FIG. 2. Increase of voltage between electrodes which occurs when the external circuit is opened after 73 min (curve I) and after 99 min (curve II), during the first heating cycle.

order of 10 volts excludes the possibility of interpretation as a thermoelectric effect occurring at the electrodes. After the second experiment the deep yellow color of the irradiated sample had practically disappeared; renewed heating did not produce further currents. Therefore with the fading of the color centers the sample became exhausted.

The irradiated dielectric, although macroscopically neutral, contains positive and negative carriers. Increase of temperature increases diffusion of the carriers; in a temperature gradient diffusion will be directed preferentially against the temperature gradient, i.e., toward higher temperatures. If the diffusion coefficient of one type of carriers exceeds that of the other type, a net external current results. The polarity of the observed current indicates a higher diffusion coefficient for the negative carriers, as seems natural when electron migration is admitted.

ACKNOWLEDGMENTS

Ordering and Disordering Processes in Cu₃Au. I*

LEONARD R. WEISBERG† AND S. L. QUIMBY
Columbia University, New York, New York
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Data are reported which describe the isothermal change of Young's modulus with time in a single crystal of Cu₃Au following a sudden change in temperature below the critical temperature when a specimen is initially in various states of equilibrium long-range order. The results are compared with a modification of the kinetic theory of ordering and disordering proposed by Rothstein and Dienes. It appears that both processes proceed in two distinct but merging stages, one of which is described well by the theory in each case. The other is plausibly ascribed to the growth and dissolution of isolated clusters of disordered atoms, similar to those deduced by Chipman from x-ray evidence. Phenomena observed in the immediate neighborhood of the critical temperature occur when these clusters are sufficiently large and numerous to be contiguous.

INTRODUCTION

THE present research is concerned with the kinetics of long-range ordering and disordering in a single crystal of Cu₃Au below the critical temperature T_c. The face-centered cubic structure of this crystal may be regarded as four identical interpenetrating simple cubic lattices. At temperatures below T_c (about 390°C) the equilibrium atomic arrangement is such that the gold atoms preferentially occupy one of these sublattices and the copper atoms the remaining three. This long-range order is described by a parameter S defined by the formula $S = \frac{4}{3}(r_\alpha - \frac{1}{4})$, where r_α is the fraction of gold atoms on the chosen sublattice. It is convenient, in what follows, to designate the gold and copper atoms A and B atoms, respectively, and their ordered lattice sites α and β sites.

The variation of equilibrium order with temperature

is in principle susceptible of measurement by x-ray diffraction methods, but the data so far obtained both by the same and different observers are discordant.[1–4] It appears that the value of S decreases from unity at $T = 0°K$ to somewhat less than 0.8 at $T = T_c$, but the course of the variation remains uncertain. The very careful measurements of Chipman yielded the value $S = 0.8$ at the single temperature 380°C. Above T_c, $S = 0$.

Specification of S alone implies nothing about the way in which the disordered atoms are distributed on the lattice sites, A on β and B on α. Significant features of the average distribution can be inferred from measurements, again by x-ray methods, of short-range order parameters defined by the formula $\alpha_i = \frac{1}{3}(4n_i/c_i - 1)$, where n_i is the average number of A atoms among the c_i atoms in the ith shell of atoms about an A atom,

[1] Z. W. Wilchinsky, J. Appl. Phys. **15**, 806 (1944).
[2] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950).
[3] D. T. Keating and B. E. Warren, J. Appl. Phys. **22**, 286 (1951).
[4] D. R. Chipman, J. Appl. Phys. **27**, 739 (1956).

irrespective of its site. For example, it can be shown that $\alpha_1 = -\frac{1}{3}S^2$, *provided the distribution of disordered atoms is random.*[5] Accordingly, $n_1 = 1.08$ corresponding to $S = 0.8$, for this distribution. The value of n_1 computed from the measured value of α_1, is 0.45; hence the actual number of nearest neighbor A atoms at 380°C is, on the average, less than half that characteristic of a random distribution.[4]

Rothstein[6] and Dienes[7] have proposed theories of the kinetics of ordering and disordering based upon the assumption that the distribution of disordered atoms is at all times random, consistently with the instantaneous value of S. Their expression for the time rate of change of S is

$$dS/dt = \tfrac{3}{16}(1-S)^2\nu_2 \exp(-U/kT)$$
$$-[S + \tfrac{3}{16}(1-S)^2]\nu_1 \exp[-(V+U)/kT]. \quad (1)$$

Here V is the increase in energy of the system associated with a disordering atomic interchange, U the energy barrier against an ordering atomic interchange and ν_1, ν_2 the frequency factors for ordered and disordered atoms, respectively.

Equation (1) yields immediately the relation between equilibrium order and temperature proposed by Bragg and Williams, provided their approximations additional to the assumption of random disorder are included. Bragg and Williams neglect the variation of vibrational energy with order, implying equality of ν_1 and ν_2, and equate V to $V_0 S$, where V_0 is a constant of the material. The right hand member of Eq. (1) set equal to zero is then the equilibrium equation of their theory.[8]

Rothstein's object is to develop an approximate theory which will describe the isothermal change in a property of the material following sudden change in temperature below T_c. Equation (1) is integrated subject to the condition that U and V are constant at constant temperature. The result is, approximately,[9]

$$(1-S) = (1-S_e) \tanh(\delta t + \gamma) \quad \text{if} \quad S_i > S_e,$$
$$= (1-S_e) \coth(\delta t + \gamma) \quad \text{if} \quad S_i < S_e, \quad (2)$$

where S_i is the initial and S_e the final (equilibrium) value of S, δ is defined by the formula

$$\delta = \{\tfrac{3}{16}\nu_1\nu_2\}^{\frac{1}{2}} \exp[-(U+V/2)/kT], \quad (3)$$

and γ is a constant whose experimental value depends in part upon the time required to effect the temperature change.

