species, M , and the volume of the cell, V , by the formula

$$n' = \frac{DVN_0}{M} \quad (10)$$

where N_0 is Avogadro's number ($6.0240 \times 10^{23} \text{ mole}^{-1}$).

The theoretical (X-ray) density, D_x , based on the ideal cubic crystal, was calculated from the same relation

$$D_x = \frac{nM}{N_0V} \quad (11)$$

where n is now the ideal number of atoms per unit cell.

The results of these calculations are shown in
Table 7.

ii. Cu-In Primary Solid Solutions

Assuming that on the average, a molecule in a Cu-In alloy contains a fraction of x In atoms, the alloy was assigned the chemical formula $\text{Cu}_{1-x}\text{In}_x$. The factor is, therefore, the atomic fraction of In and was computed from the weight percentages W_{Cu} , W_{In} by the relation

$$x = \frac{W_{\text{In}}/A_{\text{In}}}{W_{\text{Cu}}/A_{\text{Cu}} + W_{\text{In}}/A_{\text{In}}} \quad (12)$$

where A_{Cu} and A_{In} are the atomic weights of Cu and In respectively.

The molecular weight, M , of the alloy $\text{Cu}_{1-x}\text{In}_x$ was obtained simply by multiplying the atomic weights of In and Cu by the respective atomic fractions and by adding together the products. The atomic weights are based on C^{12} .

The number of molecules per unit cell for a Cu-In alloy was then calculated from equation (10). The theoretical densities were calculated using equation (11). The results are shown in Table 8.

iii. Propagated Error Calculation

The calculation of actual number of molecules

TABLE VII

Actual Number of Atoms per Unit Cell
of Copper (At. Wt. 63.54 ± 0.005) and
of Silver (At. Wt. 107.87 ± 0.003)

Metal	X-Ray Density (g/cc)	Measured Density (g/cc)	Actual No. of Atoms, n' , per Unit Cell
Cu _{ASARCO}	8.9315	8.9333	$4.00072 \pm 0.00052^*$
Cu ^{**} Zone-Refined	8.9315	8.9314	3.99987 ± 0.00046
Cu _{Deformed}	8.9315	8.9316	3.99996 ± 0.00052
Ag	10.4978	10.4973	3.99972 ± 0.00042

* Represents the propagated error

** From Germany

TABLE VIII

The Number of Molecules, n' , per Unit Cell
of the Cu-In Primary Solid Solutions

At.% In	$\text{Cu}_{1-x}\text{In}_x$	Molecu- lar Mass	X-Ray Density (g/cc)	n' of Solid Soln*	n' of Rolled S. S.**
0.00	0.0000	63.54	8.9315	4.00072	3.99987
0.14	0.0014	63.6110	8.9323	3.99824	—
0.28	0.0028	63.6822	8.9329	3.99696	3.99965
0.56	0.0056	63.8251	8.9340	3.99542	4.00016
1.12	0.0112	64.1127	8.9365	3.99285	4.00000
1.68	0.0168	64.4029	8.9387	3.99105	3.99978
2.25	0.0225	64.6957	8.9409	3.98955	3.99979
4.59	0.0459	65.8943	8.9485	3.98505	4.00033

* Figure 10, densities of the slowly cooled alloys
(dashed curve).

** Figure 10, densities of the cold-rolled and
annealed alloys (solid curve).

per unit cell involves four different measurements: D , V , N_0 and M as shown. It is obvious that there is some error associated with each of these values. To estimate the total error made in the calculation of n' , the following equation as proposed by Straumanis¹⁸ was employed:

$$\frac{\Delta n'}{n'} = \pm \left[f_1 \left(\frac{\partial a}{a} \right)^2 + f_2 \left(\frac{\partial d}{d} \right)^2 + f_3 \left(\frac{\partial N_0}{N_0} \right)^2 + f_4 \left(\frac{\partial A}{A} \right)^2 \right]^{\frac{1}{2}} \quad (13)$$

