any hitherto reported, at least where values over a wide temperature range are desired, that it should become standard.

### Note on the Thermal Conductivity of Silocel

The method above described required an exact knowledge of the conductivity of the silocel insulation at all temperatures and, since this presumably depended upon the looseness of packing, a special determination was made for this material. A copper tube 4-cm o.d. and 20 cm long with an inner bore of 1-cm diameter was centered in the large iron tube above used and the intervening space packed with silocel. The iron cylinder was surrounded by about 5 cm of additional thermal insulation. A Nichrome winding on the iron cylinder allowed the cylinder and its contents to be heated to any desired temperature. A Nichrome heating coil was centered exactly in the hole drilled through the copper cylinder. This was for direct heating current. The iron cylinder was about three times the length of the copper tube, the latter centered in it and packed above and below with silocel. Thermojunctions were placed in grooves in the iron cylinder and in the walls of the copper tube. The d.c. energy input into the central third of the copper cylinder was measured as was the temperature drop across the silocel. Thus the conductivity could be determined. The silocel was tamped firmly but the degree of tamping had no observable effect on the conductivity. The value at room temperature, 0.00038, is slightly higher than the handbook value, 0.00034. The increase with temperature was found to be linear (Fig. 5).

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# The Effect of High Pressure on the Order-Disorder Transformation in Alloys*

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With electrical resistance as an index of degree of order, the behavior of the order-disorder transformation under high hydrostatic pressure has been investigated with the three alloys, CuAu, $Cu_3Au$ and CuZn. Measurements were made under pressures up to 10,000 kg/cm$^2$ and over the temperature range 50°C to 426°C. For temperatures below the critical point the course of the transition under pressure may be predicted from reported thermal expansion data and deductions from the Bragg-Williams' theory. The observed behavior of the alloys seems to be consistent with these predictions. Measurements made near the critical temperature with the alloys CuAu and $Cu_3Au$ show that the critical point is raised by pressure in both cases. One alloy, alpha brass ($Cu_3Zn$), not hitherto included in the class of the three alloys above mentioned has been examined. The conclusion is reached that a slight ordering of the constituents of the alloy occurs under high pressure.

## Introduction

The only prior work relating to this subject is apparently that of P. W. Bridgman,[1] who gave a report of the compressibilities and pressure coefficients of resistance of eighteen intermetallic compounds measured at 30°C and 75°C. Some of these compounds are capable of the order-disorder transition. The irregularity of results in all cases as compared with results for other substances was noticed and emphasized by the investigator. Sudden changes in the shape of curves, and hysteresis effects, were attributed to a shifting under pressure of the conditions of internal equilibrium, possibly to a change in the complicated type of superstructure characteristic of some of these compounds (e.g., $Sn_8Cu_{31}$ (?) with 416 atoms in the unit cell).

If the ordering process is considered simply as a rearrangement in which atoms or ions of small diameter are fitted in the interstices between those of larger diameter so that the volume of the resulting structure is a minimum, one would expect high hydrostatic pressure to accentuate the volume differences and promote an ordered structure. With this view, the shifting of the conditions of internal equilibrium, above men-

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* Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[1] P. W. Bridgman, Proc. Am. Acad. Sci. **70**, 285 (1935).

tioned, might be interpreted as due simply to changes in degree of order rather than to change in the type of structure. This seems particularly probable in the cases of compounds, such as CuZn, having a simple type of superstructure.

From the theory of the order-disorder transition and from experimental values of thermal expansion coefficients, it is, in fact, possible to predict such a change in degree of order under pressure, and to obtain a quantitative estimate of the changes to be expected. In the following, the predictions of the theory have been examined for pressures up to 10,000 kg/cm$^2$ and temperatures up to 426°C with the three alloys CuAu, $Cu_3Au$, and CuZn. Results of investigation of a fourth alloy, alpha brass ($Cu_3Zn$), are also included.

## THEORETICAL

From the fundamental law of thermodynamics the change of entropy per unit volume ($d\phi/V$) is defined as

$$d\phi/V=(dU+pdV)/TV. \tag{1}$$

If the usual assumption in thermodynamic treatments of the order-disorder process is made that the quantities in (1) may each be separated into two independent parts, one part due to the thermal vibrations of the atoms of the solid, the other a configurational part (hereafter indicated by a subscript $c$), we may write the average change in the configurational entropy per unit change of pressure at constant temperature as

$$\frac{1}{V}\frac{\Delta\phi_c}{\Delta p}=\frac{1}{TV\Delta p}\int_0^p dU_c+\frac{1}{TV\Delta p}\int_0^p pdV_c. \tag{2}$$

The left-hand side of (2) is from Maxwell's fourth relation

$$(\partial\phi/\partial p)_T=-(\partial V/\partial T)_p \tag{3}$$

equal to the negative of the configurational part of the thermal expansion coefficient to within the approximation involved in substituting an average for an instantaneous coefficient. The first term on the right of (2) may be expressed in terms of changes in the short range order $\sigma$ or in the long range order $S$. The latter definition is here chosen because it is more easily correlated with the electrical resistance, the index of order used in this investigation. The relation between configurational energy and long range order is from the Bragg-Williams theory[2, 3]

$$U_c=U_{0c}(1-S^2), \tag{4}$$

where $U_{0c}$ is the total energy required to destroy superlattice order. Therefore

$$dU_c=-U_{0c}d(S^2)+(1-S^2)dU_{0c} \tag{5}$$

and from (2), (3) and (5) we have

$$\frac{1}{V}\frac{\Delta V_c}{\Delta T}=\frac{U_{0c}}{TV}\frac{\Delta(S^2)}{\Delta p}-\delta, \tag{6}$$

where

$$\delta\equiv\frac{1}{TV\Delta p}\left[\Delta U_{0c}(1-S^2)+\int_0^p pdV_c\right].$$

Here $\Delta(S^2)$ and $\Delta U_{0c}$ refer to integrated changes in $S^2$ and $U_{0c}$ due to the change of pressure $\Delta p$ from 0 to $p$.

The value of the correction term $\delta$ may be estimated from experimental data later described. If we assume with the alloy CuAu, for example, that $\Delta U_{0c}$ is given by the change in the critical temperature with a pressure of 10,000 kg/cm$^2$, the value of $\Delta U_{0c}(1-S^2)$ for one gram-atom varies from about $0.1(10)^8$ erg at 200°C to $5.3(10)^8$ ergs at 400°C. The term $\int_0^p pdV_c$ cannot be evaluated without compressibility measurements but a reasonable guess would place its value somewhat lower in absolute magnitude than $\Delta U_{0c}(1-S^2)$ in the same temperature range, and negative, so that the two terms partly cancel. The value of $U_{0c}\Delta(S^2)$, on the other hand, varies between $1.1(10)^8$ ergs and $80(10)^8$ ergs between 200°C and 400°C, respectively, and for the same pressure. The description of $\delta$ as a correction term seems justified. It should be noted that (6) is inexact to the extent that it involves implicitly the approximation of Bragg and Williams that the ordering energy varies linearly with degree of order.

A derivation of (6) without such an assumption can be made by calculating the entropy through its statistical definition and expressing it in terms

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[2] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **145**, 699 (1934).

[3] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **151**, 540 (1935).