Now let p be a measure of some order dependent property of the material at constant temperature. Rothstein assumes that, approximately

$$p = p_0 + B(1-S), \quad (4)$$

where B is a function of the temperature alone. Accordingly, the isothermal time variation of p following sudden heating or cooling is given by the expressions

$$(p - p_0)/(p_e - p_0) = \tanh(\delta t + \gamma)$$
$$\text{for sudden heating,} \quad (5a)$$
$$= \coth(\delta t + \gamma)$$
$$\text{for sudden cooling.} \quad (5b)$$

Here p_e is the equilibrium value of the quantity and p_0 is the value it would have if the material were perfectly ordered *at the temperature of measurement.*

Recently Nowick and Weisberg[10] devised an approximate method for the integration of Eq. (1) in which the form of the functions $U(S)$ and $V(S)$ need not be specified. The right-hand member is expanded in a Taylor's series about the equilibrium value S_e of S in terms of the small quantity $(S - S_e)$, and terms of the third and higher orders are rejected. The resulting expression, quadratic in S, is readily integrated. In their application of the method these authors set $U = $ constant, but it will be argued in Sec. 8 that the quantity $Q = (U + \frac{1}{2}V)$ rather than U is in fact more nearly independent of S. On the assumption that Q is constant, the integrals of Eq. (1) have the form of Eqs. (5) very nearly provided

$$\delta = A \exp(-Q/kT), \quad (6)$$

where

$$A = (\tfrac{3}{16}\nu_1\nu_2)^{\frac{1}{2}}\{4(3S_e+1)(S_e+3)\}^{\frac{1}{2}}$$
$$\times \left\{ \frac{(1+S_e)}{(3S_e+1)(S_e+3)} - \frac{(1-S_e)}{16} \frac{V_e'}{kT} \right\},$$

and V_e' denotes the value of $\partial V/\partial S$ at $S = S_e$. The experimental data confirm the validity of the approximations involved in the reduction of the integrals to this form.

It follows from Eq. (1) that the *initial* isothermal ordering rate in a specimen quenched from equilibrium at a temperature $T_i < T_c$ to a final temperature T_f is a maximum when T_f is given very nearly by the expression

$$(1/T_f) = (1/T_i) + (k/Q). \quad (7)$$

Terms of the second and higher orders in the ratio $V/2Q$ are neglected in comparison with unity in this approximation.

The assumption that the atomic distribution is at all times random, consistently with the instantaneous value of S, is a conspicuous defect in the foregoing equilibrium and kinetic theories. It is noteworthy that any theory that offers a description of isothermal relaxation from an initial order corresponding to equilibrium at a temperature T_i to a final order corresponding to equilibrium at a temperature T_f in terms of a single parameter, e.g., S,

[5] J. M. Cowley, Phys. Rev. **77**, 669 (1950).
[6] J. Rothstein, Phys. Rev. **94**, 1429(A) (1954).
[7] G. J. Dienes, Acta Met. **3**, 549 (1955).
[8] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1939), p. 600.
[9] In this approximation, the quantities $(1-S)$ and $\tfrac{3}{16}(1-S)^2$ are neglected in comparison with unity in the bracket of Eq. (1).
[10] A. S. Nowick and L. R. Weisberg, Acta. Met. (to be published).

involves the tacit assumption that during the process the order assumes a succession of *equilibrium* values associated with temperatures between T_i and T_f. The question arises: if these equilibrium atomic distributions are not random, what are they?

The postulate of random disorder does not appear in the equilibrium theory of order proposed by Bethe[11] and applied to Cu_3Au by Peierls.[12] A detailed description of the average atomic distribution at all temperatures, in terms of the constitution of the first shell of atoms about A and B atoms on both α and β sites, can readily be deduced from Peierls' work. The departure from randomness can then be evaluated in terms of a quantity ϵ defined by the formula

$$\phi_X = 3(1-S)\epsilon, \tag{8}$$

where ϕ_X is the average number of A atoms in the first shell about an A atom on an α-site according to Peierls, and $3(1-S)$ is the value of the same quantity on the random disorder assumption. A few values of ϕ_X are given in Table II below. The factor ϵ may be included in the derivation of the right-hand members of Eq. (1), and a new expression for δ obtained as before. It is found that the small difference between the values of δ computed with this expression and with Eq. (6) is insignificant in the interpretation of the data here reported.

It is of interest that Peierls' computation of the equilibrium long- and short-range order near T_c is in much better agreement with x-ray data than that of the earlier theory. For example, his value of the short-range order parameter α_1 at 380°C is approximately -0.28. The value obtained by Chipman[4] from his x-ray observations is -0.283, and that computed with the Bragg and Williams theory is -0.092.

The configurational energy W of the atomic array is regarded, in these theories, as the sum of the mutual energies v_{AA}, v_{BB}, and v_{AB} of pairs of adjacent like and unlike atoms. The total energy can then be expressed in the form[13]

$$W = \text{constant} + 2vn_{AA}, \tag{9}$$

where n_{AA} is the number of pairs of adjacent A atoms and $v = \frac{1}{2}(v_{AA} + v_{BB}) - v_{AB}$. This equation permits an evaluation of the quantity v with the aid of such calorimetric measurements as those of Sykes and Jones,[14] together with Cowley's measurements of the short range order parameter at various temperatures above T_c (2). In accordance with the definition of α_1 previously cited, $n_{AA} = \frac{3}{8}(1+3\alpha_1)N$, where N is the total number of atoms in the crystal. The total change in configurational energy between the state of complete

order and the state of disorder immediately above T_c, observed by Sykes and Jones, is 5.3 cal/g. Cowley's value of α_1 at the same temperature is -0.16. Accordingly $v = 0.059$ ev. The value computed with the relation $kT_c/2v = 0.47$ of Peierls' theory is 0.061 ev.

Until a complete theory of order is written, experiment, guided by such approximations as the foregoing, must be relied upon to reveal true descriptions of the equilibrium atomic configurations and of the isothermal relaxation from one such configuration to another following sudden change in temperature below T_c. Measurements of various order dependent properties of the material supplement one another to this end. Electrical resistivity is employed as an indicator of order in a recent study of ordering kinetics[15] and lattice parameter in another[16]; the Young's modulus of elasticity serves the same purpose in the present work.

EXPERIMENTAL METHOD

Specimen Material

The specimen material, of atomic composition 25.15% Au and 74.85% Cu, was prepared by the firm of Baker and Company in the form of a circular cylindrical rod. A single crystal rod of diameter 4.9 mm is grown by the Bridgman method and annealed at 850°C for 4 hours to minimize segregation. A specimen of suitable length (about 3.6 cm) is cut from the crystal and further annealed at 600°C for 5 hours to eliminate strains due to cold work. The direction cosines of the cylinder axis with respect to the principal axes of the crystal are 0.165, 0.595, and 0.784. The critical temperature of the material lies between 388.2°C and 389.5°C. The value $T_c = 389$°C is adopted here.

Measurement of Young's Modulus

Young's modulus is measured by the composite piezoelectric oscillator method described by Lord,[17] modified in respect to the means for measuring the resonant frequency of the oscillator and for heating the specimen. The resonant frequency of the composite oscillator ($\sim$38 kc/sec) is measured by measuring the frequency generated by a crystal controlled electronic oscillator in which the crystal is replaced by the piezoelectric element of the composite oscillator, as shown in Fig. 1. It is found that the two frequencies differ by not more than 5 cps. The oscillator output is applied across one pair of plates of a cathode-ray oscilloscope and that of a calibrated electronic oscillator of variable frequency across the other. The frequencies of the two oscillators are identical when the oscilloscope pattern is stationary.

