PHYSICAL REVIEW VOLUME 97, NUMBER 6 MARCH 15, 1955

Ordering Processes in Cu_3Au†

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(Received October 22, 1954)

Data are reported which describe the isothermal time rate of change of electrical resistivity in a specimen of Cu_3Au following a quench from a temperature above the critical temperature (393°C) to one below it. The experimental arrangements permit observation within one minute after the initiation of the quench. At quench temperatures above 364°C the resistivity rises and then decreases, at first rapidly and then more slowly. The initial rate of fall increases as the quench temperature is lowered. Below 364°C the early rise is absent and the rate of fall decreases with decreasing temperature. The several phenomena are consistent with the hypothesis that the processes involved are the formation, by statistical fluctuation, of stable antiphase nuclei of order in the disordered matrix, the growth of these nuclei, and the coalescence of the resultant antiphase domains. An approximate quantitative theory is developed. Measurements of the isothermal time rate of change of resistivity in an annealed specimen following sudden change of temperature below the critical temperature are in accord with the kinetic theory recently proposed by Jerome Rothstein.

INTRODUCTION

THE crystalline structure of the alloy Cu_3Au is face-centered cubic. The atomic array has long range order when the gold atoms preferentially occupy a single one of the four constituent simple cubic sublattices. This order is conveniently measured by a parameter S defined by the formula

$$S=(4/3)(r_\beta-\tfrac{1}{4})=4(r_\alpha-\tfrac{3}{4}), \qquad (1)$$

where r_β is the fraction of gold atoms on the chosen sublattice and r_α the fraction of copper atoms on the remaining three sublattices. The equilibrium value of S, corresponding to a minimum in free energy, decreases from unity at 0°K to 0.84 at about 665°K.[1] At this critical temperature the values $S=0.84$ and $S=0$ are both stable, above it only $S=0$. The existence of long range order is a consequence of the fact that the mutual energy of two unlike atoms is less than that of two like atoms in the same positions. The following argument due to Bethe[2] accounts for the critical temperature and indicates the nature of the transition that occurs there.

Imagine an ordered crystal divided by a boundary surface into two regions, and the order in one of them altered by distributing the gold atoms on a different sublattice so as to leave the value of S unchanged in the region. Then the value of S for the whole crystal is decreased, since a smaller fraction of gold atoms now occupy a single sublattice; the entropy ϕ is increased by an amount $\Delta\phi$ because the original number of atomic arrangements is multiplied by the number of ways in which the boundary can be inserted; and the configurational energy E is increased by an amount ΔE due to the increase in the number of like nearest neighbors at the boundary. The new configuration is unstable at a temperature T provided $\Delta E > T\Delta\phi$. At a higher temperature the equilibrium order and hence the boundary energy ΔE are smaller, while the quantity $T\Delta\phi$ is larger. At the critical temperature the two terms are equal, and the appearance of "antiphase" regions of the sort described produces no increase in free energy. Thus, as in Cu_3Au, two values of S, one zero, may be stable at the critical temperature. The boundary energy appears as a latent heat of transition from one to the other. The foregoing ideas have been developed quantitatively by Bethe, Chang,[3] Peierls,[4] and Cowley.[5]

The order at temperatures above the critical temperature T_c is best described in terms of the atomic constitution of the several shells of atoms about, e.g., a gold atom. The parameters introduced by Cowley[6] are the α_i defined by the formula

$$\alpha_i=1-4n_i/3c_i,$$

where n_i is the number of copper atoms among the c_i atoms in the ith shell surrounding a gold atom. Cowley computed the temperature variation of the first ten α_i by analysis of the observed diffuse scattering of x-rays, and so showed that the average local order approaches that characteristic of long-range order as the temperature is lowered toward T_c. Fluctuations are superimposed on the average order, hence it is reasonable to assume that regions of appreciable order containing large numbers of atoms have a transient existence at temperatures not too far above T_c.

The purpose of this research is to study the isothermal processes by which equilibrium long-range order is achieved in a specimen which has been quenched from a temperature above T_c to one below it and held there. The extensive observations of Sykes and Evans[7] supplemented by the calorimetric measurements of Sykes and

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† Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

‡ Now at the Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] D. T. Keating and B. E. Warren, J. Appl. Phys. **22**, 286 (1951).

[2] H. A. Bethe, Proc. Roy. Soc. (London) **A150**, 552 (1935). See also F. C. Nix and W. Shockley, Revs. Modern Phys. **10**, 1 (1938).

[3] T. S. Chang, Proc. Roy. Soc. (London) **A161**, 546 (1937).

[4] R. Peierls, Proc. Roy. Soc. (London) **A154**, 207 (1936).

[5] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[6] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950).

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

Jones[8] led these investigators to the conclusion that the initial processes are the formation and growth of ordered nuclei in a disordered matrix. The present work confirms this hypothesis and affords sufficient detail to encourage rough quantitative analysis in terms of the nucleation theory of Becker[9] and Turnbull.[10] It is further found that the progress toward new equilibrium order following sudden change in temperature below T_c in a specimen effectively free of antiphase domains is in excellent agreement with the kinetic theory of ordering and disordering recently proposed by Rothstein.[11] Electrical resistivity is employed throughout these experiments as an indicator of the state of affairs in the material.