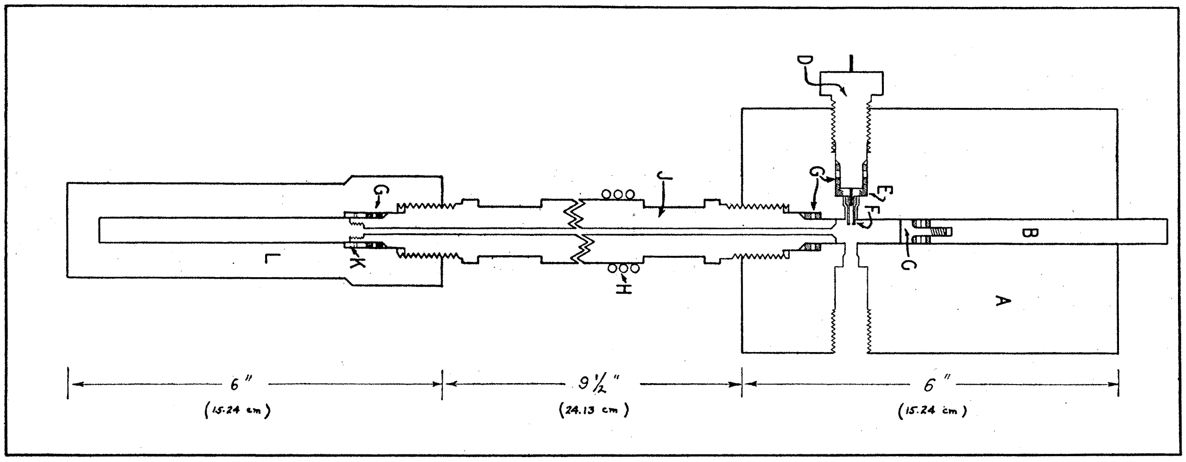

FIG. 1. High pressure unit.

of the long range order. The result for an AB alloy (the only case where a simple relation exists) is

$$d\phi_c=-\frac{kN}{2}\left\{\log\frac{1+S}{1-S}\right\}dS$$

$$=-\frac{kN}{2}d(S^2)[1+\tfrac{1}{3}S^2+\tfrac{1}{5}S^4\cdots],$$

so that the analogy to (6) becomes

$$\frac{1}{V}\frac{\Delta V_c}{\Delta T}=\frac{kN}{2V}\frac{\Delta(S^2)}{\Delta p}[1+\tfrac{1}{3}S^2\cdots]. \tag{7}$$

For comparison purposes (6) may be rewritten for the AB case as

$$\frac{1}{V}\frac{\Delta V_c}{\Delta T}=\frac{kN}{2V}\left(\frac{T_c}{T}\right)\frac{\Delta(S^2)}{\Delta p}-\delta \tag{6$_{\mathrm{AB}}$}$$

by means of the relation

$$U_{0c}=\tfrac{1}{2}NkT_c,$$

where $T_c$ is the critical temperature.

The difference between ($6_{\mathrm{AB}}$) and (7) is not large, and since (6) is applicable for all compositions, it is used hereafter. In the following, approximate values of the right side of the equation derived from measurements of electrical resistance of the alloys CuAu and CuZn under pressure are compared with reported values of the left side.

The considerations above are applicable to observations made below the critical point. At or above the critical point, the resistance measurements are of little use in evaluating the quantities of Eq. (6). However, observations made in this region may be analyzed in two ways, depending upon whether the transition occurring at the critical point is considered, in Ehrenfest's terminology, to be of the first kind or of the second kind. If it is of the first kind (a definite phase change involving a definite latent heat), then Clapeyron's equation

$$dT_c/dp=T\Delta V/L \tag{8}$$

is applicable. An observed shift of the critical point with pressure predicts at the critical point an abrupt volume change proportional to the latent heat. If, on the other hand, the transformation is of the second kind (characterized by no latent heat) one may consider the appropriate equations to be

$$\frac{dT_c}{dp}=T\frac{\Delta(\partial V/\partial T)_p}{\Delta C_p}=-\frac{\Delta(\partial V/\partial p)_T}{\Delta(\partial V/\partial T)_p}. \tag{9}$$

(It should be mentioned that the validity of these equations has been questioned by several authors.*) In the section giving the observations on the alloys $Cu_3Au$ and CuAu, deductions are made from these equations.

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* See for example the discussion in Epstein's *Thermodynamics*.

## APPARATUS

The technique for attaining high pressures was, as closely as possible, that described by P. W. Bridgman.[4] I wish to acknowledge also his personal advice on the general design of the high pressure unit of the apparatus and his generous loan to the Sloane Physics Laboratory of the hydraulic press and hand pump used in this investigation.

The high pressure unit, illustrated in Fig. 1, is in most respects of standard design. Because of the high temperatures used, the insulating plugs $D$ carrying the electrical leads are introduced in the upper cylinder $A$, kept cool by the coil $H$ on the connecting tube $J$. The lower specimen chamber $L$ is of unusually small inner diameter, $\frac{3}{8}$ in. (0.953 cm), for two reasons, (a) the fluid capacity is small and heats of compression on change of pressure therefore small; a great convenience in making readings involving change of pressure at constant temperatures—(b) the wall thickness of the chamber may be kept to a minimum 0.6 in. (1.52 cm) and temperature equilibrium between the heating bath and the specimen readily established; a desirable feature for readings at constant pressure and changing temperatures.

All parts of the unit, except the piston $B$ (which was of tool steel), were machined from Simplex forging steel, a product of the Crucible Steel Company of America and furnished through their generosity. (Special thanks are due to Mr. F. J. Dawless of their local office.) The machined parts were subjected to the heat treatment recommended for maximum hardness. For the majority of the work the steel proved eminently satisfactory. On occasion, however, experimental conditions required that the specimen chamber $L$ be held at high pressure for several hours at temperatures between 350°C and 426°C, well over its recommended annealing temperature. These conditions invariably caused slow leak, because of a gradual distortion of the recess in the specimen chamber which retains the washers $G$. The recess was rebored on such occasions and new washers fitted. For convenience in removing washers, a sleeve $K$ was placed at the bottom of the recess. This could be withdrawn with the aid of a pronged tool fitting into holes in the wall of the sleeve.

Lead and mild steel packing washers were used at connections indicated by the letter $G$. At temperatures above 300°C, however, the lead washers in chamber $L$ were replaced by washers of soft sheet aluminum and well-annealed copper.

The compression medium (the high pressure unit was vacuum filled) was kerosene. Ethylene glycol was tried originally because of its high boiling point but was discarded because it becomes conducting under pressure. Decomposition of the kerosene was noticed on only one run, that reaching 426°C. The products were a gas and a liquid fraction which evaporated readily.

A potentiometer method (Bridgman[5]) was used for making the resistance measurements. The three wires required to connect the steel sleeves $F$ with the specimen in chamber $L$ were of copper, insulated with spun glass, a product (Vitrotex magnet wire) of the Anaconda Wire and Cable Company and generously furnished by them. This insulation at low temperatures withstood the pressures applied very well, but flaked off those parts of the wire exposed to temperatures above 250°–300°C after about four or five runs, because of the necessary flexing of the wire when specimens were changed. It was considered very satisfactory to renew the wiring so infrequently, considering the conditions of its use.

In the upper cylinder $A$, the wires were soldered to the sleeves $F$, which in turn were electrically connected with the electrodes of the insulating plugs by springs. In the lower cylinder $L$, the wires were held by screw clamps to the leads on the specimen.

The resistance specimens were of narrow strip, rod, or wire, 5–7 cm in length. Short copper cross wires welded to them near the ends served as potential leads. With all alloys, the welding was assisted by first coating the copper lightly with silver solder.

The precision of the potentiometer method justifies recording resistance to $1(10)^{-6}$ ohm for the specimens used, ranging from $2(10)^{-2}$-ohm

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[4] P. W. Bridgman, *Physics of High Pressure* (Macmillan, 1931).

