

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  $\text{Cu}_3\text{Au}$ , 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<sup>23</sup> show an anomalously low  $V^*$  for self diffusion. That  $V^*$  for ordering in  $\text{Cu}_2\text{Au}$  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  $\text{Cu}_3\text{Au}$  whose rate is controlled by the mobility of the more slowly moving atom.

The observed  $V^*$  for ordering in  $\text{Cu}_3\text{Au}$  can be used to calculate the activation entropy  $S^*$ , defined as

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

by means of the relation

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

deduced by Lawson.<sup>24</sup> In this equation  $a$  is the thermal expansion coefficient and  $\beta$  the compressibility. It is found that  $S^* = 13$  cal/mole $^\circ\text{K}$  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

<sup>23</sup> P. B. McArdle, A. B. Gardener, and C. T. Tomizuka, Bull. Am. Phys. Soc. **11**, 183 (1966).

<sup>24</sup> A. W. Lawson, J. Phys. Chem. Solids **3**, 250 (1957).

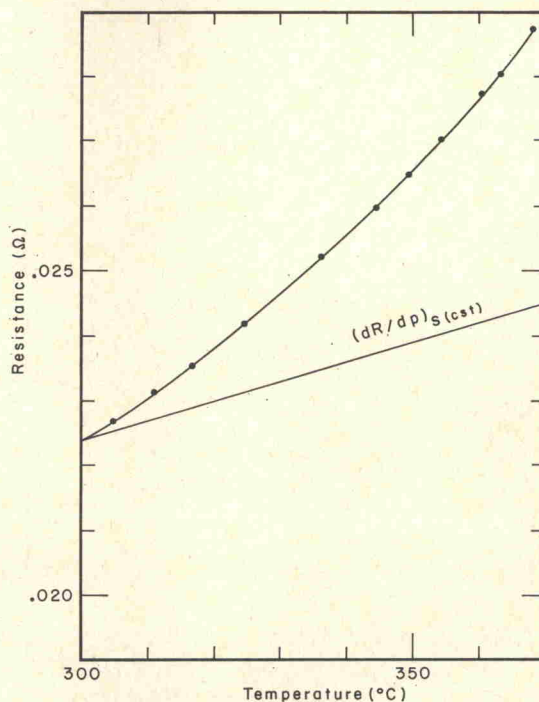


FIG. 9. The equilibrium resistance of a large domain sample as a function of temperature at 1 kbar. The straight line illustrates the temperature-dependent portion of the resistance. The difference between the curves is the order-dependent resistance.

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  $368^\circ\text{C}$  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  $25^\circ\text{C}$  was determined as follows:

(1) A large domain sample was reheated to  $368^\circ\text{C}$  in the annealing furnace and equilibrated at a series of temperatures from  $368^\circ\text{C}$  to  $298^\circ\text{C}$ . 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  $368^\circ\text{C}$ , quenching to room temperature, and measuring the variation resistance at constant order in the range from  $22$ – $38^\circ\text{C}$ . The temperature coefficient of resistance of the quenched sample at constant order,  $(dR/dT)_q$ , was  $3 \times 10^{-5} \Omega/^\circ\text{C}$ .

The assumptions are made that the temperature coefficient of resistance at constant order in the range from  $368^\circ$  to  $298^\circ\text{C}$  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.

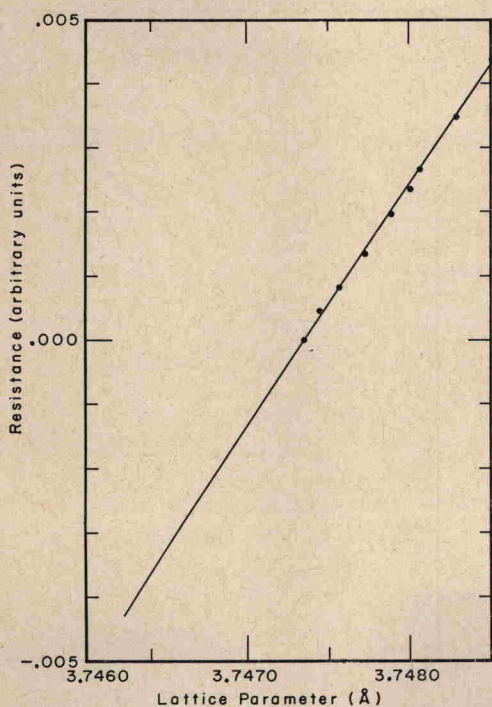


FIG. 10. The equilibrium order-dependent resistance vs the equilibrium lattice parameter as determined by Feder, Mooney, and Nowick (see Ref. 5). Temperature is the independent variable.

(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,  $R_0(25^\circ\text{C})$ , 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

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

for the monitored sample. Thus a measurement of the initial resistance of a specimen installed in the anvil apparatus is sufficient to determine  $R_0(25^\circ\text{C})$  for that specimen.

(4) In order to determine the temperature and pressure coefficient of  $R_0$  for each sample, so that  $R_0(T_{\text{anneal}})$  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

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

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

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,  $1/R_0(dR_0/dT)_{P,S}$ , by the constant of proportionality 0.76.

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