EXPERIMENTAL METHOD

Specimen Material

The specimen material was prepared by the firm of Handy and Harmon, Bridgeport, Connecticut, in the form of a wire 25 mils in diameter. The atomic composition is 24.96±0.05 percent gold and 75.04±0.05 percent copper, with spectroscopic traces of Fe, Pt, and Ag. The wire as received was annealed at 825°C for eight hours. The temperature variation of the electrical resistivity was then measured in exact accordance with the procedure described by Sykes and Evans[7] and Siegel.[12] The result is in excellent agreement with the observations of these investigators. Photomicrographic analysis at this stage revealed that the average linear dimensions of the constituent microcrystals are 0.12 mm to 0.15 mm longitudinally and 0.090 mm transversely. The critical temperature lies between 392°C and 393°C. The value $T_c = 393$°C is adopted here.

Temperature Control

The temperature of a solid can be raised several hundred degrees by suspending it in an evacuated transparent container and irradiating it with the output of a few General Electric Company reflector infrared heater lamps. This phenomenon is the basis of the radiation furnace perfected in this laboratory by Mr. Leonard Weisberg and employed in the present research.

Figure 1 is a sectional drawing of the cylindrical irradiated element. The specimen wire, 10 cm in length, lies on the axis. It is surrounded coaxially over most of its length by two cylindrical copper skirts constructed by drilling nearly through two pieces of quarter inch copper rod, so as to leave 15 mils wall thickness. The solid ends of the skirts are drilled axially to fit the wire, and a 10-mil longitudinal slit terminating in a small hole is cut in each skirt wall. The potential leads for the resistance measurements are pieces of the specimen material drawn down to 8 mils diameter. Two symmetrically placed holes of the same diameter are drilled 6 cm apart through the specimen, and the leads are inserted and affixed with a minute application of silver solder.

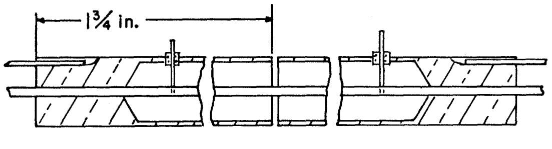

FIG. 1. Cross sectional drawing of the irradiated assembly.

The skirts are threaded on the specimen so that the potential leads pass through the holes in the skirt walls, from which they are insulated by bits of ceramic tubing. The solid ends of the skirts are then squeezed in hard on the specimen with a hydraulic press. The two skirts are almost but not quite in contact at the center. Two longitudinal slots, 10 mils wide and 18 mils deep, are cut in the solid ends of each skirt, and into these the ends of No. 30 chromel and alumel thermocouple wires are peened. Lastly, the slits in the skirt walls are closed with Dupont silver No. 4887.

The assembly shown in Fig. 1 is mounted axially on glass threads in a horizontal glass tube 2 inches in diameter and 18 inches long. One end of this tube, closed by a brass fitting and O-ring, is connected to the pumping system, and through it pass the current, potential and thermocouple leads. The other end is connected through a manifold of three valves with three chambers of 1.4 cubic inches capacity containing helium at predetermined pressure for quenching.

Each skirt is irradiated radially by four 250-watt heat lamps arranged quadrantally about the axis. The temperature of each skirt is stabilized by its own thermocouple, which is connected to a potentiometer. The light beam from the potentiometer galvanometer is deflected by a right angled prism into one of two photocells. The amplified photocurrents operate a relay which inserts or removes a small resistance in series with the variac through which power is supplied the lamps. A portion of the light beam is reflected to a visible scale. The device stabilizes the temperature of the specimen within 0.1°C at 400°C.

Resistance Measurement

The resistance of the specimen is measured with a Kelvin double bridge of the Wolff type operated with a sinusoidally varying emf of 1000 cycles/sec frequency. The components of one pair of ratio resistances are 500 ohms each, while those of the other pair are variable and are mechanically coupled so as to remain always equal. The latter are four decade resistors whose resistances per step are 100, 10, 1, and 0.1 ohms respectively. The bridge detector is a cathode ray oscilloscope

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[8] C. Sykes and F. W. Jones, Proc. Roy. Soc. (London) **A157**, 213 (1936); **A166**, 376 (1938).

[9] R. Becker, Ann. Physik **32**, 128 (1938).

[10] D. Turnbull, Am. Inst. Mining Met. Engrs., Tech. Publ. No. 2365 (1948).

[11] J. Rothstein, Phys. Rev. **94**, 1429(A) (1954).

[12] S. Siegel, Phys. Rev. **57**, 537 (1940).

preceded by a two stage amplifier. The voltage gain of the amplifier and bridge transformer is 700. The comparison resistance in the bridge is 6 cm of No. 16 manganin wire located in a thermally insulated box outside the specimen chamber. The returning current lead from the specimen passes through this box, and is there flexible. The emf of mutual induction between the current leads in the two bridge arms is annulled by manipulation of this flexible portion. The bridge sensitivity permits detection of a resistance change of 1 part in 5000.

Accuracy

The chromel-alumel thermocouples are calibrated by comparison with a platinum resistance thermometer certified by the U. S. Bureau of Standards. The wires are cut near the calibrated junctions and the ends are peened in the skirts.

The relation between the temperature of the skirts and that of the specimen is established by measurements made on an assembly identical with that of Fig. 1 except that the specimen is replaced by a length of No. 18 platinum wire, which is treated as a resistance thermometer. The observations reveal that the temperature of the platinum wire is lower than that of the skirts, but that the departure is no more than 1°C at 400°C. It is assumed that the specimen behaves similarly.

