magnesium rod displays; (d) good agreement between the theoretical curve and the most reasonable experimental curve out to 610 kc.

The theoretical curves for the magnesium rods were calculated with $\mu = 0.25$ and $V_0 =$ velocity at low audible frequencies $= 4900$ m/sec.

Silver

The two rods studied were of hard drawn silver, pure to within one part in two thousand. The graph for the smaller silver rod (see Fig. 5) shows: (a) fairly good agreement with the theoretical curve out to 400 kc, although the experimental curve has a change of curvature, whereas the theoretical one cannot have a change of curvature; (b) experimental points in the theoretical "dead zone"; (c) no evidence of "second series" velocities; (d) less dispersion for a given frequency than occurs for the other silver rod (whose graph is not shown). The theoretical curve was calculated with $\mu = 0.39$ and $V_0 = 2700$ m/sec.

Nickel

The two rods studied were of commercial nickel, about 99 percent pure. The graph for the smaller nickel rod (see Fig. 6) shows: (a) less dispersion for a given frequency than occurs for the other nickel rod (whose graph is not shown); (b) good agreement with the theoretical curve out to 530 kc; (c) experimental points in the theoretical "dead zone"; (d) one unaccountable point at high frequency like the two in Fig. 3. The theoretical curve was calculated with $\mu = 0.30$ and $V_0 = 4980$ m/sec.

To summarize, it is seen that the agreement between the experimental results and the Giebe and Blechschmidt theory is quite good out almost to the "cut-off"—i.e., the frequency at which the so-called "dead zone" begins. Nevertheless, there is no evidence whatsoever for the existence of such a region and nothing more than material for speculation about the presence of anomalous dispersion. It seems clear that the theory in its present state is able to account satisfactorily only for the low frequency dispersion. In the opinion of the authors, further development of the theory is called for, starting with the removal of the simplifying assumption discussed above.

We wish to express our sincere thanks to Professor R. B. Lindsay for suggesting the problem and for his help throughout the investigation.

The Variation of the Principal Elastic Moduli of Cu₃Au with Temperature

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Single crystals of a copper-gold alloy containing 24.92 atomic percent gold were prepared in a vacuum furnace. The crystals were brought to the ordered state at room temperature by an annealing procedure similar to that described by Sykes and Evans. The elastic moduli were measured by the method of the composite piezoelectric oscillator. The elastic moduli are tabulated as a function of temperature over the range 20°C to 450°C. At the critical temperature, 387.5°C, there is a discontinuity in each modulus-vs.-temperature curve. The results indicate that the elastic constants are closely related to the degree of local order.

INTRODUCTION

IN recent years there has been an increasing interest in binary alloy systems which exhibit superlattice formation near simple stoichiometric concentrations.[1] In the copper-gold system, ordered superstructures are observed near the

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[1] F. C. Nix and W. Shockley, Rev. Mod. Phys. 10, 1 (1938). G. Borelius, Zeits. f. Electrochem. 45, 16 (1939).

ION GAGE

WINDING MECHANISM

COOLING COILS
TUNGSTEN WIRE
GROOVED ALUNDUM TUBE
STAINLESS STEEL RADIATION SHIELD
CRUCIBLE
MOLY. WINDING

0   3   6 IN.

POWER LEADS

TO PUMPS

WESTINGHOUSE RESEARCH LABORATORIES
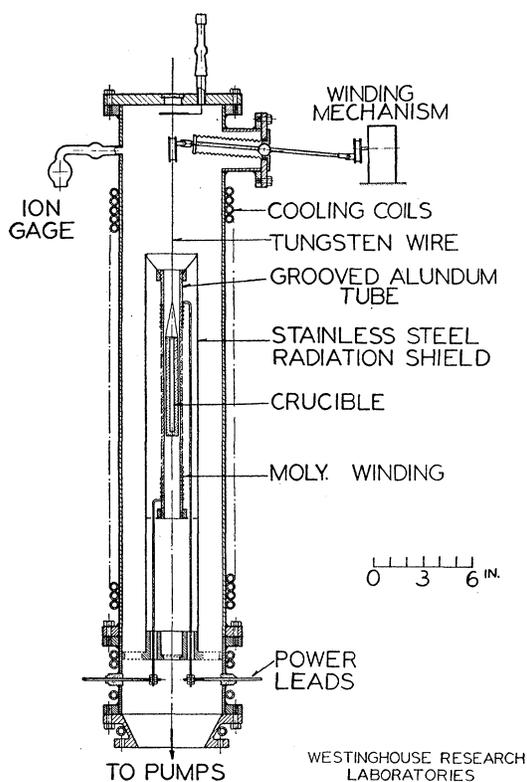
FIG. 1. Cross-section diagram of the vacuum furnace used to prepare the single crystals.

