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On the Kinetics of Ordering in  $\text{Cu}_3\text{Au}$ F. A. Mohamed, K. Linga Murty and J. E. Dorn<sup>†</sup>

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Several resistometric studies<sup>1-10</sup> have been made on the kinetics of ordering in  $\text{Cu}_3\text{Au}$  following quenching. Minor discrepancies exist in some of the reported data and some differences in opinions have been expressed regarding interpretation of these data. Furthermore, several facets of the subject have not been adequately explored. Nevertheless there now appears to be a fair agreement on all major issues. The research of Benci et al.<sup>10</sup> is most pertinent to the present discussion: Following quenching thin wires .04 mm in diameter from a series of temperatures covering the range  $T_c < T < 1073^\circ\text{K}$ , they determined  $\frac{R_T - R_{T_c}}{R_T}$  where R is the resistivity measured at room temperature and the subscripts refer to the temperature from which the specimens were quenched.  $(R_T - R_{T_c})/R_T$  decreased as T was first increased above  $T_c$ , reached a minimum value at about  $T = 723^\circ\text{K}$ , and increased as T was increased above  $723^\circ\text{K}$ . Obviously at least two factors are responsible for the variation of the resistivity of quenched  $\text{Cu}_3\text{Au}$  as a function of the quenching temperature. The resistivity of  $\text{Cu}_3\text{Au}$  is known to increase with both increasing vacancy concentration<sup>1</sup> and increasing absolute degree of short-range order,<sup>4</sup> and it decreases with increasing

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<sup>†</sup> deceased, Sept. 1971.

degree of long-range order.<sup>11</sup> The possibility that increasing degrees of long-range order can account for the decreasing values of  $(R_T - R_{T_c})/R_T$  with increasing values of  $T$  over the range  $T_c < T < 723^\circ\text{K}$  can be disqualified on the basis of several observations, the most direct being the fact that isothermal annealing of quenched specimens at  $438^\circ\text{K}$  results first in a decrease in the resistivity followed by an increase in resistivity. The latter can only be due to predominance of short-range ordering over other factors. Furthermore as shown by Dugdale<sup>2</sup> specimens quenched from just below  $T_c = 663^\circ\text{K}$  exhibit upon annealing only decrease in resistivity coincident with elimination of excess vacancies and long-range ordering. Consequently, the variations of  $(R_T - R_{T_c})/R_T$  with quenching temperature must be ascribed to short-range order and vacancy effects. Over the lower range of quenching temperatures where  $T_c < T < 723^\circ\text{K}$  the predominant factor appears to be the decreasing value of the quenched-in absolute degree of short-range order with increasing quenching temperature, whereas above  $723^\circ\text{K}$  the effect of increasing excess vacancies plays the predominant role. These conclusions are also in agreement with those presented earlier by Damask.<sup>12</sup> Thus  $\text{Cu}_3\text{Au}$  can be quenched sufficiently rapidly from above  $T_c = 663^\circ\text{K}$  to avoid long-range ordering. Furthermore the absolute degree of short-range order under equilibrium conditions at the quenching temperature must be frozen into the as-quenched  $\text{Cu}_3\text{Au}$  with no, or at most, negligible increases in value.

Whether excess quenched-in vacancies can be retained over several days in as-quenched specimens might be estimated from annealing kinetics. In the light of the previous discussion the early stages of annealing could involve two simultaneous trends, a decrease in resistivity arising from migration of excess vacancies to sinks and an increase in resistivity due to short-range order. Since the resistivity is more sensitive to vacancy concentration, this effect will predominate at first, resulting in a decrease in resistivity, followed subsequently, when the excess vacancy concentration is small, by an increase in resistivity due to an increase in the absolute degree of short-range order. Only following much longer times will the resistivity decrease again as a result of transformation from short-range to long-range order. Such general trends upon annealing have been reported by Benci et al.<sup>10</sup> and Brinkman et al.<sup>1</sup>

Annealing data at a series of temperatures from 363°K to 473°K were obtained by Benci et al.<sup>10</sup> following quenching from 803°K. The ratio  $R/R_0$ , of the instantaneous to initial resistivity initially decreased rapidly, reached a minimum value and then increased very slowly with time. Obviously over the initial stages of annealing the decrease in resistivity due to migration of excess quenched-in vacancies to sinks predominated over the minor concomitant increase in resistivity resulting from short-range ordering, whereas in the final stage the excess vacancy concentration was so low that the effects of short-range ordering on the resistivity predominated. The fact that about the same minimum value of  $R/R_0$  was obtained regardless of the annealing

temperature can be attributed to the fact that the differences in the equilibrium concentration of vacancies over the range of annealing temperatures was negligibly small in contrast to the excess quenched-in vacancy concentration. Since both the migration of excess vacancies to sinks and short-range ordering are dependent on the migration of vacancies, the annealing data for all temperatures should correlate as shown in Fig. 1 to give a single curve in terms of the temperature compensated time,  $t_e (-E_m/R_T)$ , where  $E_m = 16.6$  kcal/mole is the activation energy for migration of vacancies. Similar values for  $E_m$  have been obtained by a number of investigators.<sup>2,10,13,14</sup> The upper scale in Fig. 1 gives an extrapolation of these data in terms of the time of anneal at 290°K. Assuming that most of the excess vacancies have been eliminated when  $R/R_0$  reaches its minimum value, it is noted that the excess vacancy concentration in quenched  $\text{Cu}_3\text{Au}$  becomes small after a 3000 hr hold at room temperature.