where ∂a , ∂d , ∂N_0 and ∂A are standard deviations of the separate measurements; $\partial a/a$, $\partial d/d$, etc. are the relative errors, and the f 's are the safety factors to cover the systematic errors. The values of f 's are equal to or greater than unity depending on the precision of each kind of measurement. The precision attained in measuring the lattice parameters by the asymmetric method used in the present work is such that it covers the systematic errors. The accuracy of the internationally accepted values of the atomic weights of the elements is high, and the Avogadro's number of $6.024 \pm 0.0003 \times 10^{23}$ is correct. The density measurements, on the other hand, are of relatively low accuracy which decreases even more with the decreasing weight of specimens. Based on such considerations, the values of the safety factors were assumed to be:

$$f_1 = f_3 = 1 \quad \text{for all samples}$$

$f_4 = 1$ for pure Cu
 $f_2 = 3$ for samples weighing more than
10 grams
 $f_2 = 4$ for samples weighing less than
10 grams.

CHAPTER V
DISCUSSION OF RESULTS

A. Lattice Parameters and Coefficients of Thermal Expansion

By using the X-ray technique described in Chapter III, it was possible to obtain a precision of the order of 1:200,000 in determining the lattice parameters of the Cu-In alloys. This high degree of precision was achieved by the method of asymmetric film mounting, eliminating the errors due to incorrect knowledge of camera radius and uniform film shrinkage, also by the use of thin powder samples (less than 0.2 mm in diameter) minimized the absorption effect, and by the thermostat, keeping the temperature of samples and, hence, the lattice parameter constant. Thus it was not necessary to extrapolate the lattice parameter values obtained from many diffraction lines to the Bragg angle 90° in order to obtain precise lattice constants.

The lattice parameters of the alpha-phase solid solutions of the Cu-In system obtained in this investigation are compared with the data from other sources in Figure 6. For the purpose of comparison, all the values have been reduced to 18°C and converted to the

Angstrom unit with the conversion factor 1.00202. The figure shows a close agreement between the values obtained presently and those of the others.

As expected, In was found to expand the lattice of Cu. Within the alpha-phase region, the lattice expanded linearly with In content up to the limit of solid solubility. The expansion of the lattice of Cu by In is a natural consequence of substitutional solid solution formation because of the replacement of Cu atoms by larger In atoms, the atomic radii of Cu and In being 1.28 Å and 1.63 Å (average), respectively, for the coordination number 12.

Within a small temperature range such as 15° - 65 °C, the lattice parameters of the alpha-phase Cu-In alloys are linear functions of temperature as shown in Figure 5. The thermal expansion coefficients are increasing to a limiting value with increasing In content (Fig. 8). On the basis of this curve it is estimated that the error in determining the thermal expansion coefficients is well within ±1%.

The shape of the curve suggests that the thermal expansion coefficient of Cu increases rather rapidly with the addition of In up to about 6 weight per cent

and then reaches a plateau continuing up to the solubility limit. The physical significance of this change is not easy to assess and no explanation is attempted here.

B. Maximum Solubility of Indium in Copper at 650 °C

Figure 7 shows that the expansion is in agreement with Vegard's law:

$$a_x = 3.6149 + 0.0091 x$$

where a_x is the lattice parameter of any alpha-phase Cu-In alloy and x is its indium concentration in atomic per cent; 3.6149 is a of Cu at 25 °C.

It follows from Figure 7 that the maximum solubility of In in Cu is 10.50 atomic-% at 650 °C. This solubility limit is higher than that reported by Weibke and Eggers, and by Hume-Rothery et. al. (as 10.4 and 10.35 at.-% respectively), but is in close agreement with the results of Owen and Roberts, and of Jones and Owen (10.50 at.-%). In view of the high precision of the present measurements, the solubility limit of 10.50 at.-% In is considered to be correct.