The fundamental frequency of free longitudinal vibration of the specimen cylinder f_T is computed from

[11] H. A. Bethe, Proc. Roy. Soc. (London) **A150**, 552 (1935).
[12] R. Peierls, Proc. Roy. Soc. (London) **A154**, 207 (1936).
[13] F. C. Nix and W. Shockley, Revs. Modern Phys. **10**, 1 (1938).
[14] C. Sykes and F. W. Jones, Proc. Roy. Soc. (London) **A157**, 213 (1936). See also Rubin, Leach, and Bever, Trans. Am. Inst. Mining Met. Engrs. **203**, 420 (1955).

[15] F. Burns and S. L. Quimby, Phys. Rev. **97**, 1567 (1955).
[16] Feder, Mooney, and Nowick, Acta Met. (to be published).
[17] N. W. Lord, J. Chem. Phys. **21**, 692 (1953).

the observed frequencies of the composite oscillator and the quartz crystal alone with the formulas of the method,[18] and this is related to the Young's modulus of the specimen material E_T by the expression

$$E_T = 4\rho_{20}L_{20}^2 f_T^2 (L_{20}/L_T)[1+\tfrac{1}{2}\pi^2\bar{\sigma}^2 a^2/L_{20}^2], \quad (10)$$

where ρ is the density, L the length, a the radius of the cylinder and $\bar{\sigma}$, the mean Poisson's ratio. The quantities $\bar{\sigma}$ and (L_{20}/L_T) are evaluated with the data of Siegel[19] and Nix and MacNair,[20] respectively. The value of the term containing $\bar{\sigma}$ is 0.0012. The measured value of ρ_{20} is 12.12 ± 0.08 g/cm³. Changes in length due to change in order during the kinetic experiments are so small as to be without significant effect on the value of E_T computed with Eq.(10).[21] Throughout thepresent paper Young's modulus is evaluated in arbitrary units (a.u.) which are related to cgs units by the formula $E_{cgs}=6.790\times10^9 E_{a.u.}$. The precision of the measurements is ±0.03 a.u., but their accuracy, as measured by the reproductibility of data taken after reconstructing the oscillator and remounting it, is ±0.3 a.u.

Temperature Control

The experimental arrangements are nearly the same as those described in reference 15 hence the description is here abbreviated. The composite oscillator is mounted horizontally on glass threads along the axis of a Pyrex glass tube 2 inches in diameter and 12 inches long. The tube is evacuated from one end and means are provided for admitting helium in bursts at the other for quenching. The oscillator is irradiated radially by four General Electric Company 250-watt reflector infrared heat lamps arranged quadrantally about the axis. Its temperature is stabilized with a calibrated chromel-alumel thermocouple of No. 30 wire constructed by inserting each wire into a hole 10 mils in diameter drilled radially at the center of the specimen's length. Thermal contact with the specimen is insured with a minute application of Dupont conductive silver No. 4887 which, in the course of experiment, is fired at 400°C. The thermo-

Fig. 1. The piezoelectric oscillator circuit.

[18] P. M. Sutton, Phys. Rev. **91**, 816 (1953).
[19] S. Siegel, Phys. Rev. **57**, 537 (1940).
[20] F. C. Nix and D. MacNair, Phys. Rev. **60**, 320 (1941).
[21] Measurements of isothermal change of length with time in quenched specimens have recently been made in this laboratory by Mr. William Gross. A report is in preparation.

couple controls fluctuations in the power supplied the lamps. Specimen temperatures in excess of 600°C can be obtained with this radiation furnace, and stabilized within 0.1°C.

The radiation furnace serves an additional purpose. When the composite oscillator is irradiated the temperature of the quartz crystal, which must be known, is not the same as that of the attached specimen. In order to relate the two temperatures, as described in reference 17, it is necessary to measure the temperature variation of the resonant frequency of the quartz crystal alone, and of a composite oscillator in which the specimen is replaced by a copper cylinder when both components of the latter are at the same temperature. To this end, the irradiated element in the furnace is a hollow copper cylinder 1.4 inches in diameter and 5 inches long which is completely closed to radiation. The item to be heated is mounted inside this cylinder, and the control thermocouple is brazed to the outside. The temperature within the cylinder is uniform to 1°C at 400°C and is stabilized within 0.02°C.[22]

Experimental Procedure

The procedures for producing rapid changes in temperature, which are described in reference 15, are executed by one observer. Another records frequencies and corresponding times. The calibrated oscillator is set at a predetermined frequency higher or lower than that of the piezoelectric oscillator and the instant when the oscilloscope pattern is stationary is noted on a stopwatch. Observations can be made every 6 seconds if desired. The specimen cools roughly 3 deg/sec down to 5° from the end temperature, after which about 8 seconds are required to stabilize at the end temperature. Heating is effected at about 1.5 deg/sec, and only 2 seconds are required for stabilization. The specimen is never undercooled or overheated more than 0.2°.

RESULTS AND DISCUSSION

1. Young's Modulus at Equilibrium Order, E_e

The heat treatment preceding the measurement of Young's modulus corresponding to equilibrium order is as follows. The specimen is annealed at 370°C for 70 hours, after which its temperature is raised to 380°. Observations are made at intervals of 2° as the temperature is lowered to 370°, 5° to 350°, 10° to 200°, and 20° to room temperature. The specimen is then reheated to 380°C and observations made at intervals of 1° as the temperature is raised to 384°, 0.5° to 391°, 1° to 394°, 2° to 400°, 5° to 420°, and 10° to 470°. The temperature is held constant at each point until the modulus appears to reach a stationary value. This period varies from a minimum of 20 minutes at 380°
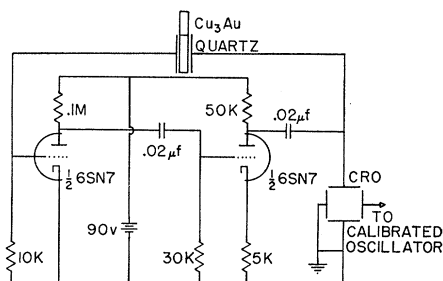
[22] Details of a modification of this furnace for the production of temperatures as high as 1000°C are reported by L. R. Weisberg and G. R. Gunther-Mohr, Rev. Sci. Instr. **26**, 896 (1955).

TABLE I. Variation of Young's modulus at equilibrium order
with temperature.

$T°C$	E_e(a.u.)	$T°C$	E_e(a.u.)
290.0	162.91	385.9	148.20
300.0	161.96	386.4	147.95
310.0	160.99	386.8	147.66
320.0	159.82	387.3	146.95
329.9	158.62	387.8	146.54
340.1	157.23	388.0	146.47
350.0	155.78	389.0	135.82
355.1	154.99	390.0	135.60
359.9	154.06	392.0	135.21
365.0	153.18	394.0	134.88
370.0	152.26	396.0	134.58
371.9	151.85	398.0	134.27
374.1	151.46	400.0	134.03
376.0	151.03	405.0	133.36
378.0	150.57	410.0	132.75
379.9	150.07	415.0	132.19
381.1	149.91	420.0	131.61
382.0	149.61	430.0	130.53
383.0	149.33	440.0	129.57
384.0	149.06	450.0	128.56
384.4	148.80	460.0	127.57
384.9	148.60	470.0	126.59
385.4	148.43		

and above 415°, to many hours at temperatures near T_c.