It is well known that following the previously described initial period of adjustment,  $\text{Cu}_3\text{Au}$  quenched from above  $T_c$ , can be held for very long periods of time at room temperature without material changes in its ordering-sensitive properties. This shows that the equilibrium concentration of vacancies is so low and their rate of migration at room temperature is so slow that they provide infinitely slow rates of short-range ordering. Consequently the terminal slow increase in resistivity documented in Fig. 1 must be due to excess vacancies. Such order will continue until the excess vacancy concentration reaches some terminal residual value.

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TIME OF ANNEAL AT 290°K, HRS.

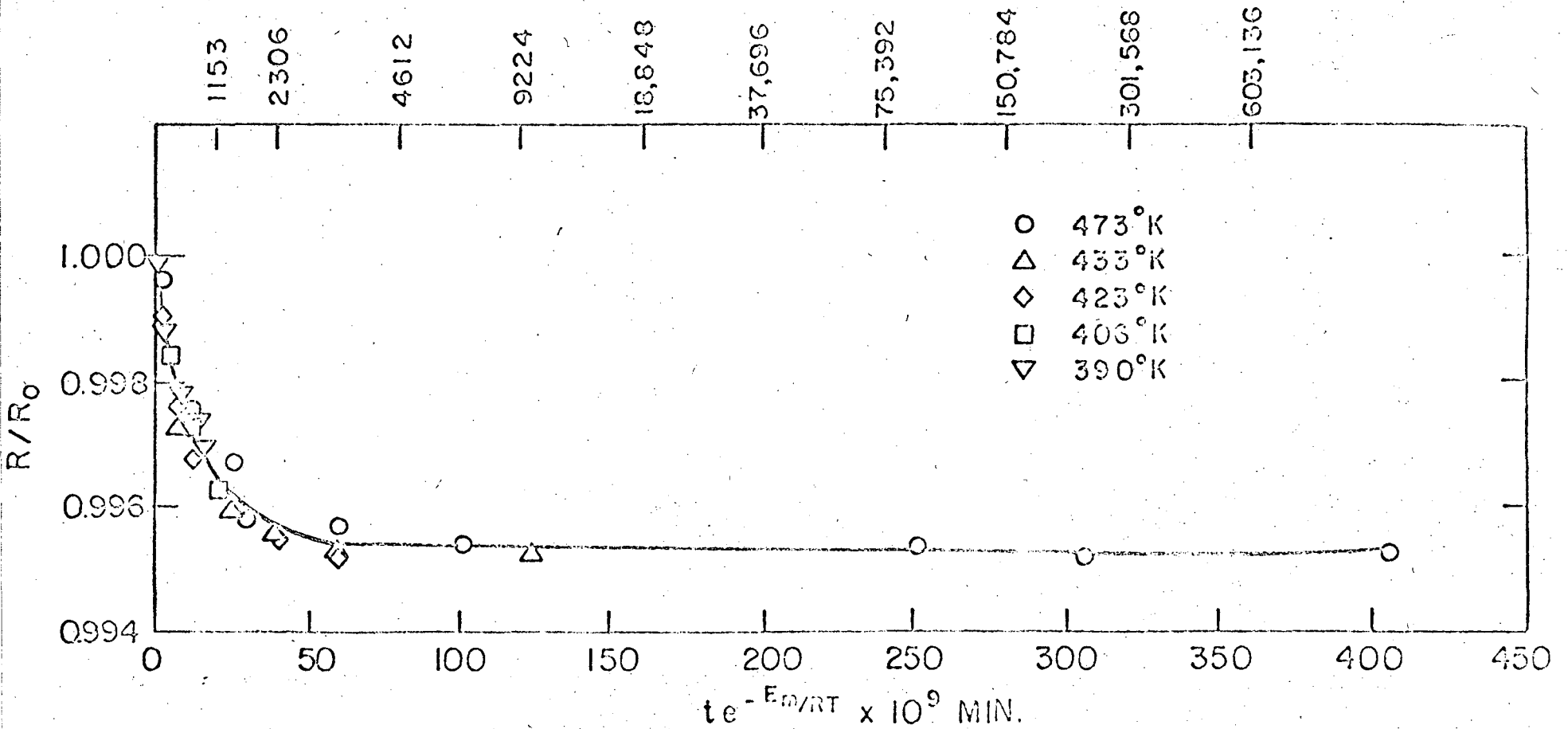


FIG. 1. RATIO OF THE INSTANTANEOUS TO INITIAL RESISTIVITY vs.  $t e^{-E_m/RT}$ .

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