[5] P. W. Bridgman, Proc. Am. Acad. Sci. **56**, 61 (1921).

to $1(10)^{-3}$-ohm total resistance, a fact emphasized by adjusting the size of the points on the resistance-pressure graphs for the different alloys. Deviations of the readings from a smooth curve generally occur and are attributed mostly to slight departures of the specimen from an equilibrium condition. Contributing factors of minor degree are the various parasitic e.m.f.'s. Such troubles were minimized by immersing all copper-to-iron junctions in constant temperature baths. In general, the accuracy of the measurements of changes in resistance must be judged by the scatter of the points on each curve. The scatter changes from specimen to specimen and varies with temperature.

Measurements of pressure were made by recording changes in resistance of a manganin coil, wound upon the electrode of one of the four insulating plugs in cylinder $A$, and connected in one arm of a Wheatstone bridge circuit.

While measurements of relative changes of resistance were made with high precision, absolute values of resistance are probably correct only within about 2 percent. Likewise the absolute values of pressure readings cannot be regarded as fixed to better than about 4 percent. Such absolute errors, however, affect the conclusions in only a slight degree.

The heating bath was a welded steel container of about 1.5 gallons' (6 liters) capacity, around which was wrapped a heating coil—used however only as an auxiliary for high temperatures. The whole was suitably insulated and swiveled on a forked lever so that it could be conveniently brought up to or dropped away from the specimen chamber. Most of the heat was supplied to this bath by three immersion heaters in liquid tight copper tubing. The removable Transite cover carried these heaters, a tube containing the thermocouple, a mercury thermostat, and the stirring device. Because of the temperatures used, the latter rotated in a ball bearing lubricated with graphite, being driven through flexible shafting by a motor some distance away.

The mercury thermostat was satisfactory at temperatures under 300°C (the range initially contemplated), maintaining temperatures constant to within 0.05°C. Above 300°C, temperatures were manually controlled, the temperature fluctuations noted and appropriate corrections made to the readings.

For a range of temperatures up to 200°C, Russian mineral oil was used for the thermostatic liquid. Above this point a salt bath was employed, a product of a local company, supplying baths for the heat treatment of steels. It is stated by them to be a "eutectic mixture of salts melting at about 175°C." It proved eminently satisfactory, being very fluid, odorless, and noncorrosive.

Temperatures were measured with a Chromel-Alumel thermocouple in conjunction with a Wolff potentiometer, the thermal e.m.f.-temperature relation being taken from the *International Critical Tables*. The standard cell used was recalibrated just prior to use, the whole unit being checked against the melting point of test lead. It is believed that all temperature measurements are accurate to within ±0.4°C.

TABLE I. *Values of resistivity of* CuAu.

| AUTHORS | COMPOSITION ATOMIC % AU | $\rho(20)°C \times (10)^6$ ohm·cm | | $T_c$ (HEATING) °C |
|---|---|---|---|---|
| | | ANNEALED | QUENCHED | |
| Haughton and Payne[6] | 49.8 | 5 | — | 405 |
| | 50.2 | 5 | — | 421 |
| | 50.3* | 5 | — | 422 |
| Kurnakow and Ageew[10] | 50.24 | 4.86 | 14.2 | 400–450 |
| Johansson and Linde[a] | 49.2 | 4.24 | — | — |
| | 50.0 | 3.63 | 14.1 | — |
| | 50.5 | 3.98 | — | — |
| Grube *et al.*[12] | | 3.79 | — | 420 |
| Wilson | | 4.30 | 14.52 | 415 |

* Oxygen-free sample.

[a] C. H. Johansson and J. O. Linde, Ann. d. Physik 5, 1 (1936).

Table II. *Values of resistivity of* $Cu_3Au$. *All values of* $\rho \times (10)^6$ *ohm·cm.*

| Authors | $(\rho)_{22^\circ}$ Ordered | $(\rho)_{400^\circ}$ | $(\rho)_{22^\circ}$ Quenched | $T_c$ (Heating) °C |
|---|---|---|---|---|
| Sachs and Weerts[a] | 4.7 | 14.35 | 11.4 | — |
| Grube *et al.*[12] | 4.15 | — | — | 395 |
| Haughton and Payne[6] | 7 | — | — | 392 |
| Sykes and Evans[7] | 4.5 | 14.2 | 11.5 | 386 |
| Sykes and Jones[b] | — | — | — | 391* |
| Borelius *et al.*[c] | — | — | — | 390 |
| Wilson | 4.31 | 14.4 | 11.35 | 391.5 |

* From specific heat measurements

[a] G. Sachs, and J. Weerts, Zeits. f. Physik **67**, 507 (1931).

[b] C. Sykes, and F. W. Jones, Proc. Roy. Soc. **161**, 440 (1937).

[c] G. Borelius, C. H. Johansson, and J. O. Linde, Ann. d. Physik **86**, 291 (1928).

## Experimental Methods and Results

### CuAu alloys

Numerous investigators have shown that with both CuAu and $Cu_3Au$, it is extremely difficult to obtain resistivity values characteristic of an equilibrium condition when cooling a disordered alloy from above its critical point to room temperature. In cooling, values of the resistivity at any given temperature are higher than those on the heating curve of an ordered alloy, the difference being greater, the faster the cooling. On the other hand, Haughton and Payne[6] have indicated that in heating an ordered alloy resistivity values are inappreciably affected by the rate of heating. It would seem to follow that resistivity measurements may be used as a good index of order in these CuAu alloys only when the specimen is being transformed by a rise of temperature from an ordered to a disordered state. This conclusion is further supported by the fact that different resistivity investigations of $Cu_3Au$[6, 7] indicate from heating curves a critical temperature of about 390°C (compared with the temperature 391°C accurately determined from specific heat data[8]) while cooling curves may indicate temperatures from 10°C to 30°C lower, depending on the rate of cooling.

For these reasons all measurements of resistivity as an index of order, here reported, were made at selected temperatures during heating of initially ordered alloys.

Small ingots of the alloys CuAu and $Cu_3Au$ (1 to 3 grams) were prepared by Handy and Harman of Bridgeport, Connecticut for the purpose of the experiment. These were prepared under charcoal and contained by synthesis the exact composition indicated by the chemical formulae. No analysis was made subsequently.

The castings of CuAu and $Cu_3Au$ were rolled and drawn into wires 0.58 mm diameter and 0.44 mm diameter, respectively. The frequent annealings necessary were carried out in hydrogen. After drawing, the wires were further homogenized by annealing for a period of one hour at about 850°C.

Potential leads were welded on, the specimens sealed in evacuated Pyrex tubes and heat treated for ordering as follows:

CuAu: 24 hours at 450°C, gradual cooling to 210°C over a period of 150 hours, then to room temperature in 12 hours.

$Cu_3Au$: 50 hours at 370°C, gradual cooling to 210°C over a period of 100 hours, 50 hours at 210°C, further cooling to 135°C over a 50-hour period, then to room temperature in one hour.

The resulting values of the resistivities of the specimens used are given in the last lines of Tables I and II, together with other characteristics of the alloys. Listed in these tables for comparison are corresponding values reported by other investigators.

Table I indicates that the specimens of CuAu here used deviated slightly from the equi-atomic composition. An assumption that a few tenths of one percent of silver was present (perhaps introduced from the silvered potential leads) would explain the lowering of the critical temperature (Hultgren[9]) and might also explain the slightly high values of the resistivity in both quenched and annealed states. Two specimens

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[6] J. L. Haughton and R. J. M. Payne, J. Inst. Metals **46**, 457 (1931).