C. Density and Perfection of the Structure

1. The Accuracy of Density Measurement

In the determination of the densities of Cu and Cu-In alloys, it was found that the density of a solid sample is affected by several factors: homogeneity, cold work, surface imperfections (shrinkage pits, the adsorption of gases on the surfaces, etc.), internal solidification microporosity, and purity or composition of the sample. It is important to have samples well defined with regard to these conditions in order to obtain reproducible results. In carrying out this investigation, the X-ray diffraction method was used to check the homogeneity of the alloys as described; the surface imperfections were removed by filing; the state of cold work of the alloy samples for density determinations was known; and since the alloys were prepared under vacuum, the composition could not have changed during melting and solidification, because the weight loss after annealing amounted to less than 1 part in 4,000 in all ingots. The only factor which might have caused density anomalies in the alpha-phase solid solutions was the solidification microporosity. This effect, nevertheless, was remedied to a large extent by successive cold rolling or compression and subsequent annealing of the samples.

When one is assured of the sample homogeneity, its mechanical state, its correct composition, absence of

surface defects and of visible microporosity, the accuracy of density measurements by the hydrostatic weighing method is then dependent mainly upon the accuracy in determining the density of the immersion liquid and of weighing. Other errors, such as those introduced by converting the density values measured at one temperature to the densities at another temperature can be reduced by measuring the densities at the desired temperature and by stabilizing the temperature of the specimen in the immersion liquid for a long enough time. Thus, by weighing with a precision of 0.01 mg, an accuracy of ± 0.0005 g/cc should be attained.

2. Densities of Pure Cu and Ag Single Crystals

The observed densities of Ag compare favorably with the results of other authors as shown in Table 6. A further, more accurate check is the comparison with its X-ray density, calculated from equation (11) by using the value of $N_0 = 6.0240 \times 10^{23}$ and the factor $\Lambda = 1.00202$ for conversion of kX to \AA units. The measured density of 10.4973 gm/cm^3 of Ag falls within the error limits of the X-ray density of silver, 10.4978 gm/cm^3 . The observed density of the ASARCO copper, 8.9333 , on the other hand, does not agree very well with the calculated X-ray density of 8.9315 , with which the measured density of zone-refined copper agrees much better: 8.9314 g/cm^3 . However, with

the new Avogadro's number of 6.02252×10^{23} and the new $\Lambda = 1.002056$, a value of 8.9328 was obtained for the ASARCO copper, in good agreement with the observed value of 8.9333 g/cm^3 at 25°C .

The effect of mechanical treatment on the density of a solid is exemplified by the measured values of three Cu samples. While there is no apparent difference between the densities of a copper single crystal and the annealed polycrystalline specimen, the deformed copper shows a slightly lower density, of the order of 0.002 g/cm^3 . While this difference is not significant in itself, it is of importance in evaluating the perfection of crystal structures.

Although the number of atoms, n' , per unit cell of the annealed ASARCO Cu was 4.00072 (or 4.00028 using the new values of N_0 and Λ), it was only 3.99996 for the plastically deformed specimen, with a propagated error of ± 0.00052 . This represents 4.5×10^{-17} vacant sites per c. c. in the crystal. Taking into consideration both wavelengths and both Avogadro's numbers, the average n' for copper is 4.00050, the deviation being completely within the limits of the propagated error.

The value of n' for silver is calculated to be

3.99972 as shown in Table 7, and the deviation from 4.00000 is within the limits of error.

3. Densities and Lattice Perfection of the Alpha-Phase Solid Solutions

The densities of the alpha-phase Cu-In solid solutions measured immediately after homogenization heat treatment were low because a large percentage of defects in the form of cavities could be seen under the microscope. These defects might be a consequence of shrinkage porosity since it was noted that the drop in density increased with increasing solute concentration (Figure 10). While pure Cu gave 4 atoms per unit cell (within the limits of error), this number decreased substantially when In was added to the Cu (Table 8). The only explanation of this density decrease is the microporosity formed during solidification of the alloys. Evidently, the extent of initial microporosity increases with the amount of solute. This phenomenon becomes apparent, as pointed out by Dodd et al^{12,13,14}, when the phase diagram (Figure 1) is consulted. From the diagram it is seen that the temperature interval of solidification becomes larger at higher solute concentrations; and as the solidification range of the alpha-phase solid solution increases, more shrinkage voids are formed

during the course of solidification. Even the low rate of freezing used in the present work could not eliminate the formation of these defects. Then, subsequently, the micropores at least partially collected into larger voids, while the temperature was just below that of solidification. Apparently, the micropores and the larger voids can not be annealed out.

