The Order–Disorder Transformation in Cu₃Au at High Pressure*†

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The order–disorder transformation in the alloy Cu₃Au has been studied at pressures ranging up to 21 kbar by means of electrical-resistance measurements made while the sample is at high temperature and under pressure. The rate of change of the critical temperature with pressure is 2.1°K/kbar from 7 to 21 kbar. The kinetics of the order transformation below T_c are adequately described by the homogeneous reaction rate equation and an activation volume of 6.8 cm³/mole of atoms. The magnitude of this activation volume indicates that the formation of vacancies on the gold sublattice is the rate-limiting step in the homogeneous ordering process.

INTRODUCTION

APPLICATION of pressure often stabilizes new, equilibrium phases in a substance. An equally important, and as yet hardly studied effect of pressure, is to change phase-transformation kinetics. This paper reports the results of an investigation of the effect of high pressure on the kinetics of the order–disorder transformation in the alloy Cu₃Au. This particular transformation in this particular alloy was chosen because, among all solid-state phase transformations, it is one of the most fully studied and best understood at room pressure.[1] Because of this, identification of the influence of pressure is made easier and more certain than would otherwise be possible.

The rate of the order–disorder transformation in Cu₃Au is most effectively studied by means of isothermal experiments: The alloy is equilibrated at temperature T_1 and then suddenly brought to temperature T_2, which may be higher or lower than T_1, and the progress of the transformation observed over a period of time. If $T_1 > T_c > T_2$, where T_c is the critical temperature for ordering, the transformation involves the heterogeneous growth of small regions of ordered material into the antiphase structure characteristic of the ordered state. However, if T_1, $T_2 < T_c$ and if the alloy has been properly prepared with a large antiphase domain size, the transformation is homogeneous and is fully described by a single rate equation. It is with this aspect of the transformation that we deal in the present work. The theory of the homogeneous change in order within a domain is developed in papers by Rothstein,[2] Dienes,[3] and Nowick and Weisberg.[4] Formulation of the theory in terms of experimentally measurable quantities, as well as comparison with experimental results, is given in a paper by Feder,

Mooney, and Nowick.[5] They show that changes in the electrical resistivity of the alloy measured at constant temperature are linearly related to changes in the degree of long-range order and that the time-dependence of the resistivity change at temperature
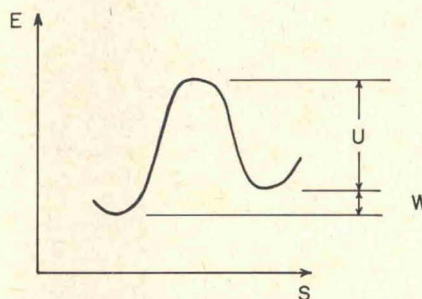

FIG. 1. Energy diagram for the homogeneous ordering step in Cu₃Au. U is the energy barrier to be overcome in taking a pair of atoms from right to wrong sites; W is the resultant change in internal energy of the alloy.

T_2 is given by the equation

$$\frac{R-R_0}{R_e-R_0} = \left\{ \begin{matrix} \coth \\ \tanh \end{matrix} \right\} (\alpha t + \beta), \qquad (1)$$

where the coth function applies if $T_2 < T_1$, the tanh functions holds when $T_2 > T_1$, R is the resistance measured at any time t, R_e is the equilibrium resistance at T_2, and R_0 is the resistance of the perfectly ordered alloy at $T = T_2$, and α and β are constants independent of t. It is also shown that, below 320°C, the dependence of the rate constant α on temperature is

$$\alpha = \alpha_0 \exp[(U + W/2)/kT], \qquad (2)$$

where, as indicated in Fig. 1, U is the energy barrier to be overcome in taking a pair of unlike atoms from correct to incorrect lattice sites (the elementary disordering step) and W is the corresponding change in the internal energy of the alloy.

Disordering of Cu₃Au results in a volume increase. Pressure therefore stabilizes the ordered phase and in-

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[1] L. Guttman, "Order-Disorder Phenomena in Metals," *Solid State Physics*, F. Seitz and E. Turnbull, Eds. (Academic Press Inc., New York, 1956), Vol. 3, p. 145.
[2] J. Rothstein, Phys. Rev. **94**, 1429 (1954).
[3] G. J. Dienes, Acta Met. **3**, 549 (1955).
[4] A. S. Nowick and L. R. Weisberg, Acta Met. **6**, 260 (1958).