The variation of Young's modulus at equilibrium order, E_e, with temperature is given in Table I. The values are uniformly 8.7 a.u. or about 5.6% lower than those computed with the values of the s_{ij} reported by Siegel.[19]

2. Young's Modulus at Perfect Order, E_0

The quantity E_0, as it appears in place of p_0 in Eqs. (5), is the value Young's modulus would have at the temperature of observation if the order were perfect. To obtain this it is necessary to know the value at a given temperature and the temperature coefficient. Both quantities are evaluated with the aid of the
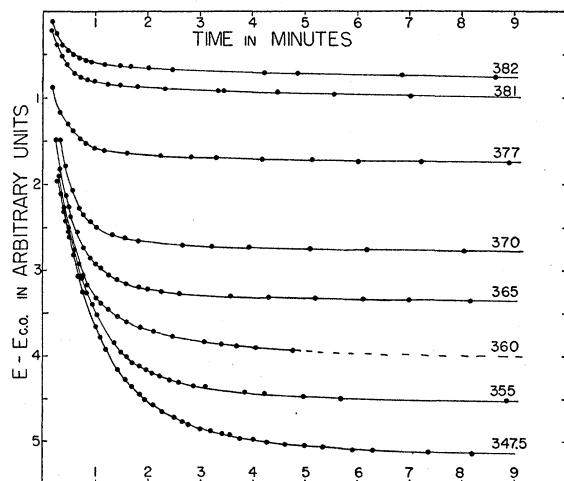

FIG. 2. Isothermal time variation of Young's modulus following a quench from 385°C to the indicated temperature.

careful measurements of equilibrium lattice constant reported by Feder, Mooney, and Nowick.[16] In the following description of the procedure for determining E_0 all data appertaining to the lattice constant are to be ascribed to these authors.

The lattice constant at 25°C is measured following anneals to equilibrium at various temperatures between 220°C and T_c and subsequent quench to 25°. The equilibrium lattice constant at 25° is deduced from these data. Incident to the measurements it is found that the anneal times required to attain equilibrium below 290° are extremely long, varying from 6 hours at 290° to over 1000 hours at 210°. Anneal times of adequate duration were not employed in the measurements of E_e below 280°, hence the latter do not represent equilibrium values and are not given in Table I. Correlation of lattice constant with E_e between 280° and T_c yields a smooth curve which permits valid extrapolation to low temperatures. Observations of E below 280° depart abruptly and systematically from this curve, indicating failure to attain equilibrium. The extrapolation yields
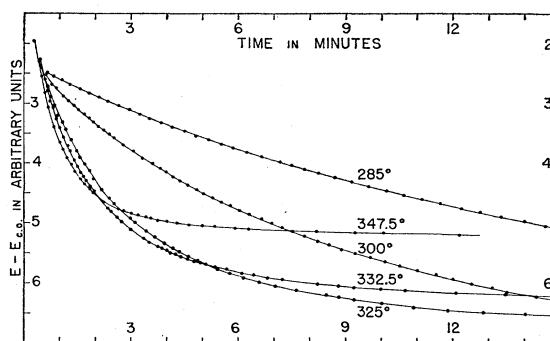

FIG. 3. Isothermal time variation of Young's modulus following a quench from 385°C to the indicated temperature.

the value of E_c at 25° and this is equated to E_0 on the assumption that the order is practically perfect at that temperature.

The observed variation of E with temperature between 40° and 230° is linear, with a temperature coefficient −0.0636 a.u./°C. This is a temperature coefficient at constant order, namely the equilibrium order at 280°.[23] Now it has been shown that the temperature coefficient of Young's modulus is nearly independent of order between 40° and 230°.[17] The same is true of the thermal expansion[20] and the temperature coefficient of electrical resistivity.[24] Hence the value −0.0636 a.u./°C is accepted as the temperature coefficient at perfect order. Lastly, this quantity is constant in the interval 40° to 230° and is assumed to remain so in the interval 230° to T_c.

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[23] Feder et al. (reference 16) argue with some cogency that the value of S_e at 280°C is 0.94.

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

The foregoing procedure yields the formula,

$$E_0 = [165.00 - 0.0636(T - 300)] \text{ a.u.} \qquad (11)$$

It is appropriate here to anticipate the result that, while values of the quantity γ computed from observations of E with Eqs. (5) are sensitive to the assumed value of E_0, those of the more significant quantity δ are not.

3. Young's Modulus at Constant Order, $E_{c.o.}$.

This quantity is introduced to afford a rough estimate of the total *order dependent* change in E to equilibrium following sudden change in temperature below T_c. Consider a specimen initially in equilibrium at temperature T_i, $E = E_i$, whose temperature is suddenly changed to T_f. Let $E_{c.o.}'$ denote the value E would assume if the order remained constant during the change. An approximate value of $E_{c.o.}'$, denoted $E_{c.o.}$, is computed with the temperature coefficient at perfect order. Thus

$$E_{c.o.} = [E_i + 0.0636(T_i - T_f)] \text{ a.u.} \qquad (12)$$

Actually, the temperature coefficient of E is undoubtedly order dependent at elevated temperatures since the data above T_c in Table I indicate that, on the present assumption, it changes at T_c from the value -0.0636 a.u./°C for $S = 1$ to the value -0.0995 a.u./°C for $S = 0$. Hence the ordinates of the curves of Figs. 2, 3, and 4 are uncertain by an unknown amount, constant for each curve. However, the observed absolute values of E can be recovered from these curves with the aid of Eq. (12) and Table I.