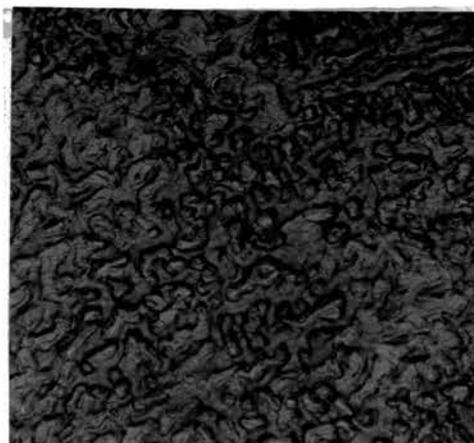
By plastic deformation, the voids were closed as shown in the photomicrograph of Figure 9, and the density values showed a marked increase. After about 70% cold reduction and stress relief at 550 °C, the densities approached the theoretical (X-ray) values. Therefore, it seems possible that the density defects of the Cu-In alloys prior to cold rolling have their origin in the process of solidification. Unfortunately Dodd, who proposed the solidification microporosity, did not elaborate how the pores were formed. But it is clear, however, that their formation is a consequence of In introduction, resulting in shrinkage porosity. The possibility of microporosity formation is further confirmed by the absence of defects in pure Cu, which is not expected to contain shrinkage porosity as it freezes at a single temperature.

In order to decide whether or not the liquid alloy

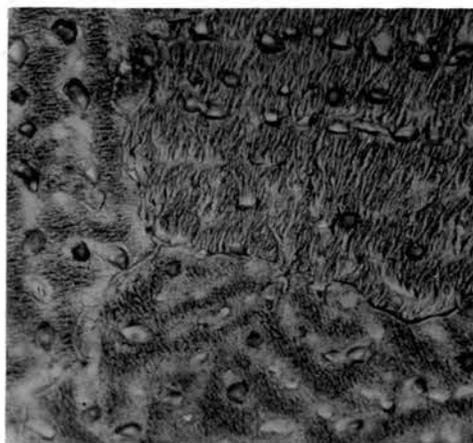
contains pores, some molten alloys (in evacuated quartz tubings) were quenched in water from the liquidus temperature and their density was determined. Sections were made for microscopic examination. It was found that while the densities of these alloys were considerably lower than the theoretical values, there was no visible microporosity present (at 750x) as shown in Figure 11. This fact suggested the existence of lattice imperfections (vacancies) or submicroscopic porosity rather than visible voids as observed with slowly cooled alloys.

Furthermore, it follows from quenching experiments of other researchers that equilibrium vacancies present at elevated temperatures can be retained^{19,20,21}. Clarebrough et al²² could even show that the vacancies can collect to form large voids so that they can be seen with an electron microscope at a magnification of 60,000x.

Finally there are some thermodynamic considerations. Swalin, in studying the diffusion of substitutional impurities in pure metals²³, has estimated the enthalpy change. Following his assumption that the atoms are compressible spheres and the lattice an elastic continuum the substitutional solute atom causes a change in enthalpy corresponding to the balance between the strain of the



(a)



(b)

Figure 11. Photomicrographs of (a) Cu-17 wt.-% In and (b) Cu-4 wt.-% In, quenched from liquidus temperature. Note the absence of microporosity. The dots represent the In-rich phase, severely attacked by the etchant. 750x

TABLE IX

Vacancies per Indium Atom Initially
Introduced into Slowly Solidified
Cu-In Primary Solid Solutions