The resistances of the specimen and comparison arms of the bridge are of the order 0.02 ohm each, and of the bridge yoke 0.011 ohm. The accuracy of the bridge ratio resistances specified by the maker is ±0.05 percent. Accordingly, it is estimated that the accuracy of the resistance measurements is ±0.2 percent. The accuracy of the resistivity computed from the resistance and the specimen dimensions is about 2 percent.

Quenching Procedure

The steps in the quenching procedure, in which two persons must participate, are the following: (1) The quenching chambers are filled with helium at the desired pressure. The latter is determined by the magnitude of the temperature change to be effected, and the speed of the diffusion pump, a VMF 20-01, and of the forepumps, two megavacs in parallel. (2) The specimen temperature is stabilized at the desired initial value. (3) The lamps are switched off. (4) One or more helium manifold valves are opened. (5) The two potentiometer settings are altered to the value corresponding to the desired lower temperature. (6) When the light beams on the visual scales indicate near approach to the new temperature, power is supplied the lamps and this is adjusted manually until the automatic control can safely take over. The pressure in the helium chambers must be such that the diffusion pump is operative at this time. (7) The decade bridge resistances are progressively altered by one observer, and the instant of bridge balance is read from a stopwatch by the other.

Temperature equilibrium is established within one minute or less after the initiation of the change. Verifi-

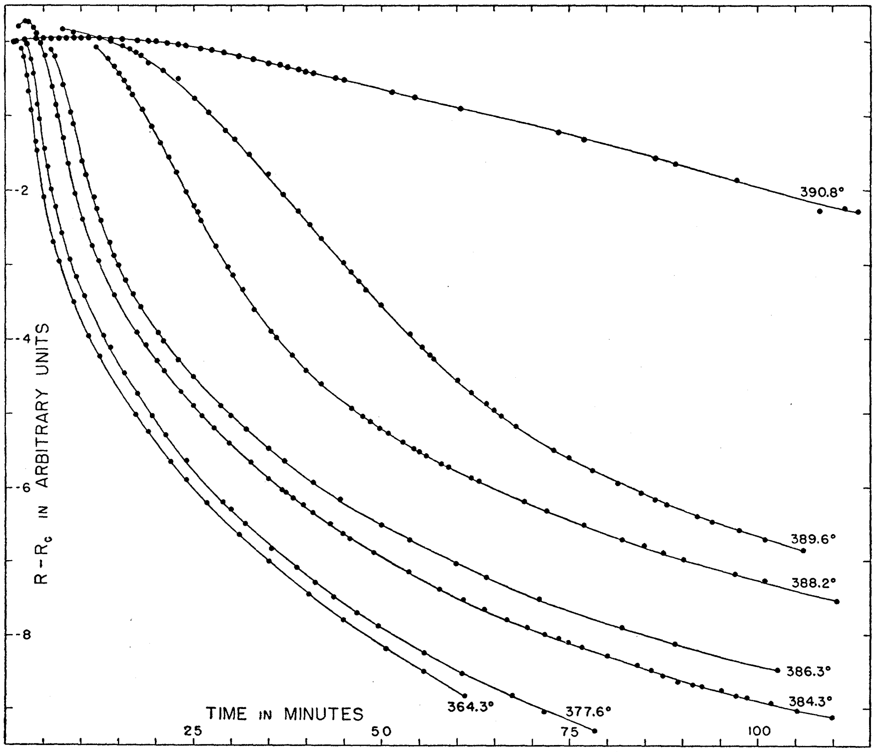

FIG. 2. Isothermal variation of resistance with time following a quench from 418°C to the indicated temperature.

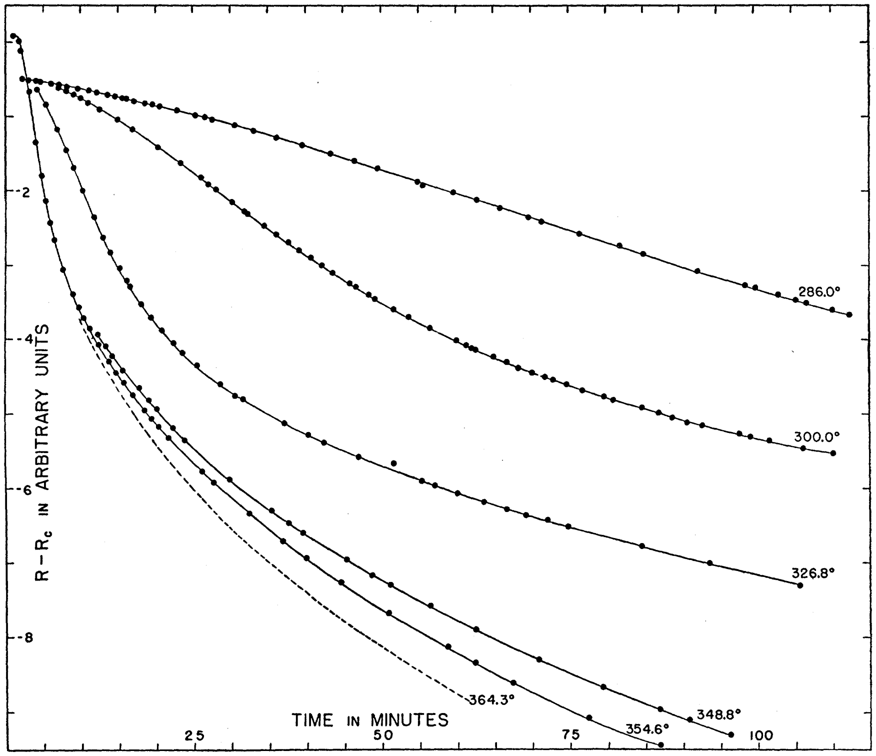

FIG. 3. Isothermal variation of resistance with time following a quench from 418°C to the indicated temperature.