concentrations Cu₃Au and CuAu, below 390° and 430°C, respectively. Many physical properties of Cu₃Au have been studied, the electrical resistivity, the specific heat, and the crystal structure by x-ray methods, most intensively. The elastic constants of Cu₃Au single crystals were measured in the ordered, partially ordered, and disordered states by Goens,[2] the actual measurements being made at room temperature. Other such measurements were made by Röhl[3] and by Sachs and Weerts,[4] but in no case was the complete curve of elastic constants vs. temperature, and hence order, obtained. Recently, Koster[5] gave a curve of Young's modulus vs. temperature for polycrystalline Cu₃Au. None of these workers followed the annealing procedure which Sykes and Evans[6] showed to be necessary

[2] E. Goens, J. Weerts and Stenzel, Zeits. f. Instrumentenk. **53**, 242 (1933).
[3] H. Röhl, Zeits. f. Physik **69**, 309 (1931).
[4] G. Sachs and J. Weerts, Zeits. f. Physik **67**, 507 (1931).
[5] W. Köster, Discussion on paper by Borelius, reference 1.
[6] C. Sykes and H. Evans, J. Inst. Metals **58**, 255 (1936).

to produce the equilibrium degree of order in the lattice.

In a completely ordered Cu₃Au lattice there is a maximum number of nearest neighbor pairs of the type Cu-Au. As disorder increases with increasing temperature, the number of Cu-Au pairs diminishes, while the number of like pairs, Cu-Cu and Au-Au, increases. The success of Fuchs[7] in calculating the elastic constants of Na and Cu made it evident that a careful investigation of the variation with temperature of the elastic constants of Cu₃Au would be of interest. For the calculations are based in part on nearest neighbor interactions, and in alloys exhibiting the order-disorder transformation, it is possible to vary the relative numbers of the different nearest neighbor pairs simply by varying the temperature, and hence the degree of order of the lattice. Cu₃Au was chosen because its properties have been studied extensively, both theoretically and experimentally. Furthermore, its structure is cubic below and above the critical temperature T_c, 387.5°C, and the latter is low enough so that measurements may be made above it without too many experimental difficulties.

PREPARATION OF THE CRYSTALS

An ingot of the alloy was made up by melting weighed amounts of Cu and Au, both better than 99.99 percent pure, in a vacuum induction furnace. This ingot was homogenized by a vacuum anneal of 100 hours at 800°C. Chemical analysis of specimens from different portions of the ingot agreed to better than 0.1 percent and gave a composition of 24.92 atomic percent Au. This ingot was cast into rods several inches long and 0.180″ diameter; these formed the material from which the single crystals were prepared. Graphite crucibles were used in all melting procedures, and spectrographic examination of the original materials and the final crystals showed no contamination during any of the melts.

The vacuum furnace used to prepare the single crystals is similar to that described by Nix.[8] Fig. 1 is a scale drawing of the furnace proper. The main improvement in the present design is the pumping system, which makes it possible to

[7] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935); **A153**, 622 (1936); **A157**, 444 (1936).
[8] F. C. Nix, Rev. Sci. Inst. **9**, 426 (1938).

maintain a pressure lower than 10^{-5} mm of Hg even when the melt is at 1200°C. A four-inch glass-metal oil diffusion pump[9] is attached directly under the funnel shaped member at the bottom of the furnace. This pump is backed by a reservoir of 15 liters capacity, and forevacuum maintained by a Megavac pump. Gas is emitted from the melt in bursts rather than steadily, and the reservoir serves to maintain at all times a forevacuum pressure low enough to prevent the main diffusion pump from stalling. Pressure in the furnace is measured by an ion gauge and by a thermocouple gauge in parallel. The indicating instrument for the latter is a sensitive relay,[10] and if the furnace pressure increases above 10^{-2} mm of Hg the furnace and diffusion pump power is cut off. The temperature of the crucible is measured by sighting on it with an optical pyrometer through a plate glass window in the top of the furnace. This window is protected by a shutter when temperature measurements are not being made.