4. Kinetics of Ordering and Disordering below T_c

Figures 2 to 5 depict the isothermal variation of E with time following rapid change in temperature below

FIG. 4. Isothermal time variation of Young's modulus following rapid heating from 340°C to the indicated temperature.
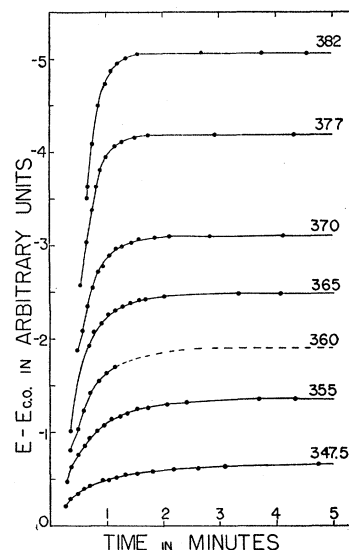
T_c. The zero of time on these graphs and those that follow is the instant at which the temperature change is initiated. Young's modulus increases with increasing order, while length and electrical resistivity decrease; therefore, to facilitate comparison with similar studies of the latter phenomena increases in E are plotted *downward* and decreases upward. The following features of the graphs are particularly to be noted for future reference:

(a) Despite the rapidity with which the temperature changes are effected, roughly half the total order dependent change in E occurs before the first observation is made: hence only the latter half of the complete ordering and disordering process is observed. In Figs. 2 and 3 the observed change varies from 48% of the
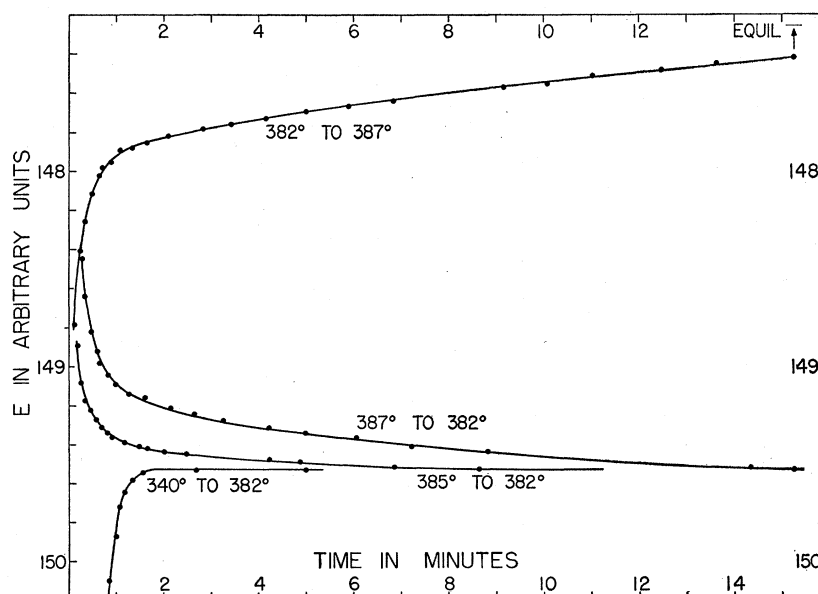

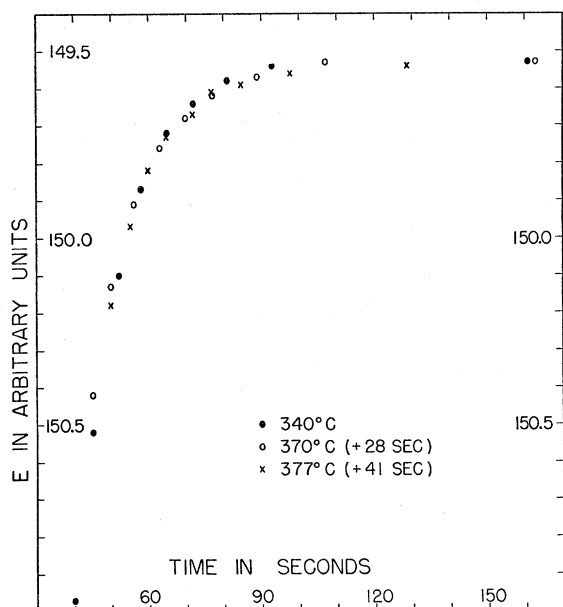FIG. 5. Isothermal time variation of Young's modulus following rapid changes in temperature as indicated.

FIG. 6. Isothermal disordering curves at 382°C following rapid heating from the indicated temperature can be superposed by shift of the time scale.

the latter quantity is related to the variation in equilibrium configurational energy, referred to perfect order, measured calorimetrically by Sykes and Jones.[25] Here the temperature is the independent variable for the evaluation of both quantities. In accordance with Eq. (9), it is suggested that the order dependent change in Young's modulus is proportional to the change in the number of "wrong" bonds, n_{AA}. If this is true, Young's modulus depends upon the short-range and not upon the long-range order.

The kinetic theories reviewed in the introduction are concerned with the temporal variation of the number of wrong atoms. If descriptions of the curves of Sec. 4 are to be sought in these theories, then it must be assumed that the ratio of wrong bonds to wrong atoms remains constant during the observed portions of the processes. Estimates of this ratio may be deduced from Peierls' theory as described in Sec. 7, and it is found that its variation is 2.2% or less in these intervals. If the distribution of wrong atoms were random, the

total at 377° to 65% at 325°, and in Fig. 4 it varies from 31% at 382° to 68% at 347.5°.

(b) The initial isothermal disordering rate increases monotonically as the ordering temperature is raised, while the initial ordering rate following a quench from 385° is a maximum in the neighborhood of 355°.

(c) Referring to Fig. 5: Disordering at 387° (two degrees below T_c) is enormously slower than disordering at 382°. Also, ordering at 382° following a quench from 387° is much slower than that following a quench from 385°. (The initial state of order for the former ordering curve is not the equilibrium value at 387° but that represented by the terminal point on the disordering curve labeled "382° to 387°.")

(d) Isothermal disordering curves following rapid heating from various lower temperatures can be superposed by shift of the time scale. An example is shown in Fig. 6.

(e) Isothermal ordering curves following quench from various higher temperatures *cannot* be superposed by shift of the time scale. The higher the initial temperature, the slower the ordering at the same value of E. Examples are shown in Fig. 7. Reproducibility of the data is indicated by two sets, taken several weeks apart, plotted on the curve labeled "385° to 340°."

5. Dependence of Young's Modulus on Order

Before attempting a comparison of the foregoing data with theory it is relevant to examine the way in which Young's modulus depends upon order. The equilibrium value E_e and its variation with order $(E_0 - E_e)$ may be employed for this purpose. In Fig. 8
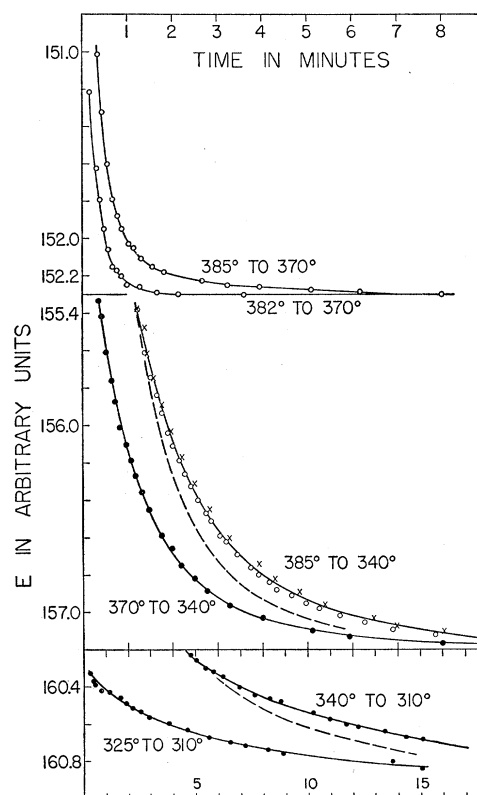

FIG. 7. Isothermal ordering curves following quench from different initial temperatures cannot be superposed by shift of the time scale. The dashed curves are curves to the left of them translated parallel to the time axis. A repeated measurement is shown on the 385° to 340° curve.