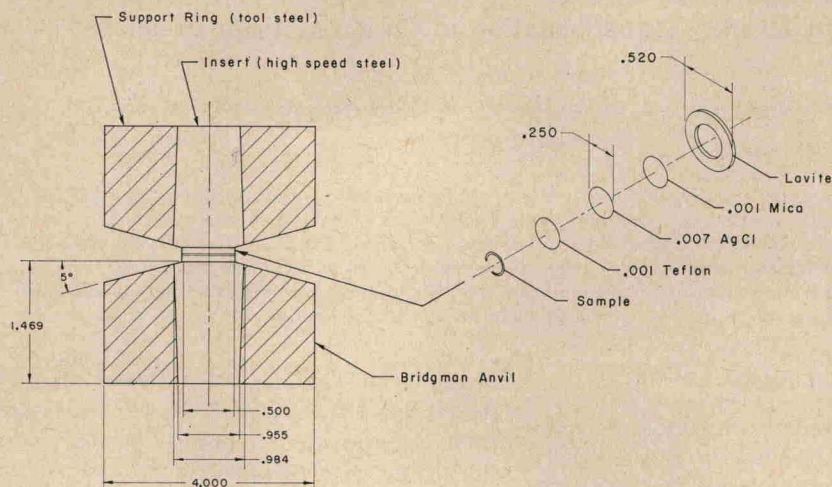[5] R. Feder, M. Mooney, and A. S. Nowick, Acta Met. **6**, 266 (1958).

FIG. 2. Bridgman anvil and split-gasket assembly used for the high-pressure measurements.

creases the ordering energy. It will also increase the energy barrier to be overcome in taking a pair of atoms from correct to incorrect lattice sites. To allow for this in Eq. (2), both U and W should be replaced by the free energies G_U and G_W. Since $(\partial G/\partial P)_T = V$ and $(\partial G/\partial T)_P = -S$, a consistent first-order approximation to the effect of pressure will be to add terms PV^* and PV_t to Eq. (2):

$$\alpha = \alpha_0 \exp[(U + PV^* + 1/2W + 1/2PV_t)/kT], \qquad (3)$$

where V_t is the volume increase of transformation for a disordering interchange of a pair of atoms and V^* is the activation volume associated with the activated process represented in Fig. 1. To a higher order of approximation, the pressure- and temperature-dependence of V and S defined by the above equations would have to be considered. However, most high-pressure experiments on atomic mobility are sufficiently accurate to require use of only the first-order approximation. The assumption is made that resistivity mains linearly related to S in the alloy under pressure.

If the activation-volume model of the effect of pressure on the order–disorder transformation is adequate and the resistivity remains linearly related to S, then Eqs. (3) and (1) should fully describe the ordering rate observed at constant temperature and pressure. The first aim of the experiments is to test this; the second is to determine the value of V^*. Knowledge of V^* should help elucidate the nature of the rate-controlling step in ordering.

EXPERIMENTS

The high-pressure technique for the proposed experiment must satisfy a number of requirements. Studies of the effect of pressure on the atomic mobility in fcc metals indicate that pressures of the order of 20 kbar will be required to produce measurable effects on the order–disorder transformation. The pressure must be very nearly a true hydrostatic pressure since the transformation is known to be sensitive to plastic strain. Since electrical resistivity changes are to be used to follow changes in the state of order, four electrical leads as well as four thermocouple leads must be introduced into the sample space. Finally, temperatures up to about 450°C must be attained while the sample is under pressure and it must be possible to both hold the temperature constant for long periods of time and to change it rapidly from one value to another.

APPARATUS

It was found that these requirements could be met economically with Bridgman anvils in conjunction with a multilayered gasket. The anvil and gasket design used is shown in Fig. 2. For the temperature and pressure range of these experiments it is not necessary to use tungsten carbide-anvil inserts; "Hypercut" high-speed steel has the requisite hardness and hot strength. Proper alignment of the anvils is assured by use of a close fitting steel guide. The sample is contained between two halves of a split gasket, each half consisting of mica, AgCl and Teflon discs contained in a lavite washer. The AgCl is used to transmit nearly hydrostatic pressure to the sample while the mica and Teflon discs protect the anvil faces and the sample, respectively, from the corrosive behavior of AgCl at high temperature. Electrical leads are carried between the two lavite rings into the sample space. The thickness of each ring is 0.0125 in. while that of the stack of inner discs is 0.009 in. The extra thickness of the lavite rings is required to avoid overloading the gasket as the sample and electrical leads slightly increase the thickness of the cavity components. When the anvils are forced together, the rings crumble and the high friction between lavite and steel retains the sample by preventing extrusion of the sample cavity materials.

The nature of the pressure distribution in the Bridgman anvil-pressure generator has been treated theoretically by Jackson and Waxman[6] and investi-

[6] J. W. Jackson and M. Waxman, in *High Pressure Measurement* (Butterworths, Washington, 1963), p. 39.

gated empirically by Montgomery *et al.*[7] The dimensions of the components comprising the gasket and the orientation and shape of the sample contained in the gasket considerably influence the pressure distribution and, without calibration, it cannot be assumed that the pressure on the sample is the load applied to the anvils divided by their face area. Montgomery *et al.* report that at room temperature a radial pressure gradient exists in the sample cavity. Consequently, a fine wire sample bent into the arc of a circle is utilized so that the sample will lie on an isobar. A series of experiments described below were done to establish the pressure calibration and to demonstrate that a sufficiently hydrostatic pressure is attained.