The crucible has three holes $5\frac{1}{2}''$ long and $\frac{3}{16}''$ diameter carefully reamed in it. The lower end is closed with a plug which may be unscrewed for the removal of the crystals. The crystals are grown by first melting the alloy with the crucible in the central uniform temperature region of the furnace, and then lowering the crucible at the rate of 3 inches per hour through the temperature gradient which exists near the lower end of the heating coil. When the rods are solid the furnace temperature is reduced to 900°C, the rods brought back to the central region of the furnace, and there homogenized for four hours. After this anneal they are allowed to cool slowly to room temperature during the next 24 hours. Several rods thus prepared were analyzed for possible segregation by determining the chemical composition of sections cut from the top and bottom ends. In no case did the segregation exceed 0.1 atomic percent.

The rods are etched electrolytically in a 10 percent KCN solution, agitated by a stream of air bubbles. Visual observation reveals whether the rods are single crystals. About 75 percent of the specimens thus prepared were suitable for further work on them.

DETERMINATION OF ORIENTATION

The orientation of the cylinder axis of a crystal rod with respect to the principal axes of the lattice is determined by the back-reflection Laue method devised by Greninger.[11] The crystal is set up with its axis coplanar with, and perpendicular to, the x-ray beam. A set of four pictures is taken, with 90° rotations of the cylinder about its own axis between successive exposures. Each film furnishes the direction cosines of a line, the x-ray beam, perpendicular to the cylinder axis of the crystal. From these direction cosines four values of the cylinder axis direction are obtained by taking the vector cross product of any two mutually perpendicular x-ray beams. From these four values a mean is calculated. The precision of the orientation is estimated at 20' by the deviations of the mean from the individual values.

HEAT TREATMENT OF THE CRYSTALS

Various investigators have shown that the properties of Cu_3Au below the critical temperature depend on the rate of cooling from 450°C to room temperature. The thermal treatment necessary to produce the best possible degree of order has been established in a careful research by Sykes and Evans[6] and their recommendations were followed here.

Five single crystal rods, of the best orientation for the contemplated elastic constant work, were chosen. These rods, protected by loosely fitting glass sleeves, were placed in holes in a massive copper block. A sixth crystal, provided with four leads by means of which resistivity measurements could be made, was placed in a hole closely adjacent to the others, and to a thermocouple by means of which the temperature of the crystals could be measured. The whole assembly was mounted in a quartz tube furnace which can be evacuated.

The resistivity of the sixth crystal was used as an indication of the progress of the heat treatment in producing an ordered structure. The temperature was first raised to 450°, maintained there for one day, and then slowly reduced, resistance measurements being made as cooling progressed. At 400°C, the cooling was arrested for several hours. The resistance very soon reached a final

[9] Manufactured by Distillation Products, Inc.
[10] Weston Sensitrol Relay, Model 705.
[11] A. B. Greninger, Zeits. f. Krist. **A91**, 424 (1935).
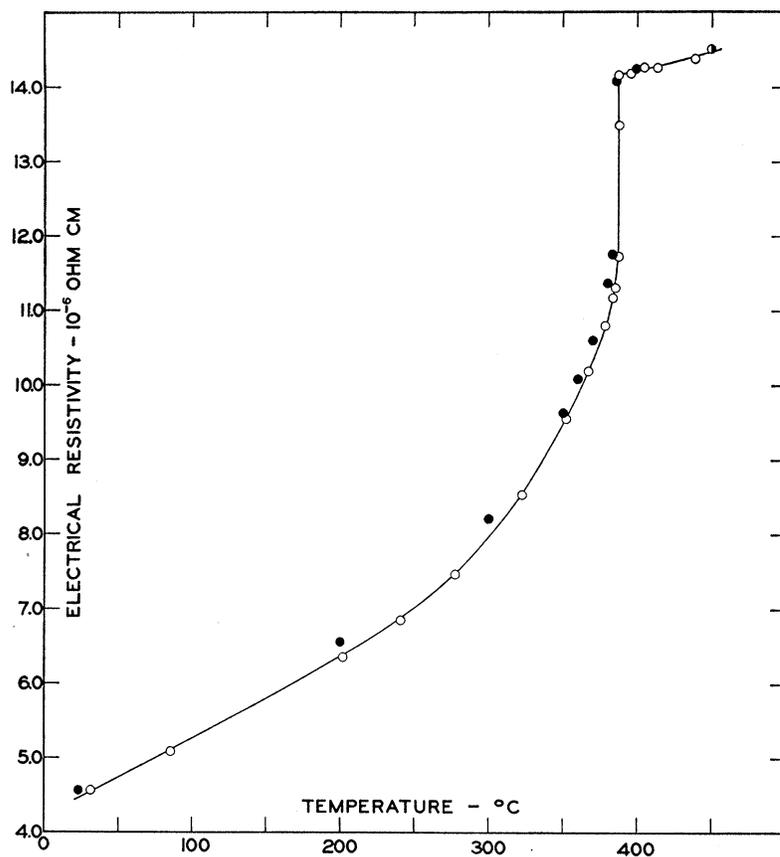
FIG. 2. The variation of the specific resistance of Cu_3Au with temperature when cooled from 450°C as described in the text. The closed circles are points taken from the data of Sykes and Evans.