Composition Wt.% In	At.% In	x in Cu _{1-x} In _x	*No. of In Atoms per Unit Cell	**Vacancies per In Atom
0.25	0.14	0.00138	0.00055	0.3178
0.50	0.28	0.00277	0.00111	0.2743
1.00	0.56	0.00559	0.00223	0.2054
2.00	1.12	0.01116	0.00446	0.1605
3.00	1.68	0.01683	0.00672	0.1333
4.00	2.25	0.02254	0.00899	0.1162
8.00	4.59	0.04591	0.01829	0.0817

$$* \left(\begin{array}{c} \text{No. of In Atoms} \\ \text{per Unit Cell} \end{array} \right) = \left(\begin{array}{c} x \text{ in} \\ \text{Cu}_{1-x}\text{In}_x \end{array} \right) \cdot \left(\begin{array}{c} \text{No. of Molec.} \\ \text{per Unit Cell} \end{array} \right)$$

$$** \left(\begin{array}{c} \text{Vacancies per} \\ \text{In Atom} \end{array} \right) = \left(\begin{array}{c} \text{Vacancies per} \\ \text{Unit Cell} \end{array} \right) / \left(\begin{array}{c} \text{No. of In} \\ \text{Atoms per u.c.} \end{array} \right)$$

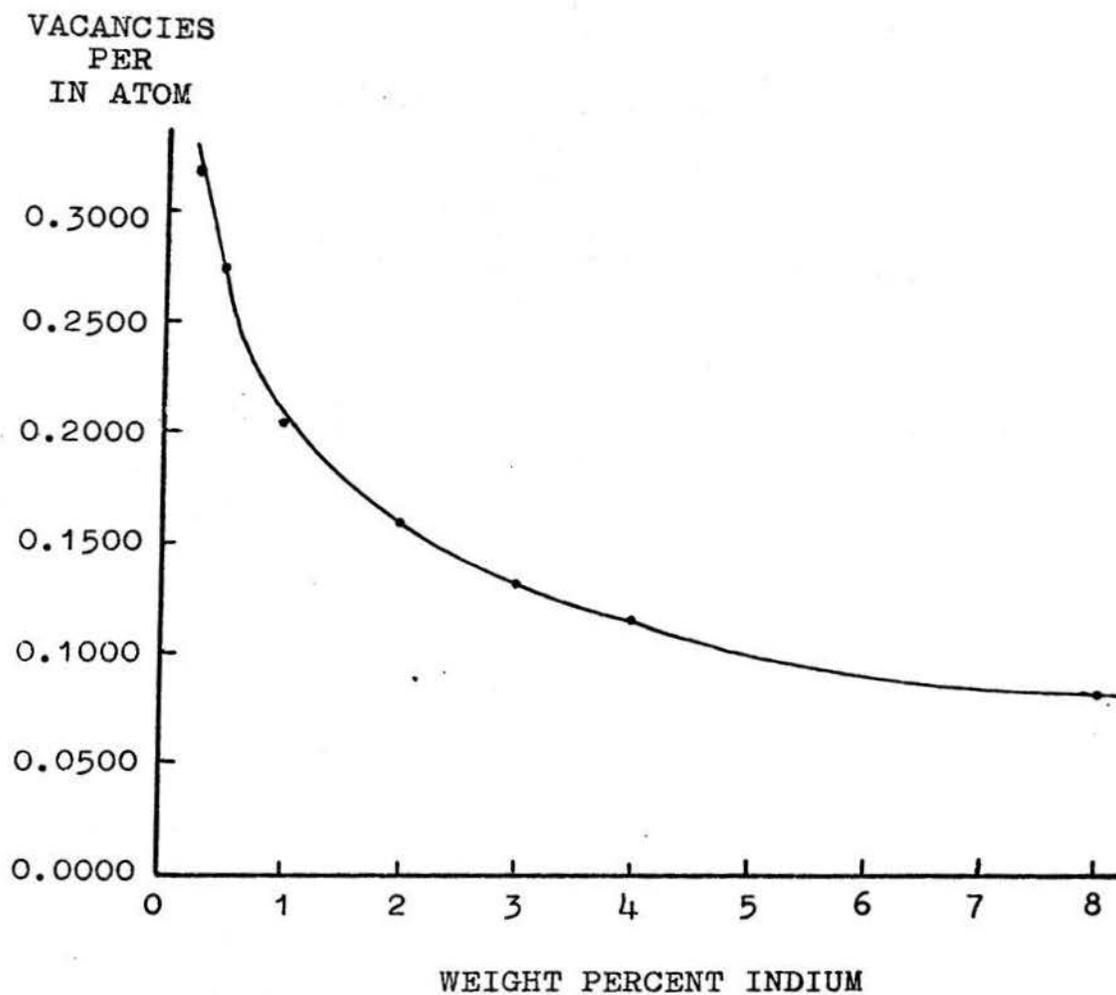
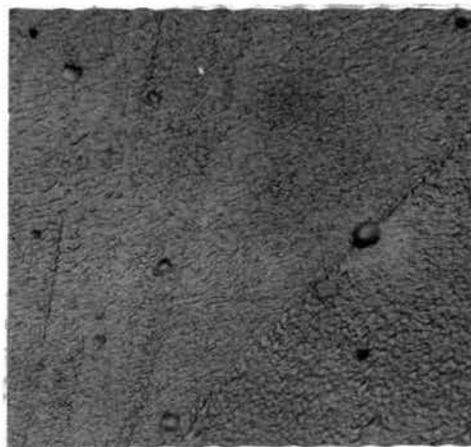