[25] See reference 14. The critical temperature of the specimen used by these authors was 664°K. Accordingly, their energy measurements were replotted as function of T/T_c. The energy values cited in Fig. 8 correspond to the critical temperature 662°K of the specimen used in the present research.

variation would be still less. It is proposed therefore to present in the next section a comparison of theory with observation.

6. Comparison of Theory and Observation

The quantitative basis for the following comparison of theory and observation is due in large measure to the work of Feder, Mooney, and Nowick.[16] These authors present a careful analysis of all available kinetic and equilibrium data, including the present measurements of Young's modulus and their own of lattice parameter. The latter extend over the temperature interval 200°C to 300°C, in which many of the approximations made in the theory disappear in virtue of the high state of equilibrium order present in the material. In consequence certain constants of the theory can be evaluated with plausible accuracy. Values employed without
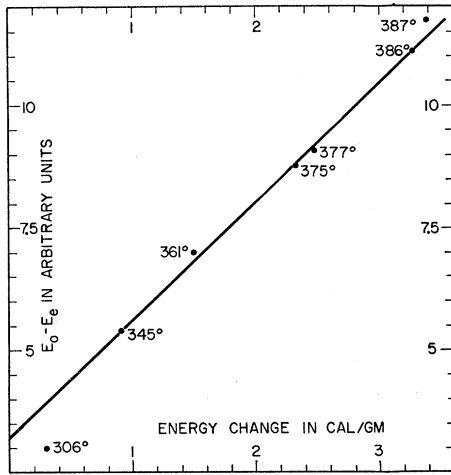
Fig. 8. Correlation of order dependent change in Young's modulus with order dependent change in configurational energy at equilibrium. Temperature is the independent variable.

further reference in what follows are

$$(\tfrac{3}{16}\nu_1\nu_2)^{\frac{1}{2}} = 3.6 \times 10^{14}\ \mathrm{sec}^{-1}; \quad Q = 2.03\ \mathrm{ev}; \quad V_e' = 0.5\ \mathrm{ev},$$

a constant. In addition, the authors obtain a relation between S_e and T which, conforming exactly to Chipman's observation at 380°C, is probably the most reliable now available. It is here used to evaluate the quantity A in Eq. (6).

The maximum in the *early* ordering rate, evident in Figs. 2 and 3, is in accord with Eq. (1) as previously noted. It appears to occur at about 355°, but it is not possible to estimate the temperature at which the *initial* ordering rate is a maximum within ten degrees. The value given by Eq. (7), with $T_i = 385°$, is 366°, but the accuracy of this is also uncertain because the temperature change from T_i to T_f is not effected instantaneously.

Disordering data of the sort depicted in Fig. 4, but taken with various initial and final temperatures, are
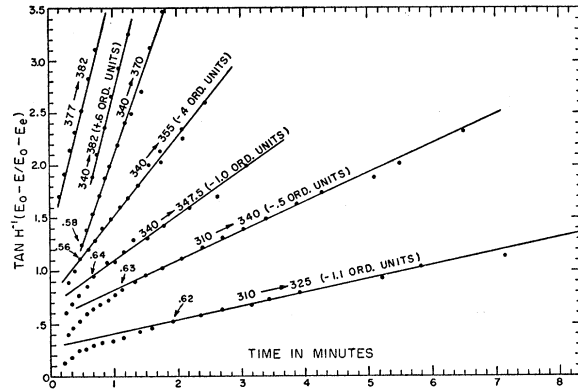
Fig. 9. Analysis of observations of isothermal disordering in accordance with Eq. (5a). The ordinates of several curves are altered as indicated to separate the curves.

plotted in Fig. 9 in such manner as to exhibit in detail the agreement with Eq. (5a). The initial and final temperatures are given for each curve, as is also, attached to an arrow, the fraction of the total change completed at the instant the observation indicated by the arrow was taken. The agreement with Eq. (5a) is seen to be excellent over the *latter* portion of each plot. The slopes of the representative lines are corresponding values of the quantity δ. The early data indicate disordering rates greater than the theoretical.

Ordering data of the sort depicted in Figs. 2 and 3, but again taken with various initial and final temperatures, are plotted similarly in Fig. 10. The numbers attached to the arrows have the same meaning as before. Good agreement with Eq. (5b) subsists over the *early* portion of each plot. The late data indicate ordering rates less than the theoretical. The lengths of the lines adjacent to the curves at $t = 3^m 25^s$ show the uncertainty in the value of the ordinate at that instant due to the uncertainty in the measured value of E.

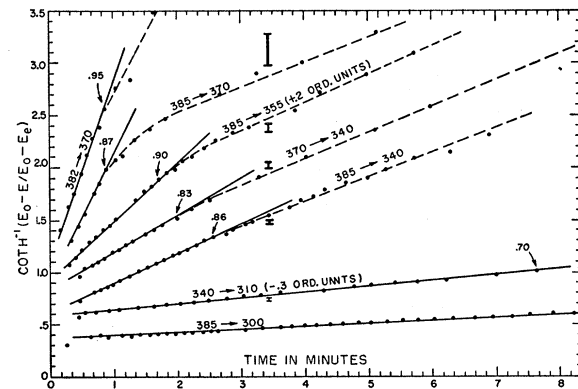In accordance with Eq. (6),

$$\ln\delta = -Q/kT + \ln A. \qquad (13)$$

Fig. 10. Analysis of isothermal ordering in accordance with Eq. (5b) The ordinates of two curves are altered as indicated to prevent overlap with others.
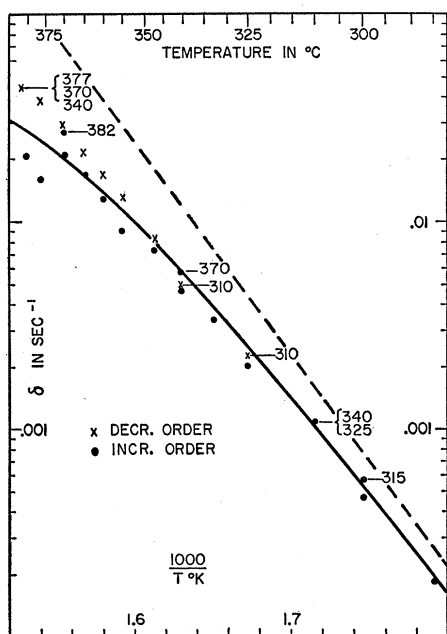
FIG. 11. The variation of δ with temperature. The initial temperatures for ordering and disordering are 385°C and 340°C, respectively, unless otherwise indicated by numbers attached to the points.