[7] C. Sykes and H. Evans, J. Inst. Metals **58**, 255 (1936).

[8] C. Sykes and F. W. Jones, Proc. Roy. Soc. **157A**, 213 (1936).

[9] R. Hultgren and S. Tarnopol, Metals Technology (January, 1938).

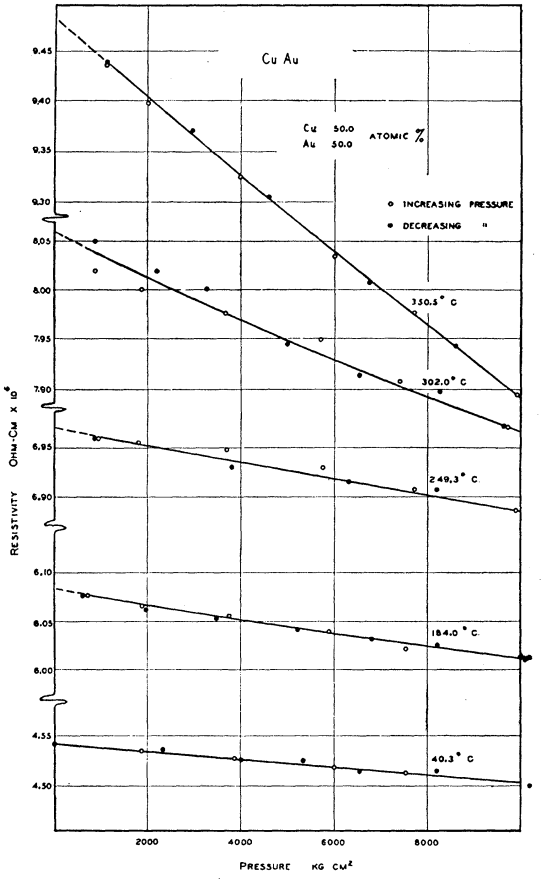

FIG. 2. Variation with pressure of resistivity of CuAu at various temperatures. The identification of the ordinate should read "Pressure, kg/cm²."

of $Cu_3Au$ were used, their resistivities coinciding within the limits set by the measurements of dimensions. Table II indicates a fair agreement of the values obtained with those reported by other workers.

*CuAu—results.*—Pressure runs at constant temperature were made successively on one specimen at the temperatures indicated in Fig. 2, with the results there shown. With the exception of the runs at 249.3°C and 302.0°C the points taken on increasing and decreasing pressure fall fairly well on single smooth curves, the sample not exhibiting irregularities (to be expected in samples not seasoned under pressure) on the first run at 40.3°C.

It should be noted that the values of $\rho$, the resistivity, shown in this graph are uncorrected for the change in volume of the specimen, so that the ordinates are proportional to what may be called atomic resistivity. This statement applies to all other data (or to calculations where they are used) in this investigation.

The average pressure coefficients of resistance measured to 10,000 kg/cm² as derived from the curves of Fig. 2 are given in Table III and are plotted against temperature in Fig. 3.

A further constant temperature-pressure run was attempted at 390°C, after completion of the run at 350.5°C, but was abandoned after the first increase in pressure due to the slow drift of the readings of resistance; caused either by the impossibility of holding the temperature absolutely constant (it was manually controlled) or by the well-known sluggishness of the reaction in CuAu near the critical point. The pressure was accordingly then increased to 8700 kg/cm² (the increase being accompanied by an immediate drop in resistivity of $0.4\times(10)^{-6}$ ohm·cm) and the temperature slowly raised. The course of the resistivity under these conditions is shown in Fig. 4 by the upper part of the dashed curve. Just below point $A$, the rate of heating was greatly reduced. At $A$ (427°C) the pressure had dropped to 8200 kg/cm². There seemed to be no change in the resistance of the specimen at this point which could not be attributed to a small decrease in the pressure due to slow leak,

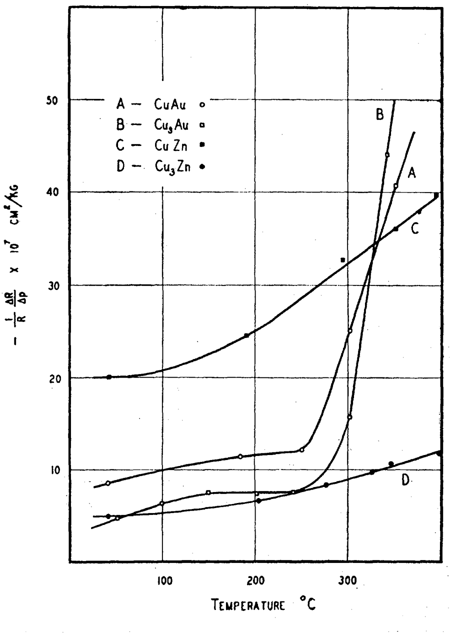

FIG. 3. Average pressure coefficients of resistance.

indicating that equilibrium conditions were closely approached. On release of pressure to 5000 kg/cm$^2$ the resistivity changed immediately to point $B$, and on a further release to about 1000 kg/cm$^2$, it moved more gradually to $C$. The rise in temperature between $A$ and $C$ was of the order of 1°C.

In view of the resistance-*vs.*-temperature readings later made on the same specimen at atmospheric pressure (full line, Fig. 4) it would appear that the critical point of the CuAu alloy was raised by about 1.7°C per 1000 kg/cm$^2$ pressure.

*Analysis of data on CuAu.*—Data taken below the critical temperature allow a comparison to be made of the ordering effect of pressure with the experimentally reported values of the thermal expansion coefficient, by means of Eq. (6).

To make such a comparison, the factor $\Delta(S^2)$ must first be evaluated from the resistivity measurements by finding $S$, the degree of order, and $\Delta S$ the change in order under pressure. (Calculations of the latter quantity are made for an arbitrary pressure change $\Delta p$ of 10,000 kg/cm$^2$.) The only useful theory relating resistivities to degree of order is that of Bragg and Williams.[2] They assume that the resistivity of an ordered alloy behaves like that of a pure metal, while the resistivity of the disordered phase of the same alloy behaves like that of an impure metal, or that a portion of its resistivity, $\rho_{0\ \text{disorder}}$, is temperature independent. Referring to Fig. 4 where $\rho_0$, the resistivity of the disordered phase, and $\rho_1$, the resistivity of the ordered phase, are plotted against temperature it follows from their assumptions that the degree of order at a temperature of 330°C is given by

$$S=(\rho_0-\rho)/(\rho_0-\rho_1)=DE/DG.$$

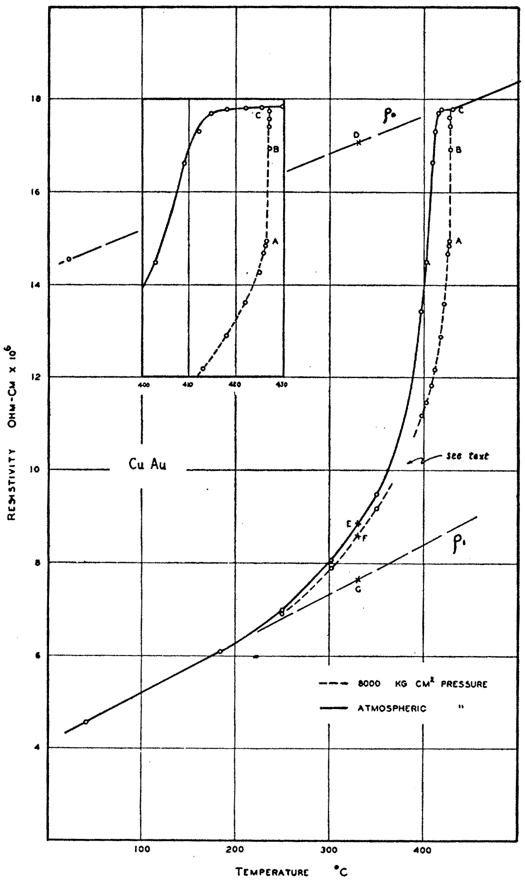

FIG. 4. Variation of the ordered and disordered resistivity of CuAu with temperature.