For the ordering experiments, a sample of Cu₃Au wire of 0.010-in. diam. is bent into a circular arc 0.125 in. in diameter and then flattened by rolling to a thickness of 0.007 in. The composition of this wire as determined by chemical analysis is 50.13 wt % Cu and 49.85 wt. % Au. Stochiometric wire would be 49.17 wt. % Cu. For pressure calibrations, samples of bismuth wire ($D=0.003$ in.) and lead wire ($D=0.007$ in.) were used. The current and potential leads to the sample are pure iron wires 0.004 in. in diameter. These are brought out of the sample chamber between the two lavite gaskets. Electrical leads of lower-strength material are broken off when pressure is applied. In addition to the electrical leads, two Chromel–Alumel thermocouples are placed in the sample cavity. One, placed in contact with the specimen, serves to measure its temperature; the other activates a temperature controller. Before use, the thermocouples are calibrated against a certified, standard couple. After being pressurized several times the couples retain their calibration; this is taken as evidence that they are not significantly cold worked during pressurizing.

To attain high temperature the entire anvil assembly is heated by a surrounding electric furnace and by heaters built into the anvil support blocks.

Pressure Calibration

A calibration at room temperature was made by placing a bismuth wire in the space ordinarily occupied by the Cu₃Au sample. The I–II transition was found to occur at an indicated pressure (load on the anvils divided by bearing area) of 24.6±1 kbar. This is to be compared with the accepted transition pressure of 25.5 kbar.[8] A calibration at high temperature was made by observing the pressure-dependence of the melting point of lead. Lead wire was substituted for the sample and its resistance observed at constant pressure as the temperature was raised at a rate of 5°C per minute. The onset of melting was indicated by an erratic be-
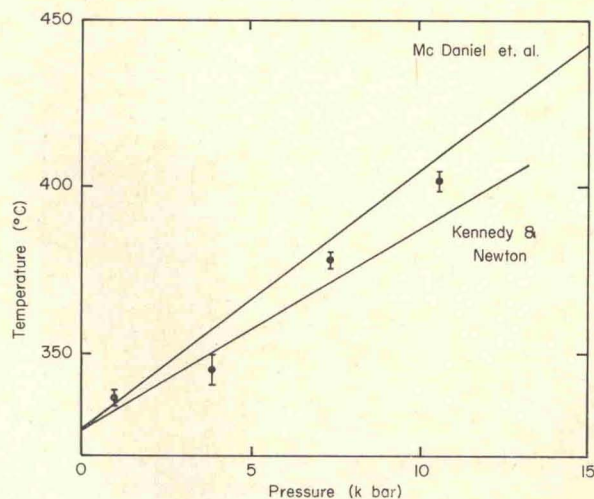

FIG. 3. Observed melting temperature of lead as a function of indicated pressure in the Bridgman anvil device.

havior of the resistance apparently associated with flow of liquid lead along the current and potential leads. That melting had actually occurred at this point was verified by inspection of the sample heated to successively higher temperatures; the flow of the liquid was clearly seen under a low-power microscope when the anvil assembly was taken apart. The melting temperature at several indicated pressures is shown in Fig. 3. For comparison, the melting curves of lead determined by McDaniel, Babb, and Scott[9] (extrapolated) and by Kennedy and Newton[10] are shown.

From the results of these experiments it was concluded that, to within the reproducibility attained with the anvil apparatus, it suffices to take the actual pressure as equal to the indicated pressure.

That the pressure generated with the composite gasket assembly shown in Fig. 2 is sufficiently hydrostatic for ordering experiments is demonstrated by comparing the resistance changes in a cold-worked sample of Cu₃Au held at constant pressure and slowly heated with the changes in an annealed sample treated the same way. The annealed sample shows a steady increase of resistance with temperature due to disordering and to the thermal component of the resistance; the previously cold-worked sample shows a resistance decrease as the cold work is annealed out under pressure and then shows the same resistance-temperature behavior as the initially annealed sample.

THE CRITICAL TEMPERATURE FOR ORDERING

The order–disorder transformation in Cu₃Au is of the first order, i.e., is characterized by a discontinuity in the volume and entropy at the critical temperature,

[7] P. Montgomery, H. Stromberg, G. H. Jura, and G. Jura, in *High Pressure Measurement* (Butterworths Scientific Publications, Ltd., London, Washington, 1963), p. 1.

[8] G. Kennedy and P. LaMori, in *Progress in Very High Pressure Research*, F. P. Bundy, W. R. Hibbard, Jr., and H. M. Strong, Eds. (John Wiley & Sons, Inc., New York, 1961), p. 304.

[9] M. L. McDaniel, S. Babb, and G. J. Scott, J. Chem. Phys. **37**, 822 (1962).