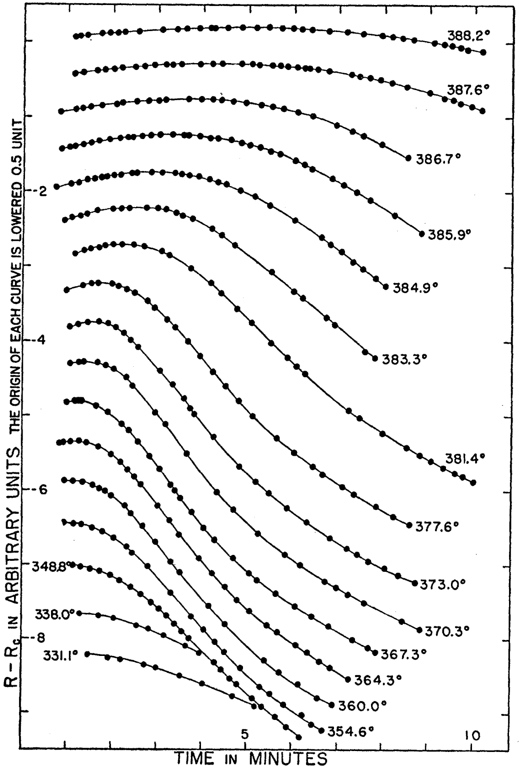

FIG. 4. Details of the initial portions of curves similar to those of Figs. 2 and 3. The origin of each curve is 0.5 a.u. less than that of the curve above it.

cation of this is afforded by observation of resistance changes associated with quenches completed at temperatures above T_c, where no ordering occurs, and also with quenches made on the platinum wire assembly.

The steps in the procedure for effecting a sudden increase in temperature below T_c are the same as (2), (3), (5), and (6) above except that in step (3) maximum power is supplied the lamps, and in step (6) the power is lowered to a value appropriate to stabilization at the new temperature.

RESULTS

The curves of Figs. 2, 3, and 4 show the isothermal variation of specimen resistance with time following a quench from 418°C to the indicated temperature. The resistivity ρ of the material is related to the resistance R (or R_c), expressed in the arbitrary units (a.u.) here employed by the formula $\rho = (0.2255 \times 10^{-6} R_{\text{a.u.}})$ ohm cm. R denotes the observed resistance at time t after the initiation of the quench, and R_c the resistance of the disordered specimen at the temperature of measurement. The temperature coefficient of resistance of the disordered material is 0.028 a.u./°C, and the resistance at 418°C is 63.56 a.u. Accordingly, $R_c = [63.56 - 0.028 \times (418 - T)]$ a.u., where T is the temperature in degrees centigrade.

The curve of Fig. 5 shows the variation of resistance with temperature immediately above T_c. The solid circles indicate the relative positions of the maxima of the curves of Fig. 4.

The curves of Figs. 6 and 7 represent observations made upon a specimen after annealing at 388°C for 50 hours. The constituent microcrystals are then essentially single domains, as is indicated by the close proximity of the resistance to the equilibrium value for the temperature. Accordingly, these data describe the true kinetics of the ordering and disordering processes below T_c, free from phenomena associated with antiphase domains.

The curves of Fig. 6 show the isothermal variation of resistance with time following a quench from 388°C to the indicated temperature. Here R denotes, as before, the observed resistance at time t after the initiation of the quench, and R_c the resistance of the specimen at the temperature of measurement and in the state of order associated with 388°C. Sykes and Evans[7] have shown that the temperature coefficient of resistivity of the material near equilibrium order is very nearly independent of order. The value is 0.051 a.u./°C. Accordingly, $R_c=[R_i-0.051(388-T)]$ a.u., where R_i is the resistance at 388°C.

The curves of Fig. 7 show the isothermal variation of resistance with time after the temperature is suddenly raised from 338°C to the indicated value. Here $R_c=[R_i+0.051(T-338)]$ a.u., where R_i is the resistance at 338°C. The values of R_i at 388°C and 338°C decreased about 2 parts in 500 during the several days of observation following the 50-hour anneal. The initial values were 50.37 a.u. at 388°C and 39.70 a.u. at 338°C.

DISCUSSION

Ordering Processes

A specimen disordered at a temperature above T_c and quenched to a temperature below T_c is in a state of metastable equilibrium. Local fluctuations in free energy produce small ordered regions called "embryos" throughout the material. In virtue of the increase in surface energy associated with the formation of an embryo, most embryos are unstable and vanish; however, embryos of greater than a certain critical size are stable and grow, with accompanying decrease in the free energy of the system composed of the ordered embryo and the disordered matrix. It is likely that neighboring stable embryos are antiphase, and growth persists with concurrent increase in the order within the embryo toward the equilibrium value for the temperature, until the boundaries of adjacent antiphase regions coincide. Stable embryos thus constitute "nuclei" for the establishment of equilibrium order within numerous contiguous antiphase domains in the medium.