TABLE III. *Average pressure coefficient of resistance of* CuAu.

| TEMPERATURE °C | $\frac{1}{R}\left(\frac{\Delta R}{\Delta p}\right)_{10,000}$ CM$^2$/KG. |
|---|---|
| 40.3 | $-8.45(10)^{-7}$ |
| 184.0 | $-11.4$ |
| 249.3 | $-12.1$ |
| 302.0 | $-25.1$ |
| 350.5 | $-40.6$ |

The change in the degree of order ($\Delta S$) due to 10,000 kg/cm$^2$ pressure is obtained in an analogous fashion. At any given temperature there is a total change $\Delta\rho_T$ in the resistivity due to a pressure of 10,000 kg/cm$^2$. Part of this change $\Delta\rho_N$ is a normal change, being due simply to a decrease in the amplitude of the atomic thermal vibrations. This is subtracted from $\Delta\rho_T$ giving $\Delta\rho_{\text{order}}$, the portion of the total change in resistivity due to the ordering effect. As above

$$\Delta S=\frac{\Delta\rho_{\text{order}}}{\rho_0-\rho_1}$$

The seemingly arbitrary choice of the normal decrease in resistivity should actually be governed by the behavior of pure metals under pressure, in view of the above assumptions. The variations of the average coefficients with temperature of the three pure metals concerned in this investigation, as derived from Bridgman's results are given below.

*Values of* $(1/R)(\Delta R/\Delta p)_{12,000}$.

| | 0°C | 100°C |
|---|---|---|
| Au | $-2.87(10)^{-6}$ | $-2.92(10)^{-6}$ |
| Cu | $-1.83$ | $-1.77$ |
| Zn | $-4.70$ | $-4.50$ |

One would conclude that changes in the pressure coefficients with temperature are small, a conclusion which Bridgman generalizes to apply to most metals.

The assumption has therefore been made that the average pressure coefficient of resistance of an ordered alloy, measured at 50°C (where the ordering effect of pressure must be very small) defines its normal decrease of resistance under pressure. The value of $(1/R)(\Delta R/\Delta p)$ at 50°C is therefore subtracted from the values of the pressure coefficients at higher temperatures and the remainder used to calculate $\Delta\rho_{\mathrm{order}}$ from the resistivity $\rho$ appropriate to these higher temperatures.

From the resulting values of $S$ and $\Delta S$, with $U_{0c}$ equal to $\frac{1}{2}RT_c$, $T_c=420°\mathrm{C}$, and with $V=8.71$ cm$^3$ (Hultgren[9]), the left side of Eq. (6) may be evaluated to within the factor $\delta$. The results, for seven different temperatures, are given in Table IV together with values of the thermal expansion coefficients for CuAu determined from the heating curve of Kurnakow and Ageew.[10]

Considering the approximations used in evaluating the quantities appearing in the third column of Table IV, and the approximate character of the thermal expansion data, it is considered that the quantitative agreement between the third and fifth columns is sufficiently close to confirm the deductions made from the Bragg-Williams theory.

TABLE IV. *Values of* $\Delta S^2/\Delta p$ *and of the thermal expansion coefficient of* CuAu *alloy.*

| TEMP. °C | $\frac{\Delta(S^2)}{\Delta p}$ CM²/DYNE | $\frac{1}{V}\frac{\Delta V_c}{\Delta T}$ | $\left(\frac{1}{V}\frac{dV}{dT}\right)_{\mathrm{EXP}}$ | $\left(\frac{1}{V}\frac{dV_c}{dT}\right)^*_{\mathrm{EXP}}$ |
|---|---|---|---|---|
| 50 | 0 | 0 | $48(10)^{-6}$ | 0 |
| 200 | $0.38(10)^{-12}$ | $2.6(10)^{-6}$ | 48 | 0 |
| 250 | 0.51 | 3.2 | 50 | $2(10)^{-6}$ |
| 300 | 0.71 | 4.1 | 58 | 10 |
| 350 | 5.4 | 29. | 66 | 18 |
| 375 | 13. | 66. | 74 | 26 |
| 400 | 28. | 138. | 105–135 | 57–87 |

* $\frac{1}{V}\frac{dV_c}{dT}$ is taken to be $\frac{1}{V}\left(\frac{dV}{dT}\right)_T-\frac{1}{V}\left(\frac{dV}{dT}\right)_{50°}$.

The observed shift of the critical point of CuAu with pressure is about $1.7(10)^{-9}$°C·cm²·dyne⁻¹. With $T_c=420°\mathrm{C}(693°\mathrm{K})$, we may conclude that if a latent heat exists, there is an abrupt volume change given by Eq. (8) as

$$\Delta V=2.5(10)^{-12}L.$$

If no latent heat exists, then from Eq. (9) the relation between the change of the specific heat and the change of the thermal expansion coefficient is

$$\Delta(\partial V/\partial T)_p=2.5(10)^{-12}\Delta C_p.$$

Experimental evidence is insufficient for a choice to be made between these two expressions. Theoretical considerations due to A. H. Wilson[11] point to a definite latent heat and therefore to the first expression. Theories of Bragg-Williams, Bethe, Peierls, and Shockley predict zero latent heat and therefore require the second expression. In particular the theory of Bragg-Williams predicts a value for $\Delta C_p=1.5R$ erg·g atom$^{-1}$·degree$^{-1}$ ($1.43(10)^7$ c.g.s. units). The predicted change in the thermal expansion coefficient is therefore

$$\frac{1}{V}\Delta\left(\frac{\partial V_c}{\partial T}\right)_p=36(10)^{-6}°\mathrm{C}^{-1}.$$

The rather rough thermal expansion data on CuAu[10, 12] indicate values much higher than this for the actual change in the thermal expansion coefficient, in fact more than three times the predicted change. The discrepancy may lie in either the predicted value of $\Delta C_p$ or in defects of Eq. (9). Inasmuch, however, as the Bragg-Williams prediction on $\Delta C_p$ is known to be in error by a factor of about three in the case of beta brass, the evidence points to the applicability and the validity of Eq. (9).

*$Cu_3Au$ results.*—The results of the pressure runs made at successively higher constant temperatures on the initially ordered specimens are plotted in Fig. 5. The irregularities of the readings on the first two runs, at 51.0°C and at 99.0°C, are quite noticeable, being so marked at

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[10] N. S. Kurnakow and N. W. Ageew, J. Inst. Metals **46**, 481 (1931).

[11] A. H. Wilson, Proc. Camb. Phil. Soc. **34**, 81 (1938).

[12] G. Grube, G. Schonmann, F. Vaupel, W. Weber, Zeits. f. anorg. Chemie **201**, 41 (1931).

51.0°C that only points taken on decreasing pressure are plotted. These irregularities are attributed to the process of seasoning which most metals undergo on initial applications of pressure. On the successively higher runs at 149.4°C, 201.1°C and 240.8°C, equilibrium conditions seemed to be fairly well maintained, points taken on increase and decrease of pressure falling on the same smooth curve. At 301.5°C, however, the curves for increasing and decreasing pressure form a well marked hysteresis loop. The sluggish nature of the reaction indicated by this behavior was expected to be even more marked at 342.0°C. The run at that temperature was therefore conducted by increasing the pressure immediately to 8200 kg/cm$^2$ and holding it constant there for one-half hour. Strangely enough the resistivity did not change during this period from the value obtained at the end of the first six minutes by an amount greater than that ascribable to small temperature fluctuations. Subsequent readings on decreasing pressure fell fairly well on the curve drawn.