[10] G. Kennedy and R. C. Newton, in *Solids Under Pressure* W. Paul and D. Wanschaeur, Eds. (McGraw-Hill Book Company, Inc., New York, 1963), p. 163.
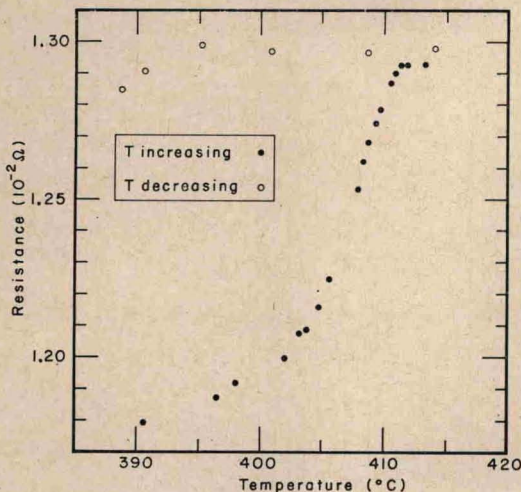
FIG. 4. Resistance of Cu_3Au wire during heating and subsequent cooling through T_c at a pressure of 10.5 kbar.

T_c, above which long-range order no longer exists. As an ordered alloy is heated, the long-range order decreases slowly and continuously until T_c is reached at which temperature the remaining long-range order vanishes. The critical temperature can be conveniently observed by means of resistivity measurements: If the sample is heated slowly and is at a uniform temperature throughout, there will be a discontinuity in the resistance vs temperature curve at T_c. Determination of T_c is made most effectively by a heating curve; when the disordered alloy is cooled through T_c considerable supercooling is often observed.

To find the change in T_c in Cu_3Au under pressure, slow heating experiments were performed on ordered wire samples. In most of the experiments the sample was first subjected to pressure and then heated, but in a few cases the sample was held at 300 bars and then heated to 200°C before the desired pressure was applied. In the latter case the sample would be subjected to smaller stress gradients during application of pressure. Equally satisfactory results were obtained by both methods, indicating again that the deviator stresses within the sample chamber are too small to influence the ordering behavior. After pressure is attained, the samples are heated at the rate of 20°C/h from 200°C to about 450°C; near T_c the heating rate is 0.3°C/min or less. Investigation at 1-atm pressure of the effect of heating rate on the observed value of T_c indicates that for the rate employed here, no measurable superheating occurs. Results of a typical experiment are shown in Fig. 4. From curves of this kind T_c is determined to within ±1°C. While holding the sample near T_c the following procedure can be used to determine whether or not T_c has been exceeded: The sample is held at constant temperature and its resistance observed as a function of time. If the resistance decreases with time the sample has not disordered, since the resistance decrease is indicative of

continued antiphase domain growth, a relatively slow process at all temperatures below T_c. With these techniques it is found that $T_c = 389 \pm 1$°C at $P = 300$ bars, a pressure low enough so that the shift in T_c is less than 1°C. A determination of T_c on the same sample material immersed in a fluid at 1 bar gave 388 ± 2°C, indicating that good accuracy is attained in the temperature measurements in the anvils. The experimental results of Hanneman and Strong[11] show no significant change in the calibration of Chromel–Alumel thermocouples in the pressure range of our experiments.

The observed values of T_c at various pressures are shown in Fig. 5. The initial slope of the curve of T_c vs P can be found from Clapeyron's equation, $dT/dP = T_c V_t/H_t$, where V_t is the volume change and H_t the enthalpy change at the critical temperature. The transformation volume at 1-atm pressure is known from the high-temperature x-ray-lattice parameter measurements of Keating and Warren[12]; it is 2.25×10^{-2} cm^3/mole of atoms. The enthalpy change at the critical temperature measured by Schkolnick and Quimby[13] is 277 cal/mole. Using these values, $dT/dP = 1.3$°K/kbar. The curve in Fig. 5 is drawn to have this initial slope.

THE KINETICS OF ORDERING

The kinetics of the ordering reaction below T_c were studied in samples annealed for 90 h at 368°C so as to attain an antiphase domain size of about 100 lattice spacings. These samples were quenched and then held
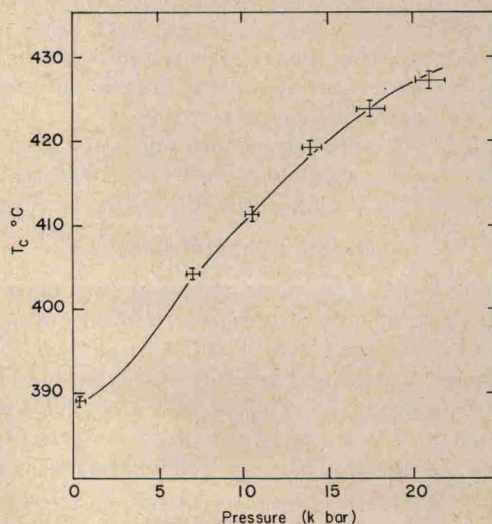

FIG. 5. Observed dependence of the critical temperature for ordering on the pressure.

[11] R. E. Hanneman and H. M. Strong, ASME Publication 61-WA/PT-21 (1964).
[12] D. T. Keating and B. E. Warren, J. Appl. Phys. **22**, 286 (1951).
[13] L. J. Schkolnick and S. L. Quimby, *The Temperature Variation of the Order Dependent Configurational Energy and the Latent Heat of the Order-Disorder Transformation in* Cu_3Au (Thesis by L. J. Schkolnick, Columbia University, 1962).