Figure 12. Vacancies introduced by indium as a function of alloy composition



(a)



(b)

Figure 13. Voids in (a) Cu-17 wt.-% In and (b) Cu-4 wt.-% In alloys, formed due to the coalescence of vacancies. 750x

solute atoms and the matrix. Since the solute atom (In) is larger than the solvent (copper) atom, the addition of In to the Cu lattice will elastically strain the lattice, giving rise to an increase in enthalpy. In addition, during cooling of the solid solutions, a primary non-equilibrium Cu-rich phase is crystallized out (Figure 11-a and b). The Cu- and In-rich phases have, however, different expansion coefficients (Figure 8). Although the coefficients were obtained at low temperatures, it is very possible that similar or even larger differences exist at elevated temperatures. Besides, the alloys upon cooling have to go through the low temperature range anyway. Thus, strains (maybe even beyond the elasticity limit) are created within the alloys causing the creation of voids of sizes below the microscopic visibility. It can also be assumed that single vacancies are formed initially which quickly collect to larger entities²¹ in a process causing a decrease of enthalpy. Thus the introduced solute (In) atoms can be regarded as vacancy sources. Assuming that initially single vacancies may be formed, the number of them introduced by each In atom can be calculated from the lattice parameter and the density measured before rolling of the samples. The results are summarized in Table 9 and plotted against alloy composition in Figure 12. The plot shows that in slowly solidified alloys the number of vacant lattice

sites introduced by one indium atom is highest at lower indium concentrations but reduces rapidly with larger amounts of the alloying element. Approaching the solubility limit (10.50 at-% In at 650 °C), the number of vacancies per In atom remains nearly constant.

To provide further proof for the coalescence of vacancies into larger entities, the alloys originally quenched from liquidus temperatures were annealed for 5 days at 700 or 800 °C, depending on their composition. A microscopic study showed that the vacancies indeed had collected into voids as revealed by Figure 13, in resemblance with those in ingots slow-cooled from the molten state. Since the voids represent zero mass, the observed densities of the alloys with voids naturally gave density values lower than those in which the voids were closed by severe rolling, followed by annealing.