steady value. The temperature was lowered in steps of 1°, with similar arrests, and similar behavior of the resistance, until the critical temperature was reached. At this temperature the resistance was not single-valued, but decreased with time, until the final steady value was reached after about 50 hours. The temperature was then further reduced in steps of 1°, with 5 hour arrests at each temperature, to 380°. From 380° to 350° the cooling rate was 1° per hour, from 350° to 250° the rate was 4° per hour, and from 250° to 20° the rate was 15° per hour. Fig. 2 shows the curve of resistance vs. temperature obtained during the progress of cooling; comparison may be made with the lowest values of resistance obtained by Sykes and Evans, shown as solid circles.

MEASUREMENT OF ELASTIC CONSTANTS

A dynamical method is used which has been described completely in previous papers.[12] Longi-

tudinal or torsional vibrations are set up in the crystal cylinders by means of suitably cut crystalline quartz rods. A quartz rod is cemented to a metal crystal with a thin layer of Insulate No. 1 cement.[13] The two rods are held together under slight pressure for 24 hours at 65°C while the cement dries. Subsequently it is possible to heat the composite oscillator to 450°C, and bring it back to 20°, several times without damage. Four composite oscillators, two longitudinal and two torsional, are mounted at once in the furnace. The oscillators are supported, at nodes of vibration, in small annular knife edges made of lava. These knife edges are hung from a structure made of fused silica tubes so that the four oscillators are radially symmetric about the axis of the furnace, and about a Chromel P vs. Alumel thermocouple placed there. The leads to the piezoelectric quartz rods are brought out of the furnace through the tubes used as supports, and the entire furnace can be evacuated. Four

[12] L. Balamuth, Phys. Rev. 45, 715 (1934); F. C. Rose, Phys. Rev. 49, 50 (1936).

[13] Obtainable from Fisher Scientific Company, Pittsburgh, Pennsylvania.

elastic measurements can be carried out simultaneously during a single run, and the identity of the thermal history of the four specimens is thus assured. These data provide sufficient information for the calculation of the three independent elastic moduli, and for one check on these calculations.

The furnace used in these temperature runs is the same as that used for annealing the specimens. The winding on it is tapered to produce a uniform temperature region at the center. Tests showed that the temperature over the central 10 cm of the furnace does not vary by as much as 1° *in air*. With specimens no longer than 7 cm, the gradient *in the specimen* is probably considerably less than that.

The furnace temperature can be maintained at any desired value to ±0.1° for several days. The controlling element is a thermocouple placed closely adjacent to the windings of the furnace. The e.m.f. of this couple is balanced by a Type K potentiometer; the difference in e.m.f. between the desired temperature and the winding temperature actuates a Type R galvanometer whose sensitivity is 20 cm/°C. The light spot reflected from this galvanometer falls on either of two photo-cells, which control the furnace current through an electronic relay circuit. If the furnace winding is too hot, cell 1 is illuminated, reducing the furnace current by about 10 percent. When the winding cools down slightly, cell 2 is illu-

minated and the current increased by about 7 percent of its normal value.

The furnace winding temperature oscillates with an amplitude of ±0.1°C, and a period of 1 minute. The temperature of the interior of the furnace, as measured by the central couple near the specimens does not vary by as much as 0.01°. However, slow drifts in the working battery for the potentiometer make the variations as large as 0.1°C if the apparatus is left unattended for several days.

In one run, four rods are mounted in the furnace and measurements of the longitudinal resonance frequencies are made on two, and of the torsional frequencies on the remaining two at various temperatures. The procedure is to bring the furnace to the desired temperature, maintain it there for one hour, and then make frequency measurements. If no change in frequency occurs during the next hour, the temperature is raised to a new value, and the procedure repeated. Points are taken at 40° intervals up to 250°, and more closely together at higher temperatures. From 380° to the critical temperature points are taken 1° apart. At the critical temperature, T_c, it is found that holding the temperature steady does not soon yield a constant frequency, independent of time.