FIG. 6. Resistance changes during anneal at 286°C and 1 kbar of sample first equilibrated at 368°C. The curve is calculated to give the best fit to the datum points as described in the text.
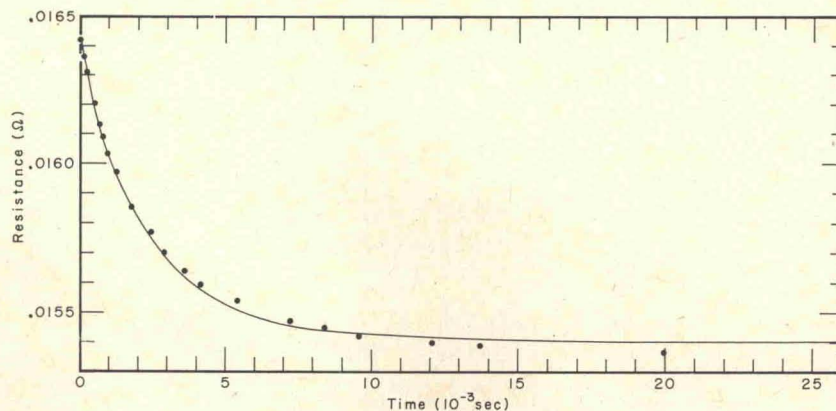
at constant temperatures ranging between 247° and 290°C under various pressures. During this second anneal, the degree of long-range order within the domains increases with no significant change in the domain size itself. Thus, changes in the sample resistance, R, are directly related to changes in the long range order parameter, S, and are expected to follow the equation

$$(R-R_0)/(R_e-R_0) = \coth(\alpha t + \beta).$$

To find the pressure- and temperature-dependence of the rate constant α from this equation, R_0 and R_e must be determined as a function of T and P. R_e is the final resistance of the sample held until the homogeneous ordering is completed at the temperature and pressure of interest. The determination of R_0 as a function of temperature and pressure is more difficult. The procedure used is given in the Appendix. Essentially, it consists of relating the order-dependent resistance of a sample to the lattice parameter and then extrapolating to the value of the lattice-parameter characteristic of the fully ordered material to find R_0 at 25°C and 1 atm. The temperature and pressure coefficient of resistance of a highly ordered sample are then measured and used to find $R_0(T, P)$.

The procedure for measurement of the ordering rate is to first set up a quenched sample in the anvils and measure its resistance at room temperature and pressure. Then a pressure of a few hundred bars is applied and T raised to 100°C. At this temperature the sample is brought to the pressure to be used in the experiment; it is then rapidly heated and, when the temperature is stabilized (usually within 45 min), the resistance is measured as a function of time until the equilibrium resistance is attained. At the temperatures and pressures used, this may require a time between a few hours and a few days. During this anneal T is held to ±0.5°C and P to within ±40 bars.

The resistance changes during a typical ordering experiment are shown in Fig. 6. To the datum points shown, Eq. (1) must be fitted. In making this fit, allowance must be made for possible errors in the

determination of R_0 and R_e. This was done by means of a computer program which compares Eq. (1) with the data for the following range of the variables R_0, R_e, and α:

$$\Delta R_0 = 1.1 R_0 \quad \text{to} \quad 0.7 R_0,$$

$$\Delta R_e = 1.0 R_e \quad \text{to} \quad 0.9 R_e,$$

$$\Delta \alpha = 3.0 \alpha \quad \text{to} \quad 0.3 \alpha.$$

The starting points for the computation are the measured R_0 and R_e and a value of α estimated from room-pressure data. As successively better fits are obtained, the interval of variation of the three parameters is made smaller until, at the final fit, the intervals are

$$\delta R_e = 4 \times 10^{-5} R_e,$$

$$\delta R_0 = 1.7 \times 10^{-5} R_0,$$

$$\delta \alpha = 6 \times 10^{-4} \alpha.$$

At this interval size computational errors are negligible compared to experimental errors.

Two series of kinetic experiments were done. In one, a constant pressure of 900 bars was used and the ordering temperature was varied between 247° and 289°C; in the other, the temperature was 286°C and pressure ranged from 1 to 14 kbar. Rate constants from the first series are shown in Fig. 7 and are seen to fit Eq. (2). The activation energy for ordering obtained from this plot is 1.9±0.2 eV. This may be compared with the value of 2.03 eV obtained by Feder, Mooney, and Nowick,[5] and the 1.95-eV value found by Goering and Nowick[14] by an internal friction experiment.

The results of the second series of measurements, in which a series of pressures and one temperature were used, are shown in Fig. 8. It is seen from this figure that the data fit an equation of the form of Eq. (3). The slope of the line drawn through the points yields a total activation volume for ordering of 6.8±1 cm³/mole or $(11\pm2)\times10^{-24}$ cm³/atom.