The occurrence of an embryo of given size in a disordered material is the result of many atomic interchanges, and the chance that these occur simultaneously is slight. Smaller embryos must appear before larger ones.[13] Embryos are present at the instant the quench temperature is reached, but if these are appreciably smaller than the critical size for that temperature a finite "incubation period" must precede the formation of a nucleus.

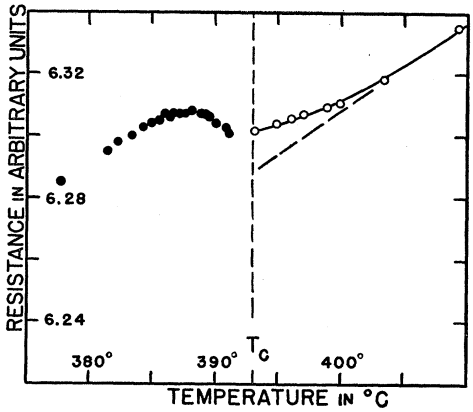

FIG. 5. The variation of resistance with temperature immediately above T_c. The solid circles indicate the relative positions of the maxima of the curves of Fig. 4.

Accordingly, the first ordering process is the formation of nuclei and the second their growth into contiguous antiphase domains of equilibrium order. The third process is the coalescence of these domains until a highly stable structure results which has been compared by Bragg to that of a stable foam.[14] In this structure the domains are nearly equal sized regular polyhedra with approximately plane bounding surfaces, and there is no tendency for one domain to absorb another. Furthermore, as remarked by Sykes and Jones, as the nuclei grow they absorb gold and copper atoms in the ratio 1:3, and any excess of atoms of either kind consequent upon initial fluctuations in atomic composition are concentrated at the domain boundaries. Addi-

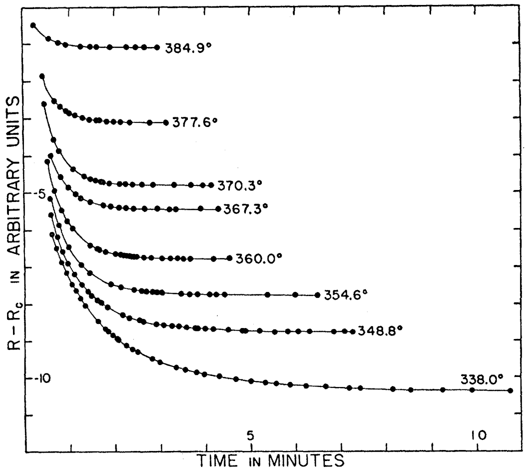

FIG. 6. Isothermal time variation of resistance of an annealed specimen following a quench from 388°C to the indicated temperature.

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[13] The mechanism of the formation of embryos in the cognate phenomenon of phase precipitation in solid solutions has been described in detail by Turnbull, reference 10.

[14] W. L. Bragg, Proc. Phys. Soc. (London) **52**, 105 (1940).

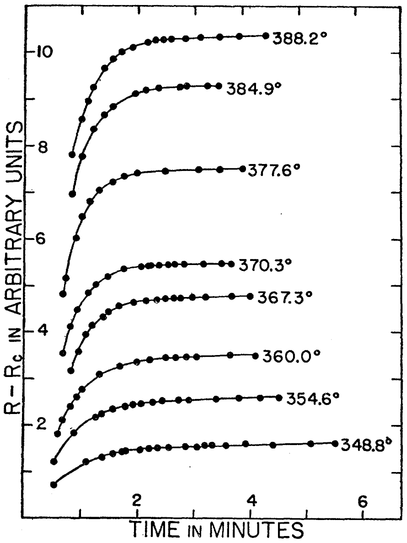

FIG. 7. Isothermal time variation of resistance of an annealed specimen following a sudden increase in temperature from 338°C to the indicated temperature.

tional coalescence involves movement of this material along the boundaries. Thus the fourth and final process in the establishment of equilibrium order throughout the specimen is extremely slow even at temperatures near the critical temperature. Owen and Sim[15] observed the time variation of domain size in a quenched specimen during annealing at 350°C. The linear dimensions of the domains increased to 71 interatomic distances in 30 hours, and showed no further change after 87 hours.

Theory of Order

The basis here adopted for a quantitative analysis of the nucleation process is the theory of order proposed by Cowley.[5] In this theory the configurational energy is assumed to be the sum of energies of interaction between pairs of atoms, one of which is in the ith shell of atoms surrounding the other. These energies are denoted by $V_{AA,i}$, $V_{BB,i}$, $V_{AB,i}$ according as the atoms of the pair are both copper, both gold, or one of each. The configurational energy E of an ordered lattice of N atoms, referred to a state of complete disorder, is given by the expression

$$E=-\tfrac{3}{4}S^2NW, \tag{2}$$

where

$$W=V_1-\tfrac{3}{2}V_2+2V_3-\cdots, \tag{3}$$

and

$$V_i=\tfrac{1}{2}(V_{AA,i}+V_{BB,i})-V_{AB,i}. \tag{4}$$

This form is valid only for values of S different from zero. The equilibrium long-range order is related to the temperature below T_c by the equation

$$\ln\left\{\frac{(\frac{1}{3}+S^2)(3+S^2)}{(1-S^2)^2}\right\}=\frac{16}{3}\frac{T_c}{T}S^2, \tag{5}$$

where

$$T_c=(3/2k)W. \tag{6}$$

The Helmholtz free energy per atom f, referred to complete disorder, is given by the expression[16]

$$f=\tfrac{1}{16}kT[(1+3S)\ln(1+3S)+6(1-S)\ln(1-S)$$
$$+3(3+S)\ln(1+\tfrac{1}{3}S)]-\tfrac{3}{4}S^2W. \tag{7}$$

Nucleation Process[17]

The parameter S is here employed as a measure of the order in nuclei. This is a valid first approximation when the nuclear size is large of the order 10 interatomic distances or more.