At this temperature the frequencies of the crystals decrease slowly with time, attaining a final steady value only after about 50 hours.

TABLE I. *Elastic properties of* Cu₃Au *at various temperatures.*

$T°C$	ELASTIC MODULI (10^{-12} CM²/DYNE)			ELASTIC CONSTANTS (10^{11} DYNE/CM²)			THERMAL EXPANSION $\Delta L/L_{20}$
	S_{11}	S_{12}	S_{44}	$C_{11}-C_{12}$	C_{44}	$1/k$	
20	1.344	−0.565	1.508	5.238	6.631	1.558	$0×10^{-3}$
100	1.380	.583	1.545	5.094	6.472	1.558	1.28
200	1.436	.610	1.593	4.888	6.277	1.543	2.92
250	1.468	.625	1.619	4.778	6.177	1.529	3.80
300	1.512	.646	1.657	4.634	6.035	1.515	4.72
325	1.548	.664	1.678	4.521	5.959	1.515	5.22
350	1.590	.684	1.699	4.398	5.886	1.502	5.79
360	1.613	.694	1.709	4.335	5.851	1.481	6.08
370	1.638	.706	1.719	4.266	5.817	1.475	6.47
380	1.666	.718	1.730	4.195	5.780	1.449	7.10
385	1.693	.730	1.738	4.127	5.754	1.431	7.63
387.5 } T_c	1.714	.738	1.750	4.078	5.714	1.401	7.73
387.5 }	1.948	.852	1.787	3.571	5.596	1.366	7.73
390	1.958	.856	1.790	3.554	5.587	1.366	7.80
395	1.970	.863	1.797	3.530	5.565	1.366	7.90
400	1.981	.868	1.802	3.510	5.549	1.361	7.99
410	2.001	.878	1.813	3.473	5.516	1.361	8.20
420	2.021	.888	1.822	3.438	5.488	1.361	8.39
450	2.073	.912	1.850	3.350	5.405	1.339	8.98
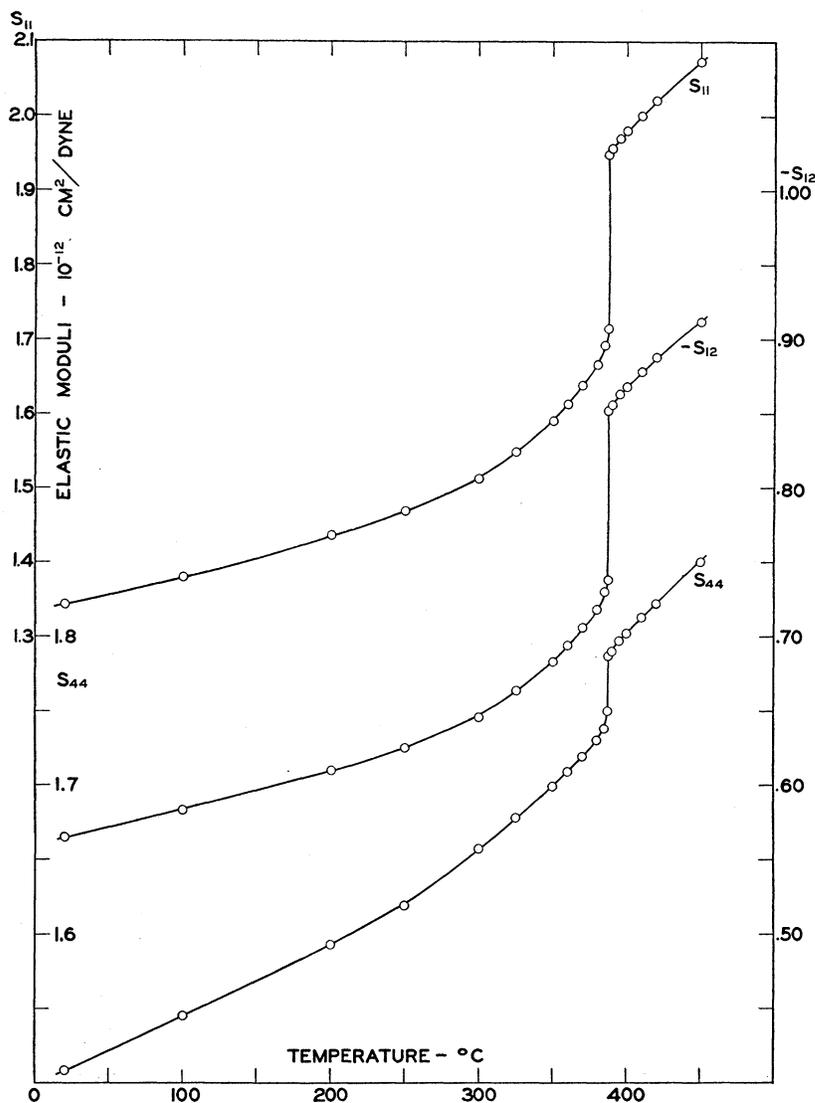
FIG. 3. The variation of the principal adiabatic elastic moduli of Cu_3Au with temperature.