The average pressure coefficients of resistance measured to 10,000 kg/cm$^2$ as derived from the curves of Fig. 5 are given in Table V and are plotted against temperature in Fig. 3.

At temperatures above 350.5°C two runs were made, the specimens being kept under high pressure and the temperature alternately raised and lowered. During the first run, leaks were troublesome, the pressure initially being 8400 kg/cm$^2$ at 355°C but falling to 6800 kg/cm$^2$ as the transition point was crossed. This occurred between 397°C and 405°C, the exact point being uncertain. On subsequent cooling the pressure held at a constant value of 3400 kg/cm$^2$, the transition point on cooling at a rate of 100°/hr. being at 382°C and on heating at a rate of 50°/hr. at 394°C.

During the second run (not immediately after the first) the transition point on heating the specimen, held at 7600 kg/cm$^2$, came at 400.5°C. The pressure was then allowed to fall to 600 kg/cm$^2$, the critical points being at 375.8°C on cooling and 392.4°C on heating under these conditions. The suggested course of the resistivity on heating at 8000 kg/cm$^2$ pressure is plotted in Fig. 6 as the dashed curve. The full line shows the resistivity on heating at atmospheric pressure, the points thereon having been taken from Fig. 5; the critical point from an extrapolation of the observations just described (from 600 kg/cm$^2$ to zero). No significance should be attached to the shape of the resistivity curve near the critical point. The only accurate resistance readings were made on the first run and are those plotted in Fig. 6. Attention thereafter was concentrated on the more accurate determination of the transition temperatures.

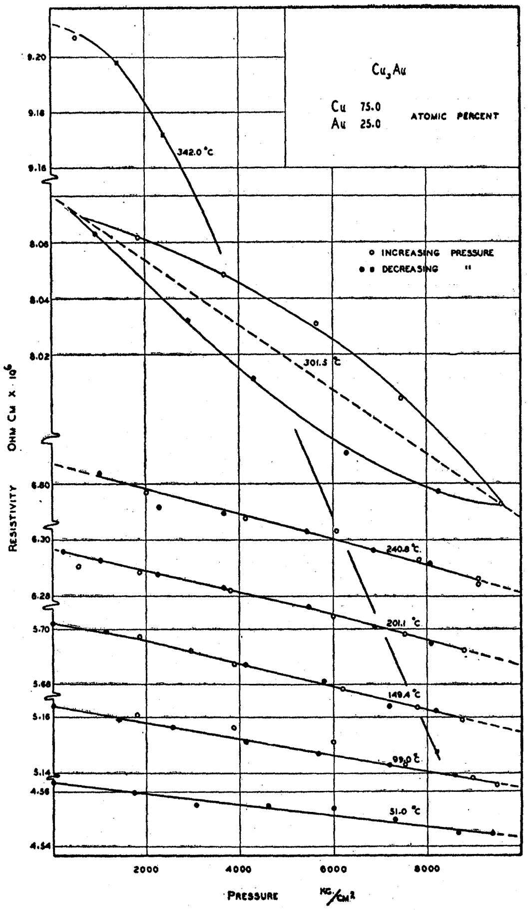

FIG. 5. Variation with pressure of resistivity of $Cu_3Au$ at various temperatures.

Several observations were made on quenched specimens. Early pressure runs at 50°C (on an impure sample, however) had indicated that no substantial change in degree of order as measured by resistivity was to be expected at this low temperature. Although slight permanent decreases in resistance were noted after applying pressure to these specimens, further decreases

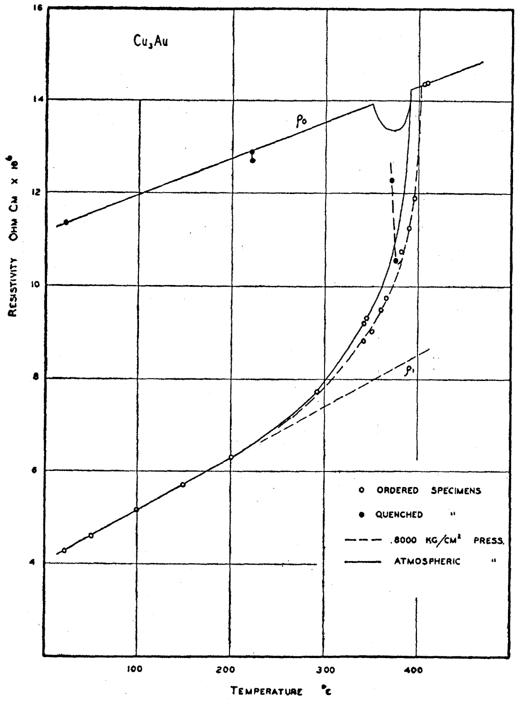

FIG. 6. Variation of the ordered and disordered resistivity of Cu$_3$Au with temperature.

were not observed in repeated runs and the initial changes were therefore attributed to seasoning effects.

A pressure run was later made (on a pure specimen) at 222°C. The results were very irregular and only significant because the resistivity declined permanently from a value of $12.81(10)^{-6}$ ohm·cm before the run to $12.71(10)^{-6}$ ohm·cm after. Following this run the specimen was heated to 370°C and a pressure of 9000 kg/cm$^2$ then applied, the temperature being slowly raised. The resistivity declined from an initial value of about $13(10)^{-6}$ at 370°C to $10.57(10)^{-6}$ at 376°C and thereafter followed the same course as that of an initially ordered alloy (Fig. 6).

TABLE V. *Average pressure coefficients of resistivity of* Cu$_3$Au.

| Temp. °C. | $\frac{1}{R}\left(\frac{\Delta R}{\Delta p}\right)$ cm$^2$/kg$\times(10)^7$ |
|---|---|
| 51.0 | −4.73 |
| 99.0 | −6.31 |
| 149.4 | −7.52 |
| 201.1 | −7.26 |
| 240.8 | −7.48 |
| 301.5 | −15.75 |
| 342.0 | −44 |

*Analysis of data on Cu$_3$Au.*—An analysis of the data taken below the critical temperature may be made in the same manner as with CuAu. The values of the configurational part of the thermal expansion coefficient derived from these data through Eq. (6) are given in Table VI. Here the experimentally determined value of 5.5 cal./g (2.81 $(10)^9$ ergs/cm$^3$ (reference *b*, Table II)) is taken for the quantity $U_{0c}$ in Eq. (6).

The reported values of $(1/V)(dV/dT)$ for Cu$_3$Au are not sufficiently precise to compare with these results.

From the data summarized above, one would infer that the shift of the critical point with pressure for Cu$_3$Au is about 1.2°C per 1000 kg/cm$^2$ or in c.g.s. units $1.2(10)^{-9}$.

Sykes and Jones[8] have investigated the behavior of Cu$_3$Au by thermal means and have concluded that the latent heat at the critical point is 1.26 cal./g ($0.64(10)^9$ ergs/cm$^3$). Eq. (8) then indicates that an abrupt volume change occurs at the critical point given by $\Delta V/V = 0.0012$ whereas the total volume change in going from a completely disordered to an ordered structure is known to be $\Delta V/V = 0.0041$. From the curves of Sykes and Jones relating size of nuclei to changes of volume of the alloy Cu$_3$Au the abrupt volume change above is consistent with a change in size of nuclei from about 10A to a negligibly small value.