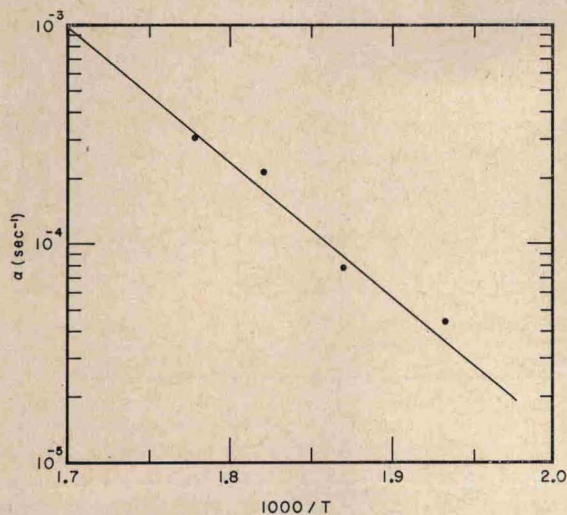[14] W. Goering and A. S. Nowick, Trans. AIME **105**, (1958).

FIG. 7. Variation of the rate constant α with temperature at 900 bars. The slope of the straight line corresponds to an activation energy of 1.9 eV.

DISCUSSION

The measured room-pressure values of V_t and H_t indicate an initial slope of the T_c vs P curve of 1.3°K/kbar. An old measurement by Wilson[15] gives an initial slope of 1.2°K/kbar. A smooth curve drawn through the data points in Fig. 5 would have a slope of 2.1°K/kbar at zero pressure. An increase in dT_c/dP
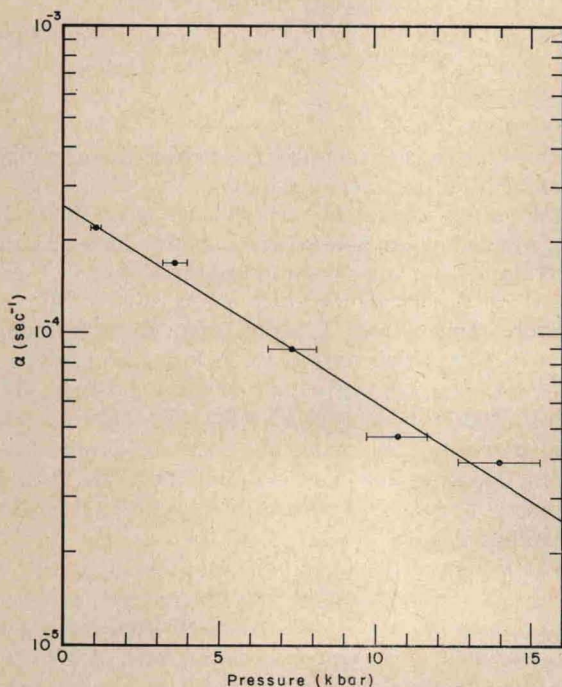

FIG. 8. Variation of the rate constant α with pressure at 286°C. The slope of the line corresponds to an activation volume of 6.8 cm³/mole of atoms.

[15] T. C. Wilson, Phys. Rev. 56, 598 (1939).

at higher pressures is expected because of the increase in T_c, but allowance must also be made for the pressure variation of V_t and H_t. The change in V_t with pressure assuming a constant degree of long range order at T_c can be estimated by using Siegel's[16] measurements of the elastic constants of the ordered and disordered phases at high temperature to compute the compressibilities of the two phases. A correction for the pressure-dependence of the elastic constants can be estimated from Lazarus'[17] data on the pressure-dependence of the elastic constants of Cu and Au. At 21 kbar, V_t is reduced from 2.25×10^{-2} to 1.94×10^{-2} cm³/mole of atoms. This decrease in V_t almost compensates the increase in T_c so that dT_c/dP would remain about constant (the change in H_t at 21 kbar due to PV_t is negligibly small). The form of the curve in Fig. 5 must result, then, from changes in V_t and H_t resulting from a shift in the amount of long-range order just below T_c and short-range order just above T_c as the pressure is increased.

TABLE I. Activation energies and volumes.

	Q	V^*
Ordering kinetics	2.0 eV	6.8 cm³/mole
Anelastic, Cu₃Au[a]	1.95	
Diffusion, Au in Cu[b]	1.95	
Diffusion, Au in Au[c]	1.81	7.2
Diffusion, Au in Ag–Au alloy[d]		7.5
Diffusion, Ag in Ag[e]		9.2
Anelastic, Ag–Zn alloy[f]		5.4
Atomic radii		
Au 1.44 A Ag 1.44 A		
Cu 1.28 Zn 1.37		

[a] See Ref. 14.   [d] See Ref. 20.
[b] See Ref. 18.   [e] See Ref. 21.
[c] See Ref. 19.   [f] See Ref. 22.

The results in Fig. 8 show that Eq. (3) gives an adequate representation of the pressure-dependence of the ordering rate below T_c. Since V_t is about 0.03 cm³/mole, the term $1/2PV_t$ can be neglected in comparison with PV^* in Eq. (3). Within the accuracy attained in these experiments, no pressure variation in V^* could be detected; more accurate determination of the sample pressure would be required for this purpose.