When this lowest value at T_c is reached, indicating that some abrupt disordering process has gone to completion at that temperature, the furnace is heated, in steps of 2°, to 400°; from there to 450° readings are taken at intervals of 10°. The temperature is then reduced, and the reverse procedure to that described above is followed. The same type of behavior is observed in the neighborhood of T_c, and after the ordering process on the cooling curve has been completed, the curve reproduces the heating curve within the precision of the measurements.

Such a run yields values of the longitudinal and torsional resonance frequencies of the crystals. Young's and the rigidity moduli at a temperature T are related to these frequencies by the equations

$$E = 4\rho_{20}L_{20}{}^2{}_Lf_T{}^2\left(\frac{L_{20}}{L_T}\right)\left[1 + \tfrac{1}{2}\frac{\pi^2\bar{\sigma}^2n^2a^2}{L_{20}{}^2}\right] \quad (1)$$

and

$$G = 4\rho_{20}L_{20}{}^2 \ _Tf_T{}^2(L_{20}/L_T). \quad (2)$$

In these, ρ_{20} and L_{20} are the density and lengths, respectively, at 20°C; $_Lf_T$ and $_Tf_T$ are the fundamental longitudinal and torsional frequencies at temperature T. The term in the [ ] of Eq. (1) is a correction due to the lateral

motion; here $\bar{\sigma}$ is the average Poisson's ratio, estimated from approximate values of the elastic moduli; n is the number of half-waves in the metal crystal; and a is the radius of the crystals. The whole correction is very nearly unity.

The term (L_{20}/L_T) is a correction, also nearly unity, arising from thermal expansion. No quantitative values of the thermal expansion can be found in the literature,[14] so this property of a single crystal of Cu₃Au was measured in a fused quartz dilatometer. The results for $\Delta L/L_{20}$ are tabulated in the last column of Table I. Since the material is cubic, it is assumed that the expansion is isotropic. The furnace used in the expansion measurements was not temperature controlled, and hence the data between 350° and T_c are probably not the equilibrium values. Very likely there is a discontinuity in length at T_c which does not appear here.

RESULTS

The principal elastic moduli S_{11}, S_{12}, and S_{44} are related to E and G by the equations

$$1/E = S_{11} - 2S\Gamma \qquad (3)$$

[14] G. Grube, et al., Zeits. f. anorg. allgem. Chemie **201**, 41 (1931) give only qualitative curves, but no absolute values.

and

$$1/G = S_{44} + 4S\Gamma - \frac{2S^2(\Gamma - 4\Gamma^2 + 3\chi)}{S_{11} - 2S\Gamma}, \qquad (4)$$

where

$$\Gamma = \alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2, \quad \chi = \alpha^2\beta^2\gamma^2,$$
$$S = S_{11} - S_{12} - \tfrac{1}{2}S_{44}.$$

The direction cosines of the cylinder axis with respect to the principal crystalline axes are α, β, γ.

Five crystals in all were run. The values of Γ for these are 0.0014, 0.1237, 0.2089, 0.2521, and 0.3110. Four of these—the first, second, third, and fifth—were measured during one run. The fourth was measured during a subsequent run. It was found to be consistent with the first four, and hence data from this crystal were included in the final calculations.