The change in free energy ΔF associated with the formation of an embryo in a completely disordered matrix can be represented by the expression

$$\Delta F=\Delta F_o+\Delta F_\sigma+\Delta F_e, \tag{8}$$

where ΔF_o is the change in free energy due to ordering within the embryo as given by Eq. (7), ΔF_σ is the work done in forming the interface between ordered embryo and disordered matrix, and ΔF_e is the elastic strain energy associated with the contraction of the material on ordering.[18] ΔF_o is intrinsically negative, but ΔF_σ and ΔF_e are positive. ΔF_e is a minimum when the bounding surfaces of the embryo are the (111) slip planes of the face-centered cubic lattice, so that the resistance to shear is a minimum, and when the shape of the embryo is a disk.[19] It is assumed that the embryos conform to this pattern, and the term ΔF_e is neglected.

The method for evaluating ΔF_σ is as follows. Imagine a volume of material in order S divided into two regions a and b by a plane surface of area σ, and the same volume of disordered material divided into regions c and d by the same area. This is the first configuration. Now let region c be joined to region a on the area σ, and d joined to b similarly. This is the second configuration. The surface energy associated with an area 2σ separating disordered material from material of order S is the energy of the second configuration minus that of the first.

The surface energy is assumed that contributed by nearest neighbors alone, and is computed for each of the four bounding surfaces by simply counting the average number of nearest neighbor bonds of the types AA, BB, and AB acting across them. For example, the average number of AB-type bonds acting across the ordered-ordered surface is computed as follows. Figure 8 is a diagram of the atomic arrangement on two adjacent (111) planes in the crystal. Here the copper sites are

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[15] E. A. Owen and M. Sim, Phil. Mag. **38**, 342 (1947).

[16] The entropy term is computed by R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 600.

[17] The method adopted follows closely that employed by R. Becker in his study of phase precipitation in solid solutions, reference 9.

[18] E. A. Owen and Y. H. Liu, Phil. Mag. **38**, 354 (1947); also F. C. Nix and D. MacNair, Phys. Rev. **60**, 320 (1941).

[19] F. R. N. Nabarro, Proc. Phys. Soc. (London) **52**, 90 (1940).

labelled α and the gold sites β, and the primed quantities refer to plane I and the unprimed to plane II. It will be noted that the nearest neighbors of the α' sites are two α and one β, while the nearest neighbors of the β' sites are three α. Now in accordance with Eqs. (1), the numbers of α' sites occupied by A and B atoms respectively are $\frac{3}{16}(3+S)N_\sigma$ and $\frac{3}{16}(1-S)N_\sigma$, where N_σ is the total number of atoms on the area σ. Similarly the numbers of β' sites occupied by A and B atoms respectively are $\frac{3}{16}(1-S)N_\sigma$ and $\frac{1}{16}(1+3S)N_\sigma$. Hence the average number of AB-type bonds contributed by the α' sites is

$$\tfrac{3}{16}\{(3+S)[r_\beta+2(1-r_\alpha)]+(1-S)[(1-r_\beta)+2r_\alpha]\}N_\sigma.$$

Similarly, the average number of AB-type bonds contributed by the β' sites is

$$\{\tfrac{1}{16}(1+3S)3r_\alpha+\tfrac{3}{16}(1-S)3(1-r_\alpha)\}N_\sigma.$$

A calculation of this sort yields the numbers of bonds of each type acting across each of the four surfaces (the two order-disorder surfaces are identical), and so the expression for ΔF_σ. The result is

$$\Delta F_\sigma = \tfrac{3}{16}S^2V_1N_\sigma, \tag{9}$$

where V_1 is given by Eq. (4).

The shape of an embryo is assumed, for simplicity, to be a square disk of edge L interatomic distances and edge to thickness ratio five. Equations (8) and (9) yield accordingly the expression

$$\Delta F = (1/5)fL^3 + (21/40)S^2V_1L^2, \tag{10}$$

in which f is given by Eq. (7). Cowley's measurements of x-ray scattering gave $V_1=358k$ and $W=371k$. The value of W computed with Eq. (6) and the observed critical temperature is $444k$. The value $V_1=400k$ is adopted here. In the foregoing expressions for V_1 and W the quantity k is to be regarded as a dimensionless constant whose value is 1.380×10^{-16}. The energies and free energies computed with the formulas here given are then evaluated in ergs.

The variation of ΔF with L at various temperatures is depicted in Fig. 9, where L^* denotes the nuclear size and ΔF^* the fluctuation in free energy required to produce a nucleus in a disordered matrix. The variation of L^*, plotted as ordinate, with S between $S=0$ and $S=1$ is a U-shaped curve at all temperatures, with a minimum at about $S=0.4$. Hence this value is used in computing the curves. Relaxation of the constituent material toward equilibrium order is concurrent with nuclear growth.