The values of Q and V^* found in these experiments are compared with other related quantities in Table I. Change in the state of order in Cu₃Au involves thermally activated movements of both the Au and the Cu atoms; the slowest-moving species will determine the

[16] S. Siegel, Phys. Rev. 57, 537 (1940).
[17] D. Lazarus, Phys. Rev. 76, 545 (1949).
[18] A. B. Martin, R. D. Johnson, and F. Asaro, J. Appl. Phys. 25, 364 (1954).
[19] R. H. Dickerson, R. C. Lowell, and C. T. Tomizuka, Phys. Rev. 137, A613 (1965).
[20] E. D. Albrecht and C. T. Tomizuka, J. Appl. Phys. 35, 3560 (1964).
[21] C. T. Tomizuka, R. C. Lowell, and A. W. Lawson, Bull. Am. Phys. Soc. II5, 181 (1960).
[22] G. W. Tichelaar and D. Lazarus, Phys. Rev. 113, 438 (1959).

ordering rate. This is expected to be the Au atom because of its greater size. The data in Table I show that the activation volumes for the diffusion of Au in Au, in Cu₃Au, and in a Ag–Au alloy are all the same (within experimental error). Since Ag and Au have almost identical atomic radii, equal activation volumes would be expected in the Au–Ag alloy. In Cu–Au alloys, there is a decrease in specific volume as Cu is added to Au. In all of these close packed structures atom movements occur by the vacancy mechanism and $V^* = V_f + V_m^*$ where V_f is the volume of vacancy formation and V_m^* is the activation volume for the interchange of a vacancy and an atom. In the close-packed metals V_m^* is only about 15% of V^*. As Cu is added to Au, V_m^* is expected to increase for the jump of Au atoms, but since V_m^* is such a small part of V^* this would not much affect the measured activation volume. Preliminary activation volume measurements for pure Cu by McArdle, Gardener, and Tomizuka[23] show an anomalously low V^* for self diffusion. That V^* for ordering in Cu₂Au is not significantly less than for self diffusion, diffusion in Au indicates that V^* in the alloy is principally determined by the formation of vacancies on the Au sublattice.

There is one other alloy for which activation volume data are available for an ordering process, viz., Ag–Zn (see Table I) where the measurements were done by an anelastic relaxation method. As in Cu–Au, there is an appreciable size difference but, in this case, there is a large decrease in V^* relative to the value in pure Ag. (Even if V^* for self diffusion in Ag proves to be too high, this would probably still be true.) It must be, then, that the anelastic, stress-induced ordering effect is responsive to the motion of the smaller, and presumably more mobile, atom in the alloy as contrasted with the homogeneous change in long-range order in Cu₃Au whose rate is controlled by the mobility of the more slowly moving atom.

The observed V^* for ordering in Cu₃Au can be used to calculate the activation entropy S^*, defined as

$$S^* = (\partial G^*/\partial T)_P,$$

by means of the relation

$$S^*/V^* = a/\beta,$$

deduced by Lawson.[24] In this equation a is the thermal expansion coefficient and β the compressibility. It is found that $S^* = 13$ cal/mole°K which is very nearly the same as the value computed for pure Au.

APPENDIX: DETERMINATION OF THE RESISTANCE R_0 AT PERFECT ORDER

The following procedure was used to determine the quantity $R_0(T, P)$, the resistance the sample would

²³ P. B. McArdle, A. B. Gardener, and C. T. Tomizuka, Bull. Am. Phys. Soc. **11**, 183 (1966).
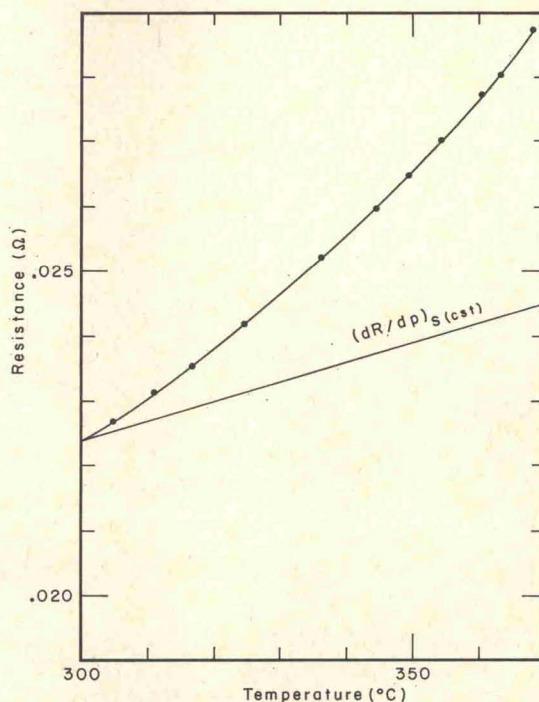²⁴ A. W. Lawson, J. Phys. Chem. Solids **3**, 250 (1957).

FIG. 9. The equilibrium resistance of a large domain sample as a function of temperature at 1 kbar. The straight line illustrates the temperature-dependent portion of the resistance. The difference between the curves is the order-dependent resistance.

have were it perfectly ordered at the temperature and pressure of the kinetic run. This quantity must be found for each sample for use in the rate equation [Eq. (1)]. All of the samples were annealed at 368°C to grow a large, stable domain size. During this anneal the resistance of one sample was monitored.