For each crystal, smooth curves of $1/E$ or $1/G$ were plotted against temperature. From these curves, values were picked off at the temperature tabulated in the first column of Table I. At each of these temperatures the best set of values of S_{11}, S_{12}, and S_{44} was calculated by the method of least squares from the five available data. These values are tabulated in the second, third, and fourth columns of Table I. The results are also exhibited graphically in the curves of
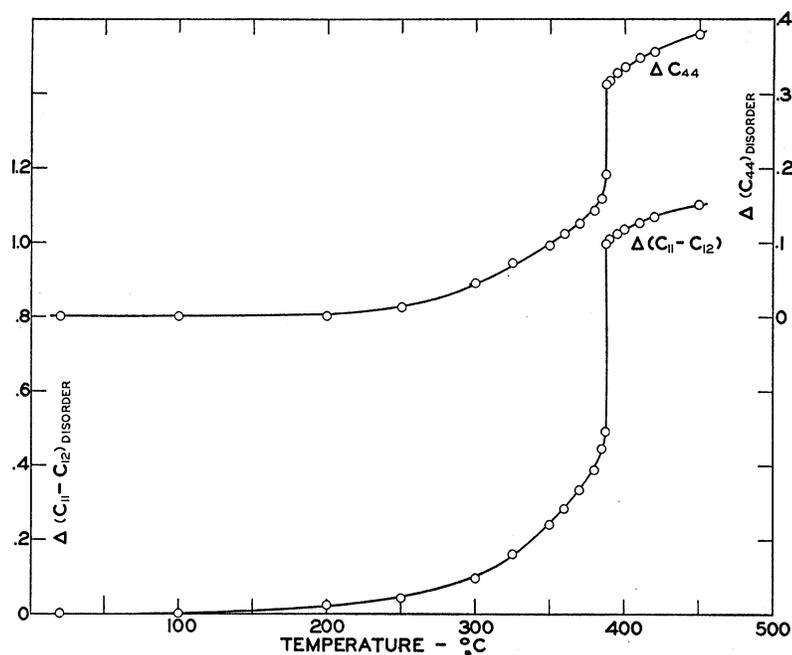
FIG. 4. The decrease in the elastic constants $(C_{11} - C_{12})$ and C_{44} due to increasing disorder, plotted against the temperature.

Fig. 3. The precision of these results is estimated at $\frac{3}{4}$ percent, by the deviation of the individual observed values of $1/E$ and $1/G$ from those calculated with the aid of the least square values of S_{ij}.

From the elastic moduli S_{11}, S_{12}, and S_{44}, another independent set of constants more useful theoretically may be calculated. These are two shear constants

$$(C_{11} - C_{12}) = 1/(S_{11} - S_{12}),$$
$$C_{44} = 1/S_{44}$$

and the reciprocal of the compressibility,

$$1/k = 1/[3(S_{11} + 2S_{12})].$$

These appear in the fifth, sixth, and seventh columns of Table I. Since the quantity $(S_{11} + 2S_{12})$ is obtained by subtracting two nearly equal quantities, the values of $1/k$ do not have as high a precision as the other constants. For errors of $\frac{1}{2}$ percent in S_{11} and S_{12} if additive, would produce an error in $1/k$ of 7 percent.

The temperature during these runs was measured with a Chromel P-Alumel thermocouple calibrated against melting ice, boiling water, and the freezing points of Sn, Pb, and Zn. The absolute values of the temperature are good to 2°.

DISCUSSION OF THE RESULTS

The elastic moduli plotted in the curves of Fig. 3 vary with temperature because of two effects. First there is the nearly linear variation which is observed in most pure metals, and which is here exhibited by the linear portions of the curves, up to about 200°. Secondly, the moduli vary because of the increasingly rapid disappearance of order above 250°, as may be inferred from the increasing curvature and slope above that temperature. At the critical temperature the abrupt discontinuity is due to a sudden large decrease in local order, and the disappearance of long range order. The large slope and downward curvature above T_c indicate that some order still persists there, however.

These conclusions are more evident from the curves of Fig. 4. These curves were obtained in the following way. The data for $(C_{11} - C_{12})$ and C_{44} were plotted against temperature, a straight line through the points up to 200° was drawn

and extrapolated to 450°. The differences between the actual observed values and these straight lines are plotted against temperature in Fig. 4. If it is assumed that the extrapolated straight lines represent the effect on the elastic constants of the temperature variation alone, if no order-disorder phenomenon took place, then these difference curves represent the effect of the disordering process alone in decreasing $(C_{11} - C_{12})$ and C_{44} below their room temperature values.

The most successful theories of the order-disorder phenomenon are those of Bethe,[15] and Peierls,[16] based on the concept of order of neighbors. The short range order parameter σ, in the case of Cu_3Au, is a measure of how well on the average each Cu atom is surrounded by Au nearest neighbors. If f_{CuAu} is the fraction of nearest neighbor pairs of the Cu-Au type actually existing in any state of the crystal, and if f_{max} and f_{random} are the values of this fraction in the perfectly ordered and random states, then we define

$$\sigma = (f_{CuAu} - f_{random})/(f_{max} - f_{random}).$$

If the curves of Fig. 4 are compared with the theoretical curve[17] for σ vs. T, it will be observed that they are quite similar in form. It seems reasonable to assume that the shear elastic constants $(C_{11} - C_{12})$ and C_{44} are relatively simple functions of σ.