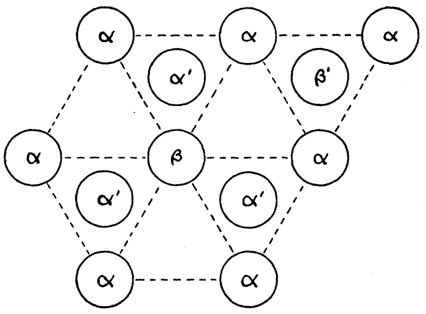

FIG. 8. The arrangement of copper α sites and gold β sites on two adjacent (111) planes of the lattice. The planes are distinguished by primed and unprimed symbols.

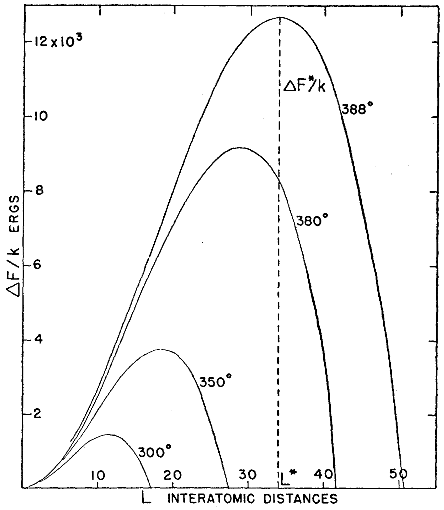

FIG. 9. Variation of embryo free energy with size and temperature.

It will be noted that as the quench temperature is lowered from T_c the number density of nuclei, which is proportional to $\exp(-\Delta F^*/kT)$, increases rapidly, while the quantities ΔF^* and L^* both decrease, and with them the incubation period for the formation of a nucleus. Furthermore, since the density increases far more rapidly than the size diminishes, a temperature is implied at which the nuclear boundaries are contiguous on formation.

The nuclear dimensions indicated in Fig. 9 are consistent with the antiphase domain sizes inferred by Sykes and Jones from the width and intensity of the superlattice lines formed by x-ray diffraction. On the present view, the nucleus must be smaller than the domain into which it grows. The average domain size is 75 interatomic distances in a specimen cooled from above T_c at 30°C per hour, and 6 to 8 interatomic distances in a specimen water quenched to room temperature and heated to 130°C, at which temperature equilibrium order within the domains is established.

Electrical Resistivity

The isothermal resistivity of a crystal ordered on a single sublattice decreases with increasing order. However, as remarked by Sykes and Jones, the presence of antiphase domains in the crystal destroys its homogeneity and so must disturb this behavior when the size of the domains is comparable with the mean free path of the conduction electrons. Electron reflections at the domain boundaries then increase the resistivity above the value corresponding to the order within. The magnitude of the change increases with diminishing domain size; when the domains are sufficiently small the resistivity is that of a completely disordered material. The mean free path λ of the conduction electrons in monovalent metals is given by the expression $\lambda=(h/\rho e^2)(3/\pi N^2)^{\frac{1}{3}}$, where ρ is the resistivity, e the electronic charge, and N the atomic density.[20] The resistivity is 10^4 emu for the ordered and 1.4×10^4 emu for the disordered material. The density is 12 g/cm^3, and the lattice constant is 3.7×10^{-8} cm. The corresponding values of λ are 38 and 27 interatomic distances.

Small embryos initially present in a specimen quenched to, say, 380°C act as scattering centers for the electrons. Nuclei of high order, as they appear, enhance the inhomogeneity with associated increase in resistivity. Subsequent nuclear growth decreases the resistivity by removal of disordered material, and domain coalescence tends still further to restore homogeneity to the medium.

The variation of the resistivity with temperature above T_c is linear except in the neighborhood of T_c, where the variation is as shown in Fig. 5. The increase of resistivity above the linearly extrapolated value indicated by the dashed line is produced by embryos whose size and number density increase as the temperature is lowered toward T_c. If α_i is a measure of the local order, the mean square fluctuation in α_i is given by the expression[21]

$$\langle(\Delta\alpha_i)^2\rangle_{\text{Av}}=\frac{kT}{n\partial^2 f(\alpha_i)/\partial\alpha_i^2},$$

where $f(\alpha_i)$ is the free energy per atom and n is the number of atoms in the embryo. The free energy is independent of local order at the critical temperature. The phenomenon is similar to critical opalescence in liquids.

Ordering in Quenched Specimens

The curves of Figs. 2, 3, and 4 will now be discussed in detail. The incubation period is identified approximately with the elapsed time after quenching before the maximum of resistivity is reached. Values of these maxima are plotted as a function of the quench temperature with the solid circles of Fig. 5.

$T=390.8$°C. The nuclei are large and their number density small. Hence the incubation period is long and the increase of resistivity slight. The entire curve represents the formation and growth of nuclei. Contiguous domains have not been established 130 minutes after quenching.

$T=389.6$°C to 364.3°C. The nuclei are progressively smaller and their number density larger as the temperature is lowered. The incubation period is not revealed by the measurements below about 360°C, where an appreciable number of embryos initially present are of nuclear size. The resistivity *rise* at first increases with the increase in the number of scattering centers (nuclei), and then decreases as the effect of scattering is annulled by the growth of nuclei present at the instant of quench.

The rate of removal of disordered material, and therefore the rate of fall of resistivity, increase with the number of *growing* nuclei. This number reaches a maximum at 364°C. Nuclear growth is stopped when the nuclear boundaries touch, and subsequent reduction of resistivity follows the removal of disordered material by the slower process of domain coalescence.