Values of δ, obtained from numerous graphs similar to those of Figs. 9 and 10, are plotted to a logarithmic scale as ordinates in Fig. 11. The abscissa is $1000/T°K$, where T is the temperature at which the process occurred. The initial temperature for ordering is 385°, and for disordering 340°, unless otherwise specified by one or more numbers attached to a point. For example, the three numbers attached to the value of δ for isothermal disordering at 382° show that the same value was obtained on heating to 382° from 377°, 370°, and 340°; those attached to the value of δ for ordering at 310° show that the same value was obtained on quenching to 310° from 340° and 325°.

As the value of S_e approaches unity the terms containing S_e in A of Eq. (6) cancel each other to unity, and $\ln\delta$ varies linearly with $1/T$ very nearly. The dashed line of Fig. 11, taken from Fig. 8 of reference 16, represents well the low temperature observations of Feder, Mooney, and Nowick. The solid line is a graph of Eq. (6), computed with the values of S_e and $V_e{}'$ quoted in Sec. 6. The latter are obtained quite independently of the data plotted in the figure: hence no adjustable parameter is employed in the computation.

The condition that the observed portions of relaxation curves such as those of Figs. 2, 3, and 4 should superpose on shift of the time scale is that a value of δ conforming to the theory should exist *and remain constant throughout.* Accordingly, the result depicted in Fig. 6 is consistent with the data of Fig. 9, and that depicted in Fig. 7 with the data of Fig. 10.

It remains to account for the notable departures

from the theory exhibited in Figs. 9 and 10, and for the extreme slowness of both the ordering and disordering processes in the immediate neighborhood of T_c revealed in Fig. 5.

7. Atomic Distributions

The symbols here employed in the description of an atomic distribution have the following meanings: $A^\alpha = A$ atom on an α site; $A^\beta = A$ atom on a β site; $A_m{}^\alpha = A$ atom on an α site with m A atoms in the first shell of surrounding atoms; $B_m{}^\alpha = B$ atom on an α site with m A atoms in the first shell; etc.

The equilibrium atomic distributions at various temperatures, described in terms of the numbers of $B_m{}^\alpha$ and $A_m{}^\alpha$ present in the medium and computed with Peierls' theory, are given in Table II. Values of the quantities ϕ and ϕ_X of the theory are also given. The quantity ϕ is the average number of A^β in the first shell about a B^α and ϕ_X is the average number of A^β in the first shell about an A^α. The average number of A^α about an A^β, denoted μ_X by Peierls, is related to ϕ_X by the formula $r_a\phi_X = w_a\mu_X$, where r_a nad w_a are the fractions of A atoms on α and β sites, respectively. The average number of A^β about an A^β, denoted λ_X by Peierls, is negligible at all temperatures. Hence, from Peierls' Eq. (19), at temperatures below T_c a close approximation to the number of wrong bonds is given by the expression $n_{AA} = \frac{1}{4}r_a\phi_X N$, where N is the total number of atoms.

High accuracy cannot, of course, be claimed for the numbers that appear in Table II, but there is no doubt that they are qualitatively correct in respect to the various types of atomic environment that exist in the medium and the way in which the relative fractions of these types vary with temperature.

8. Significance of the Quantities Q, U, and V

Figure 12 is a schematic representation of the mutual configurational energy, referred to perfect order, of a B^α and an A^β in an otherwise ordered lattice. The positions a, b, c denote β sites in successive shells

TABLE II. The numbers of $B_m{}^\alpha$ and $A_m{}^\alpha$ at various temperatures expressed in units of $10^{-3}N$, after Peierls.

$T°C$ S	200° 0.98	300° 0.94	362° 0.90	389° 0.87
$B_0{}^\alpha$	1.61	2.97	3.66	3.73
$B_1{}^\alpha$	1.61	5.11	8.12	9.92
$B_2{}^\alpha$	0.484	2.69.	5.55	8.14
$B_3{}^\alpha$	0.045	0.461	1.33	2.36
$B_4{}^\alpha$		0.022	0.094	0.22
$A_0{}^\alpha$	3.57	9.82	14.9	18.1
$A_1{}^\alpha$	0.181	1.36	3.60	5.68
$A_2{}^\alpha$	0.0026	0.067	0.281	0.561
$A_3{}^\alpha$				0.024
ϕ	0.7252	1.066	1.258	1.400
ϕ_X	0.04976	0.1383	0.2222	0.2811

about the α site. The peaks of the curve are, in fact, much higher than drawn, since the value of U_i is many times that of V_i. The quantity $Q = U_i + \frac{1}{2}V_i$ is a constant, and is the activation energy for diffusion of an A^β in the lattice.

The activation energy for the initial disordering process, which produces an A^β in the position (a), is $(U_1 + V_1)$, which may be written $(Q + \frac{1}{2}V_1)$. The activation energy for the reverse (ordering) process is U_1, which may be written $(Q - \frac{1}{2}V_1)$. Accordingly, any decrease in the value of V_1 must *increase* the disordering rate and *decrease* the ordering rate. Similar considerations apply to transitions of the A^β between positions (a) and (b). After reaching position (b) the A^β may wander through the lattice with no change in configurational energy.

9. Notion of Clusters

Figure 13 is a drawing of various atomic configurations lying in the Cu-Au layer of a (100) plane in a partially disordered lattice. The uncircled letters A and B indicate rightly occupied α and β sites, and the circled letters wrong occupied sites. Planes containing only β sites lie above and below the plane of the figure. These atomic configurations are called "clusters." The atomic constitution, in terms of the numbers of $B_m{}^\alpha$ and $A_m{}^\alpha$, and the configurational energy, in terms of v, are given for each cluster. It will be observed that, in accordance with Eq. (9), the energy is $2v$ times the number of AA pairs in the cluster.