Thus by allowing the vacancies in the solidified alloys to coalesce to large pores, they could be removed by plastic deformation from the alloys. This process is similar to the hot squeezing technique of Taylor²⁴ in which high pressure and temperature are applied simultaneously to eliminate vacancies from titanium monoxide and vanadium oxide. While in the latter case the annihilation of vacancies turned out to be reversible, it

is irreversible in the present investigation: the voids removed from the Cu-In solid solutions do not return upon heat treatment. Therefore, the vacancies formed are not "constitutional" but only voids (formed during the solidification process) which could be eliminated. This explains why under favorable conditions, e.g., by transport reactions¹², solid solutions without voids can be produced.

Thus, the close agreement between the theoretical densities and the observed density values of rolled and annealed Cu-In primary solid solutions (see Figure 10) shows that the addition of indium to copper finally does not result in a defect micro-structure.

CHAPTER VI

SUMMARY

1. The precise lattice parameters at 25 °C of Cu and Cu-In alloys are (corrected for refraction):

99.999% pure copper	3.61490 ±0.00003 Å
Cu-0.14 at.-% In	3.61616 ±0.00001 Å
Cu-0.28 at.-% In	3.61742 ±0.00003 Å
Cu-0.56 at.-% In	3.62001 ±0.00001 Å
Cu-1.12 at.-% In	3.62508 ±0.00002 Å
Cu-1.68 at.-% In	3.63024 ±0.00002 Å
Cu-2.25 at.-% In	3.63544 ±0.00002 Å
Cu-4.59 at.-% In	3.65672 ±0.00001 Å

2. The lattice parameter of Cu increases at a rate of approximately 0.0091 Å per atomic % of In.
3. The alpha-phase solid solutions of the Cu-In follow Vegard's law up to the limit of solid solubility at 650 °C.
4. The linear thermal expansion coefficients of the primary solid solutions of the Cu-In system within the range 10° to 65 °C are:

Cu-0.14 at.-% In	16.43 x 10 ⁻⁶ °C ⁻¹
Cu-0.28 at.-% In	16.48 x 10 ⁻⁶ °C ⁻¹
Cu-0.56 at.-% In	16.57 x 10 ⁻⁶ °C ⁻¹
Cu-1.12 at.-% In	16.72 x 10 ⁻⁶ °C ⁻¹
Cu-1.68 at.-% In	16.84 x 10 ⁻⁶ °C ⁻¹

Cu-2.25 at.-% In	$16.94 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$
Cu-4.59 at.-% In	$17.17 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$
Cu-7.06 at.-% In	$17.20 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$

5. The solid solubility limit at $650 \text{ } ^\circ\text{C}$ of the f.c.c. alpha-phase of the Cu-In systems is 10.50 atomic % In.
6. The number of atoms, n' , per unit cell of 99.999% pure Cu with $N_0 = 6.0240 \times 10^{23}$ and $\Lambda = 1.00202$ is 4.00072. Using the new $N_0 = 6.02252 \times 10^{23}$ and the new $\Lambda = 1.002056$, n' is 4.00024.
7. The slowly solidified Cu-In primary solid solutions show a considerably lower density than theoretically expected, which is due to the formation of cavities as a result of In addition.
8. No visible porosity is found in the alloys quenched from liquidus temperatures. Upon annealing of these alloys, however, voids are found again.
9. By rolling or compression of such alloys the voids become closed and the density raises up to the theoretical. The bulk and the theoretical densities at $25 \text{ } ^\circ\text{C}$ of the Cu-In primary solid solutions are:

Composition	d_{25}^*	d_x
Cu-0.14 at.-% In	—	8.9323
Cu-0.28 at.-% In	8.9322 ± 0.0004	8.9329

Cu-0.56 at.-% In	8.9344 ±0.0004	8.9340
Cu-1.12 at.-% In	8.9364 ±0.0002	8.9365
Cu-1.68 at.-% In	8.9382 ±0.0001	8.9387
Cu-2.25 at.-% In	8.9404 ±0.0003	8.9409
Cu-4.59 at.-% In	8.9490 ±0.0004	8.9485

* As obtained, with voids closed.

10. No point defects are formed by the alloying of Cu and In because the density defects observed (and vacancies calculated per In atom) were only a consequence of the solidification process.

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