$T=364.3$°C to 286°C. As the temperature is lowered from 364°C and the density of nuclei increases correspondingly, a greater proportion of nuclei are contiguous on formation and a lesser proportion are free to grow. Hence the rate of fall of resistivity decreases with decreasing temperature. It appears that in the neighborhood of 300°C all the nuclei are effectively contiguous on formation. The data at 286°C then represent entirely the process of domain coalescence.

Referring to Fig. 4, the initial small rate of change of resistivity with time below 360°C represents a balance between the effect of nuclear growth, which is to decrease the resistivity, and that of the formation of new nuclei, which is to increase it by scattering.

Ordering in a Single Domain

Figures 6 and 7 show the relaxation of order from one equilibrium value to another following a sudden change in temperature in a specimen effectively free of antiphase domains. These curves represent the true kinetics of ordering and disordering *per se.* In accordance with Rothstein's theory,[22] the time variation of the isothermal resistivity R_t is given by the formula

$$(R_t-R_0)/(R_e-R_0)=\coth(\gamma t+\epsilon),\tag{11}$$

or the formula

$$(R_t-R_0)/(R_e-R_0)=\tanh(\gamma t+\epsilon),\tag{12}$$

according as the initial temperature is greater than or less than the final constant temperature. Here R_e is the equilibrium resistivity and R_0 the resistivity for perfect order, both corresponding to the temperature of measurement; t is the time after quenching; γ and ϵ are temperature dependent constants. Values of R_e are obtained from the curve relating equilibrium resistivity and temperature, and R_0 from a linear extrapolation of this curve upward from low temperatures, where the

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[20] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 268.

[21] A. H. Cottrell, *Theoretical Structural Metallurgy* (Edward Arnold and Company, London, 1951), p. 232.

[22] An abstract of Rothstein's theory appears in reference 11. A complete presentation, including further discussion of the data of Figs. 6 and 7, is in preparation.

order parameter S is nearly unity. Values of γ and ϵ are determined by the data. The plotted points of Figs. 6 and 7 represent observations, and the curves are graphs of Eqs. (11) and (12).

It will be noted that the data are consistent with the assumption, introduced earlier, that the processes of nuclear growth and ordering within nuclei are simultaneous in specimens quenched from above T_c.

In conclusion the authors acknowledge with gratitude their indebtedness to Dr. Charles D. Coxe and his associates of Handy and Harmon, who prepared the specimen material; to Professor Victor K. La Mer of Columbia University for helpful advice on nucleation theory; and to Mr. Leonard Weisberg of this laboratory, who devised the radiation furnace and assisted in many of the measurements.

PHYSICAL REVIEW VOLUME 97, NUMBER 6 MARCH 15, 1955

Electrical Properties of Gallium Antimonide*

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(Received December 9, 1954)

Data are presented on the conductivity and Hall coefficient of several samples of GaSb over the temperature from −196°C to 650°C. The lowest room-temperature conductivity obtained was 12 $\text{ohm}^{-1}\text{ cm}^{-1}$. All material produced from zone-purified components was *p*-type. *N*-type material was produced by doping with tellurium, as were *p-n* junctions. The intrinsic band gap is estimated from junction rectification data to be 0.78 ev at −196°C. The mobility of electrons was found by measurement on *n*-type material to be several times greater than the hole mobility. The mobilities of both holes and electrons are found to vary approximately as $T^{-\frac{3}{2}}$ in the lattice scattering range.

INTRODUCTION

CONSIDERABLE interest in the semiconducting properties of intermetallic compounds, particularly those formed by the combination of a group three and a group five element, has developed during the last several years.[1–3] Leifer and Dunlap[4] have recently published the results of their studies of the properties of a relatively pure sample of *p*-type GaSb. The present work includes several *p*-type samples, the purest of which is comparable to that of Leifer and Dunlap, as well as an *n*-type sample. Hall effect and conductivity measurements were made over the temperature range from −196° to 650°C. In addition, the current-voltage characteristics of a grown *p-n* junction were measured at room temperature and at −196°C.

PREPARATION OF MATERIALS

GaSb was formed by the direct combination of the zone-refined components[5,6] in approximately stoichiometric properties. It was found that this could be done most conveniently by mixing the purified components in the zone-refining boat and permitting the reaction to occur as the first molten zone was passed through the charge. Any excess of either component is quickly transported to the end of the ingot. Since gallium exhibits some tendency to wet the silica boats employed, a slight excess of antimony was usually added to insure complete reaction of the gallium.

Zone-refining of antimony and GaSb and subsequent GaSb crystal growing by the Czrochralski method were carried out under a purified hydrogen atmosphere. Electrolytic hydrogen, freed of oxygen and water by passing successively through a catalytic purifier, a high-voltage discharge, a $CaSO_4$ drying tower, and a liquid nitrogen cooled trap, was passed continuously over the charge. The resulting ingots of both antimony and GaSb exhibited a very clean, mirror-like surface as compared to the dull matte surface obtained with less pure hydrogen.

All of the material produced in this fashion exhibited *p*-type conductivity, the value depending upon the purity of the gallium employed. The less pure GaSb samples were prepared from relatively impure gallium which had not been zone-refined. These facts, together with the observation that the purity of GaSb made from the same gallium after zone-refining was as high as any produced, indicates the presence in at least some gallium of an impurity which is not effectively removed from the compound by the zone-refining process.

N-type material and *p-n* junctions were prepared by doping with an alloy of about one atomic percent tellurium in GaSb when growing crystals.

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* This research was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.

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