The initial disordering process in an ordered lattice is the simple interchange of an A^α and a B^β. This forms Cluster I, which may be called, after Rothstein, an "associated wrong pair." Clusters II and III result when the A^β leaves the first shell about the B^α, and these constitute a "dissociated wrong pair." A simple free energy computation shows that the disorder at low temperatures consists predominantly of dissociated wrong pairs. Clusters I, II, and III are the primary clusters from which the remainder are built by the successive addition of a single wrong pair. The following remarks concerning the clusters are pertinent:

(a) Comparison of the atomic distributions of arrays of clusters with those of Table II strongly suggests
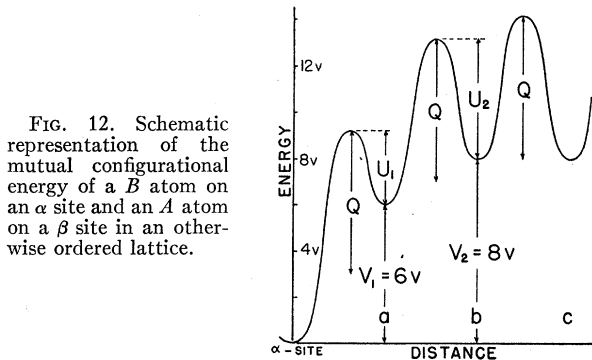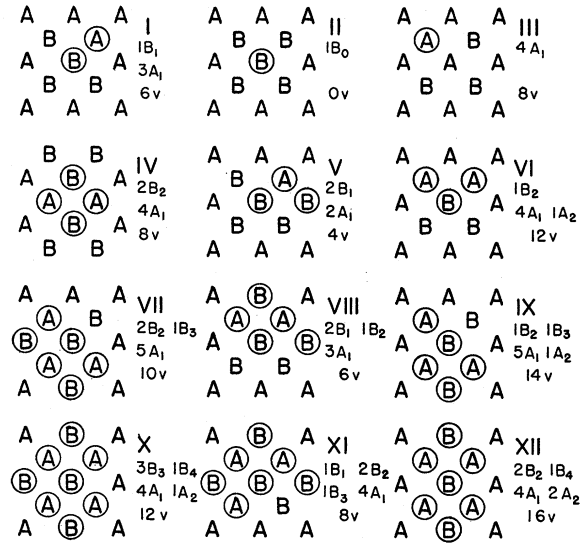

FIG. 13. Typical clusters of wrong atoms in a Cu-Au layer of a (100) plane in a partially disordered lattice. The wrong A and B atoms are circled.

that disordering and ordering do in fact proceed by the growth and dissolution of clusters. It is not difficult to construct an array of clusters of Types I to VI inclusive that reproduces Peierls' distribution at 200°C very closely. (Values of μ_X and ϕ_X are reproduced exactly, with an error of 3% in ϕ resulting from neglect of the 1.2% of $B_3{}^\alpha$, since the latter are not present in these clusters.) The computed number densities of the several types are consistent with the assumption that the clusters are effectively isolated.

(b) The presence of an appreciable number of $A_3{}^\alpha$ reveals cluster contiguity. The formation of a cluster is the inception of order in which the A atoms occupy a different sublattice. Hence only clusters lying in mutually perpendicular planes can be contiguous. Evidently, from Table II, clusters are contiguous only in the neighborhood of T_c.

(c) The process of ordering and disordering here proposed yields exactly the atomic arrangement at 380°C deduced by Chipman[4] from an analysis of the diffuse scattering of x-rays. According to Chipman this analysis "strongly suggests very tiny antiphase domains, one layer thick in a Cu-Au layer and containing about 9 atoms. The plate-like antiphase domains would be distributed at random throughout the crystal on any of the three sets of (100) planes."

(d) The energy of formation of the primary clusters is $6v$ or $8v$, and that of the first derived series is $2v$ or $4v$ additional. The remaining clusters of all types, including those derived from Nos. X, XI, and XII and their progeny, form with successive increases in energy of only $2v$. The exponential form of the Boltzmann factors governing the rate of production of right and wrong atoms leads inevitably to the conclusion that relaxation toward equilibrium order following sudden

FIG. 12. Schematic representation of the mutual configurational energy of a B atom on an α site and an A atom on a β site in an otherwise ordered lattice.

change in temperature below T_c procedes by two distinct but merging stages. One of these stages is controlled principally by an atomic interchange energy $2v$ and the other by an energy approximately $6v$. The ratio of the Boltzmann factors, $\exp[(Q+\frac{1}{2}V_1)/kT]$, corresponding to these two values of the quantity V_1 of Sec. 8 varies from 11 at 300°C to 8 at 389°C.

(e) During the growth and dissolution of large clusters the change in the number of wrong (AA) bonds is equal to the change in the number of wrong A (or B) atoms. The ratio of wrong bonds to wrong atoms associated, respectively, with clusters of Type I and of Types II and III is 3 and 4. Justification further to that mentioned in Sec. 5 is thus afforded for the correlation of theory and experiment here attempted.

(f) The clusters are not to be regarded as fixed, either in space or time. They are continually forming and dissolving. The equilibrium is dynamic. A specified numerical distribution of cluster types represents an average over a long time of a great many instantaneous atomic configurations.

(g) The configurational energy of each cluster depicted in Fig. 13 is a minimum for the number of wrong atoms in the cluster. Other clusters of higher energy containing the same number of wrong atoms will be present, but those of lower energy will predominate.

10. Kinetics of Cluster Arrays

On the present view, each curve of Figs. 9 and 10 depicts the kinetic behavior of an array of clusters. Referring to Fig. 9, at the termination of each two stage disordering process the number of large clusters is increased, as is likewise the number of clusters of Types I, II, and III. In accordance with Sec. 8 above, growth of the large clusters, governed by $2v$, proceeds much more rapidly than that of the small clusters, governed by $6v$ or $8v$. This is indicated by the departure of the initial observations from the straight lines that describe the course of the second stage. At the higher temperatures the entire first stage is completed before the first observation is recorded.

The curves of Fig. 10 reveal the two distinct merging

stages of ordering. Values of δ deduced from the straight lines agree well with those deduced from the lines of Fig. 9, as shown in Fig. 11. The early stage of ordering and the late stage of disordering represent, respectively, the dissolution and formation of small clusters governed by an atomic interchange energy approximately $6v$. The late stage of ordering, comprising roughly 10% of the total change, represents slow dissolution of large clusters.

The considerable retardation in both the ordering and disordering rates that occurs in the immediate neighborhood of T_c, will now be considered. Heretofore, clusters have been treated as isolated in an ordered matrix. As the temperature is raised the size and number density of clusters increases, in accordance with Table II; in the neighborhood of T_c the clusters are no longer isolated. In this event many atoms lying between disordered clusters are so situated that an interchange of an A^α and a B^β, or an A^β and a B^α, effects no change in configurational energy. Such atoms will not on the average participate in either an ordering or a disordering process. They are effectively neutral. The resultant decrease in the number of atoms available for participation decreases the numerical magnitude of dS/dt, alike whether its sign is positive or negative. The tails of the ordering and disordering curves between 387° and 382°, of Fig. 5, are quite similar.

It will be noted in Fig. 11 that the values of δ for ordering following a quench from 385° are about 20% less, at the same final temperature, than those following a quench from a lower temperature. Examples occur at 340° and 300°. This represents a remnant effect of contiguous clusters present at 385°. The same phenomenon was observed by Feder, Mooney, and Nowick.