Fuchs[7] calculated the elastic constants of Na and Cu, and obtained good agreement with the experimental values.[18] The shear constants were determined by calculating the energy changes accompanying pure shears. In such a deformation the volume change is zero. The calculations are based on classical electrostatic theory; the quantum mechanical exchange interactions due to the overlapping of the ion cores, which occurs in both Cu and Au, are included as repulsive terms in the electrostatic interaction. The shear constants depend mainly on the charges and degree of overlap of the ions of the lattice, according to this picture.

For the case of Cu, the relative contributions of the electrostatic and overlapping energies to

[15] H. A. Bethe, Proc. Roy. Soc. **A150**, 552 (1935).
[16] R. Peierls, Proc. Roy. Soc. **A154**, 207 (1936).
[17] E.g., Fig. 3b in reference 16.
[18] Cu: E. Goens, Physik. Zeits. **37** 321 (1936); Na: S. L. Quimby and S. Siegel, Phys. Rev. **54**, 293 (1938).

TABLE II. *Elastic constants of copper.*

	$C_{11}-C_{12}$	C_{44}
Electrostatic	5.7	26
Overlap	45	63
Total	51	89
Exp.	51	82

the shear constants are shown in Table II, taken from a paper by Shockley.[19]

We may examine the results on Cu₃Au in the light of the above remarks. In this alloy, both ions have the same charge. It is probable, however, that the overlap energies of the three possible types of nearest neighbor pairs, CuCu, AuAu and CuAu, are different because of differences in the electron distributions in the Cu and Au ion cores. In the transition from the ordered to the disordered state, f_{CuAu} goes from its maximum value to its value for a random solid solution. This redistribution in the relative numbers of the different kinds of pairs of atoms will not affect the contribution to the elastic constants arising from the pure electrostatic interaction, since the charge on each ion is the same for both Cu and Au. The disordering process may, however, affect appreciably the ionic overlap contribution, since this does depend on the type of nearest neighbor pair. On this basis it seems reasonable to expect that the shear constants depend on the degree of order of the lattice.

The constants $(C_{11}-C_{12})$ and C_{44}, reported in Table I, do in fact depend in an anomalous way on temperature, and have an abrupt discontinuity at T_c, where there is a discontinuity in σ. The change in $(C_{11}-C_{12})$ is of the order 20 percent, the change in C_{44} about 5 percent. From Table II it will be observed that the overlap contribution, which depends on σ, is more important in the case of $(C_{11}-C_{12})$ than in C_{44}. The experimental results thus confirm two of the ideas furnished by the theory—first that the shear constants depend on the degree of order, and second that the effect is more marked on $(C_{11}-C_{12})$ than on C_{44}.

The third independent elastic constant, $1/k$, is determined from calculations on a pure dila-

tation. In such a deformation there is a change in volume, but no relative change in position of the ions. The total energy of the solid is calculated as a function of volume, and the compressibility computed from the second derivative with respect to volume of this energy. The total energy also depends in part on the ionic overlap, so that here also a dependence of $1/k$ on degree of order might be expected. An examination of the seventh column of Table I, where $1/k$ is reported for different temperatures reveals that there is a dependence of $1/k$ on order, with a small discontinuity at T_c. However, the entire variation of $1/k$ here observed is only twice the possible error in this quantity, and it is therefore difficult to draw any conclusions on this point from the experimental results.

BEHAVIOR IN THE NEIGHBORHOOD OF T_c

In Table I, and the curves of Figs. 3 and 4 the critical temperature is given as 387.5°C. This is the value found on the heating curve; on cooling the discontinuity in elastic constants occurs at a slightly lower temperature, approximately 2° less. Actually, then, two vertical lines should appear on the curves of Figs. 3 and 4 at T_c, but on the scale on which these are plotted, the hysteresis curve does not show up.

Since the time required for the traversal of the vertical parts of the curve, about 50 hours, is nearly the same on either heating or cooling, it seems difficult to associate it with a time required to get rid of antiphase boundaries between domains of local order. It may perhaps be a quantity more closely associated with rates of diffusion.

A more exhaustive examination of the behavior in the neighborhood of T_c is now being carried out. The elastic constants and the resistivity are being measured simultaneously in the same furnace. It is hoped that some information concerning the kinetics of the order-disorder transformation will be obtained.

[19] W. Shockley, J. App. Phys. **10**, 543 (1939).