The resistance of the monitored sample at perfect order and 25°C was determined as follows:

(1) A large domain sample was reheated to 368°C in the annealing furnace and equilibrated at a series of temperatures from 368°C to 298°C. The equilibrium resistance of the monitored sample was measured at each temperature. The order-dependent portion of the resistance at each temperature was extracted from the measured resistance by subtracting the temperature-dependent resistance. The temperature-coefficient of resistance at constant order was measured by reheating the samples to 368°C, quenching to room temperature, and measuring the variation resistance at constant order in the range from 22–38°C. The temperature coefficient of resistance of the quenched sample at constant order, $(dR/dT)_q$, was 3×10^{-5} Ω/°C.

The assumptions are made that the temperature coefficient of resistance at constant order in the range from 368° to 298°C is only slightly dependent on the degree of order, and that this coefficient is a constant for each state of order in the temperature range of measurement. Plots of equilibrium resistance vs temperature and resistance at constant order vs temperature appear in Fig. 9.
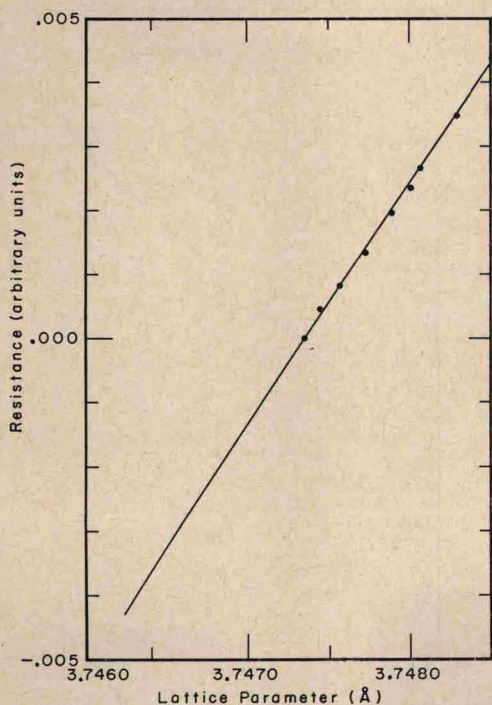
FIG. 10. The equilibrium order-dependent resistance vs the equilibrium lattice parameter as determined by Feder, Mooney, and Nowick (see Ref. 5). Temperature is the independent variable.

(2) The order-dependent portion of the resistance, represented by the difference in resistance between the two curves of Fig. 9 is plotted against the order-dependent lattice-parameter data of Feder et al., which were taken at 25°C. This plot is shown in Fig. 10. The assumption that the order-dependent portion of both the lattice parameter and the resistance reflect the degree of order in the same way is verified by the linear relation exhibited in this plot.

The resistance at perfect order and 25°C, $R_0(25°C)$, is determined by extrapolation of the plot to $a_0 = 3.7465$ Å. This is the value of the lattice parameter at perfect order and 25°C as determined by Feder et al., by equilibration of their sample at temperatures in the range from 368° to 200°C. At 200°C, the ordering

process occurs extremely slowly, and the equilibrium degree of order is nearly perfect.

(3) Since the specimens to be used in the kinetic experiments were subjected to the identical heat treatment as the monitored sample, the ratio (R_0/R_q) at 25°C should be the same for each specimen. This ratio was found to be

$$(R_0/R_q)_{25°C} = 0.564 \pm 0.001,$$

for the monitored sample. Thus a measurement of the initial resistance of a specimen installed in the anvil apparatus is sufficient to determine $R_0(25°C)$ for that specimen.

(4) In order to determine the temperature and pressure coefficient of R_0 for each sample, so that $R_0(T_{anneal})$ can be calculated, the following measurements were performed:

First, the specific temperature coefficient of resistance of a quenched sample was measured. The sample was then highly ordered, and the coefficient remeasured. The ratio of these coefficients was found to be 0.76. The pressure coefficient of resistance at constant temperature of both a highly ordered and slightly ordered sample was measured to 20 kbar at 100°C, and found to be nearly linear continuous functions. The results were as follows

$$R_q^{-1} < (dR_q/dP)_T = 0.03\%/\text{kbar; slightly ordered,}$$

$$R_0^{-1}(dR_0/dP)_T = 0.8\%/\text{kbar; highly ordered.}$$

Since the resistance of both highly ordered and slightly ordered samples was found to be a continuous function of pressure and temperature, it was assumed that the specific temperature coefficient of resistance of each specimen in the quenched condition, $1/R_q(dR_q/dT)_{P,S}$, was related to the specific temperature coefficient of resistance of the same sample in the highly ordered state, $1/R_0(sR_0/dT)_{P,S}$, by the constant of proportionality 0.76.

Once the temperature coefficient of resistance of R_0 was determined, the value of $R_0(P, T)_{anneal}$ could be calculated.