It should be noted that the thermal measurements of Sykes and Jones upon an alloy previously cooled at 30°/hour did not show a latent heat at the critical point but instead a change in the specific heat of finite amount 1.92 cal. g$^{-1}$°C$^{-1}$

TABLE VI. *Values of $\Delta S^2/\Delta p$ and of the thermal expansion coefficients of* Cu$_3$Au.

| Temp. °C. | $\frac{\Delta(S^2)}{\Delta p}$ cm$^2$/dyne | $\frac{1}{V}\frac{\Delta V_c}{\Delta T}$ |
|---|---|---|
| 50 | 0 | 0 |
| 100 | $0.24(10)^{-12}$ | $1.8(10)^{-6}$ |
| 150 | .48 | 3.2 |
| 200 | .54 | 3.2 |
| 250 | .71 | 3.8 |
| 300 | 2.60 | 13 |
| 350 | 11.1 | 50 |
| 360 | 12.9 | 57 |
| 380 | 14.8 | 64 |

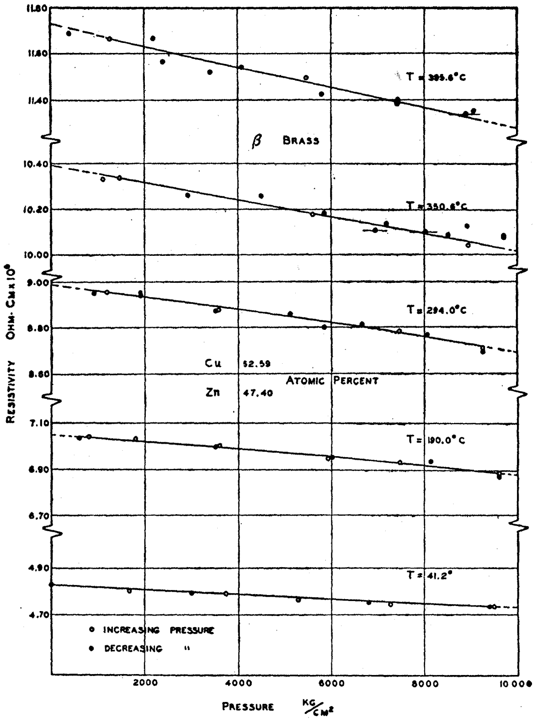

FIG. 7. Variation with pressure of the resistivity of beta brass at various temperatures.

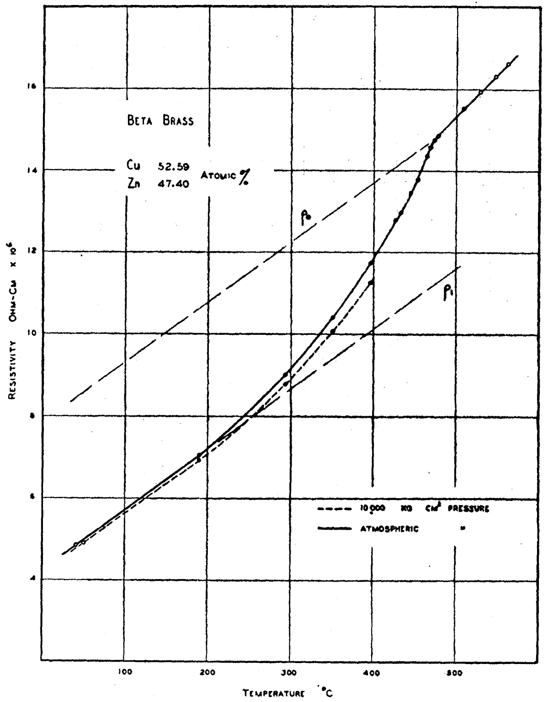

FIG. 8. Variation of the ordered and disordered resistivity of beta brass with temperature.

$(98(10)^7$ erg cm$^{-3}$°C$^{-1})$. This was attributed to presence of anti-phase nuclei. For such a case, Eq. (9) gives a finite change in the thermal expansion of

$$\frac{1}{V}\Delta\left(\frac{\partial V}{\partial T}\right)_p = 1770(10)^{-6}\text{°C}^{-1}.$$

It would be of interest to have accurate thermal expansion data to compare with the results above.

*Copper-zinc alloys.*—Alloys of both alpha and beta brass were supplied through the courtesy of the American Brass Company, Waterbury, Connecticut. Special thanks are due Dr. Cyril S. Smith, Research Metallurgist, under whose direction they were prepared.

TABLE VII. *Average pressure coefficients of resistance for beta brass.*

| TEMP. °C. | $\frac{1}{R}\left(\frac{\Delta R}{\Delta p}\right)_{10,000}$ CM²/KG |
|---|---|
| 41.2 | $-2.00(10)^{-6}$ |
| 190.0 | $-2.46$ |
| 294.0 | $-3.27$ |
| 350.6 | $-3.60$ |
| 395.6 | $-3.96$ |

*Beta brass—CuZn.*—The samples were of hot rolled rod $\frac{1}{8}''$ (0.317 cm) diameter. The analysis furnished was, in atomic percent, copper 52.59, zinc 47.40, lead 0.001, iron 0.01. Resistance specimens were prepared by grinding the rolled rod to a square form with 0.0153 cm$^2$ cross-sectional area. On sections of this rod about 5 cm in length silvered potential leads were attached by welding. The specimens were then heated above the transformation point in hydrogen and quenched. This heat treatment apparently preserved no detectable amount of disorder at room temperature, the resulting value of the resistivity at 25°C proving to be $4.60(10)^{-6}$ ohm·cm. This is slightly higher than Webb's[13] value of $4.5(10)^{-6}$ ohm·cm for annealed single crystals of this composition but lower than that of Haughton and Griffiths[14] who reported $4.62(10)^{-6}$ ohm·cm (room temperature). Subsequently, the samples under pressure

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[13] W. Webb, Phys. Rev. **55**, 300 (1939).

[14] J. S. Haughton and W. T. Griffiths, J. Inst. Metals **34**, 245 (1925).

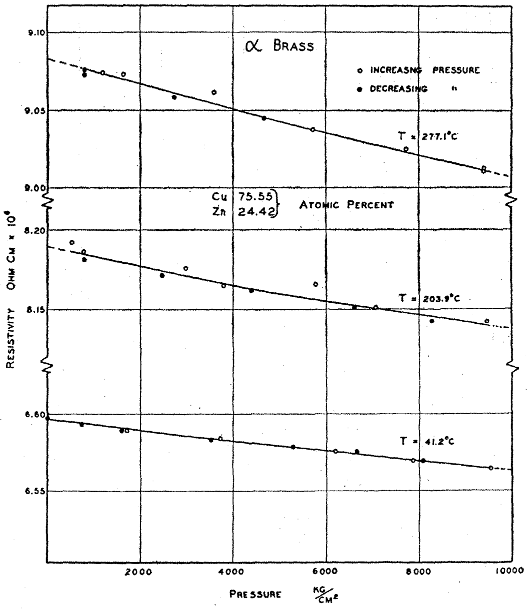

FIG. 9. Variation with pressure of resistivity of alpha brass at various temperatures.

showed no irregularities aside from those due to initial seasoning effects. They were therefore considered to be in an ordered state requiring no further heat treatment.

The five runs made at various temperatures up to 395.6°C are plotted in Fig. 7. Bridgman[1] has measured the pressure coefficient of resistance of CuZn (exact composition not stated). From his data we derive the following values

| Temp. | $\frac{1}{R}\left(\frac{\Delta R}{\Delta p}\right)_{10,000}$ cm²/kg |
|---|---|
| 30°C | $-2.06(10)^{-6}$ |
| 75°C | $-2.03(10)^{-6}$ |

The first run here made, at 41.2°C gives in the same units $-2.00(10)^{-6}$, affording a check upon the method of measurement.

The average pressure coefficients of resistance derived from the curves of Fig. 7 are given in Table VII and plotted in Fig. 3 against temperature. Values of the thermal expansion coefficient due to the configurational changes may be calculated from the values of the pressure coefficients given in Fig. 3. A difficulty arises, however, in that the line representing the behavior of the resistivity of the disordered alloy cannot be drawn on the resistivity-temperature graph (Fig. 8) below the critical point with any degree of confidence. Beta brass, unlike the CuAu alloys, cannot be retained in a disordered state below the critical temperature, and $\rho_0$ is not therefore defined by experimental points in this region. The policy, adopted by Webb,[13] of extrapolating the resistivity-temperature curve above the critical point linearly to temperatures below the critical point is not justifiable. If such extrapolation is made, the formula above derived relating resistivity to degree of order actually gives negative values of $\rho_{0\ \text{disorder}}$ in the equation $\rho_0=\rho_{0\ \text{disorder}}+\alpha_0 T$. It will be remembered that $\rho_{0\ \text{disorder}}$ is assumed to represent the contribution of the disordered state to the resistivity at 0°K, so that it cannot be negative. Moreover, such an assumed curve actually crosses the curve $\rho_1$ for the resistivity of the ordered phase. Obviously, at the intersection, and for lower temperatures, the relation between degree of order and resistivity

$$S=(\rho_0-\rho)/(\rho_0-\rho_1)$$

becomes meaningless.

In this dilemma it has been here assumed that the line $\rho_0$ is parallel to $\rho_1$ below the critical point, as drawn in Fig. 8. This involves the assumption that $\rho_{0\ \text{disorder}}$ may be equated to the value $\rho_0-\rho_1$ at the critical point.

With this assumption, values of $S$ and $\Delta S$ may be calculated for various temperatures.

With $U_{0c}=8.7$ cal./g [$3.02(10)^9$ ergs/cm³] from experimental measurements of Sykes and Wilkinson[15] for the composition used, calculated values of the left side of Eq. (6) are given in Table VIII. Given also are the thermal expansion coefficients reported by Merica and Schad[16] and

TABLE VIII. *Values of $\Delta S^2/\Delta p$ and of the thermal expansion coefficient of beta brass.*

| Temp. °C | $\frac{\Delta(S^2)}{\Delta p}$ cm²/dyne | $\frac{1}{V}\frac{\Delta V_c}{\Delta T}$ | $\frac{1}{V}\frac{dV}{dT}$ | $\frac{1}{V}\frac{dV_c}{dT}$ |
|---|---|---|---|---|
| 50 | 0 | 0 | $5.8(10)^{-5}$ | 0 |
| 200 | $2.0(10)^{-12}$ | $1.7(10)^{-5}$ | 6.6 | $.8(10)^{-5}$ |
| 250 | 3.6 | 2.7 | 7.1 | 1.3 |
| 300 | 5.2 | 3.6 | 7.6 | 1.8 |
| 350 | 6.6 | 4.2 | 8.4 | 2.6 |
| 400 | 7.1 | 4.2 | 9.4 | 3.6 |

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[15] C. Sykes and H. Wilkinson, J. Inst. Metals **61**, 223 (1937).

[16] P. D. Merica and L. W. Schad, Nat. Bur. Stand. Sci. Pap. 14, 1918.

the estimated values of $(1/V)(dV_c/dT)$ derived from these measurements.*

*Alpha brass.*—The samples were a hot rolled rod $\frac{1}{8}''$ (0.317 cm) diameter, the analysis made by the American Brass Company being in atomic percent, copper 75.55, zinc 24.42, lead 0, and iron 0.03.

Resistance specimens were prepared by rolling the samples to ribbon 0.107 mm thick, and cutting the ribbon into strips about 6 cm long and 1 to 2 mm wide. After attaching potential leads, the specimens were heated to between 500°C and 600°C, and quenched. No undue irregularities were noted on the six constant temperature-pressure runs subsequently made. The results of these runs are plotted in Figs. 9 and 10; the derived pressure coefficients of resistance are shown in Table IX and plotted against temperature in Fig. 3.

In going from 40°C to 400°C there is an increase in the absolute magnitude of the pressure coefficient of alpha brass which is about one-third the increase in beta brass for the same temperature range. The relative increase is, however, somewhat greater than that of beta brass.

If the interpretation which has been attached throughout this analysis to an increase with temperature of the pressure coefficient of resistance is correct, the conclusion must be drawn that an ordered phase in alpha brass is promoted by pressure.

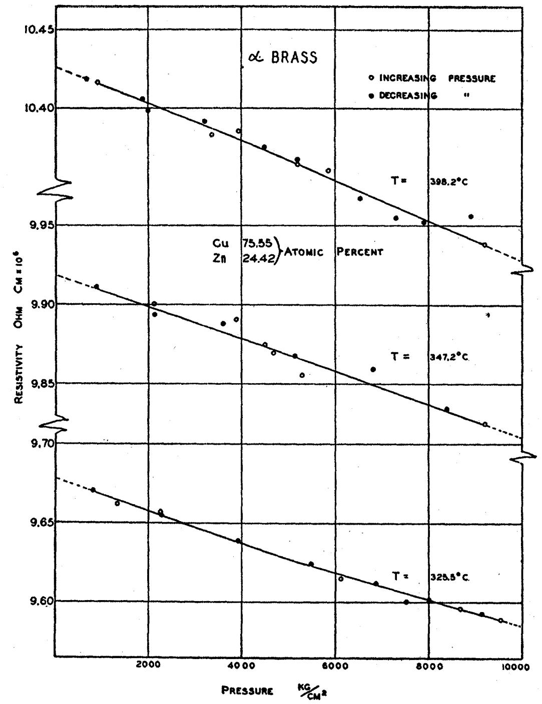

FIG. 10. Variation with pressure of resistivity of alpha brass at various temperatures.

In this connection, it should be pointed out that a specific heat measurement by Sykes and Wilkinson on a sample of alpha brass containing 36 percent Zn by weight showed an anomalous behavior below 210°C. The indication is that a slight degree of order exists in alpha brass at room temperature, which gradually vanishes on heating. The effect of pressure is apparently to enhance the ordering tendency.

TABLE IX. *Values of the pressure coefficients of resistance for alpha brass.*

| TEMP. °C | $\frac{1}{R}\frac{\Delta R}{\Delta p}$ CM²/KG. |
|---|---|
| 41.2 | $4.95(10)^{-7}$ |
| 203.9 | 6.52 |
| 277.1 | 8.30 |
| 325.5 | 9.68 |
| 347.2 | 10.52 |
| 398.2 | 11.70 |

The writer takes pleasure in acknowledging his indebtedness to Professor L. W. McKeehan under whose guidance this work was carried out. His stimulating and keen advice was invaluable throughout the course of the investigation.

Mention has already been made in the text of the material aid afforded to this research from many sources. Especially, it will be recalled that the technical difficulties were greatly simplified by the generous loan of part of the pressure equipment by Professor P. W. Bridgman of Harvard.

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* The values of $(1/V)(dV/dT$ reported by Merica and Schad are averages for the temperature ranges 0–100°C, 100–200°C, etc. These have been plotted as points at 50°C, 150°C, etc., and the values on the smooth line joining these points are given in Table VIII.