

## Investigation of the relaxation process in the $\text{Cu}_3\text{Au}$ -alloy order-disorder phase transition near the transition point

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An investigation of the relaxation process in the  $\text{Cu}_3\text{Au}$ -alloy order-disorder phase transition near the transition point has been performed by observing the time dependence of the electrical resistivity of samples which are quenched from the disordered state to the ordered one very near the phase-transition point. It is found that the relaxation time becomes longer with the approach of the temperature to the order-disorder phase-transition point. The critical index of the Ising relaxation time  $\tau$  is obtained as  $\Delta = 1.20 \pm 0.16$ .

### I. INTRODUCTION

Many authors<sup>1</sup> have been interested in the problem of the order-disorder transition in a binary alloy, which seems to be typical of the Ising spin model. The static problem of the critical phenomena related to the order-disorder phase transition has been investigated more than adequately by many authors,<sup>2</sup> but, the dynamic problem near the order-disorder phase-transition point has hardly been made clear. In order to clarify this problem, we have investigated the electrical resistivity of  $\text{Cu}_3\text{Au}$ . The  $\text{Cu}_3\text{Au}$  alloy was chosen for the following reasons. The relaxation time from the disordered state to the thermal-equilibrium state at a temperature below the phase-transition temperature is so long that experimental measurements can be carried out very easily. Moreover, a great variety of experimental results<sup>1</sup> is available which can be used for discussions. As the phase change of  $\text{Cu}_3\text{Au}$  is of the first order, it might be inappropriate to select the  $\text{Cu}_3\text{Au}$  alloy to study the critical phenomenon. However, the phase-transition point of the first order is close to a hypothetical transition point ( $T_c$ ) of the second order, which is estimated from results<sup>1</sup> on the temperature dependence of the electrical resistivity of  $\text{Cu}_3\text{Au}$  as compared with the phase change of a three-dimensional Ising spin system.<sup>3</sup> Therefore, it is thought that these circumstances are not always fatal defects for the  $\text{Cu}_3\text{Au}$  alloy.

In this study, to obtain the relaxation time from the disordered state to the ordered state near the phase-transition point of  $\text{Cu}_3\text{Au}$ , we measured the change of electrical resistance when the annealing temperature of the specimen is abruptly changed from the temperature above the phase-transition point to a certain temperature below it.

### II. EXPERIMENTS

The  $\text{Cu}_3\text{Au}$  alloy was prepared from a 99.99% pure copper sheet and a 99.999% pure gold shot by vacuum melting the constituent metals together in a silica tube at 1150 °C. The specimen with the

size of  $1.5 \times 1.5 \times 50 \text{ mm}^3$  was cut from the ingot and was annealed for 3 days at 900 °C. Chemical analysis and x-ray analysis confirmed that the alloy was homogeneous.

The electrical resistance of the specimen was measured by the following procedure. A solid resistor of 50  $\Omega$  was connected with the specimen in series and an alternating electric field of 80 Hz was applied to both. The resistance of the specimen ( $\sim 10^{-3} \Omega$ ) was negligibly small compared with 50  $\Omega$ , and an electric current passing through the specimen was unchanged despite the change in the resistance of the specimen. The voltage between the two ends of the specimen was measured with a lock-in amplifier whose output was recorded on a multipoint chart recorder. A platinum-versus-platinum-13% rhodium thermocouple with a junction spot adjacent to the specimen was used to determine the temperature and its voltage was measured with a potentiometer. The temperature of the furnace was controlled within  $\pm 0.1$  °C with a proportional-integral-derivative control system.

### III. EXPERIMENTAL RESULTS

The experiments were performed in the following sequence. First, the  $\text{Cu}_3\text{Au}$  specimen was heated in a furnace at 673 K, at which temperature Cu and Au atoms are distributed randomly. Then, the sample was suddenly quenched to and kept at a certain temperature below the transition temperature  $T_t = 664.2 \text{ K}$ . The electrical resistance decreases very slowly with time to its value in the thermal-equilibrium state,  $R_e$ .

A typical experimental result is shown in Fig. 1(a). The logarithm of  $R - R_e$  is plotted against the time  $t$  elapsed after quenching to 653.1 K. In the region  $t > 300 \text{ min}$ , the change of the electrical resistance is described by an exponential function of  $(-t/\tau)$ . Therefore, it is thought that the time dependence of the resistance has the form

$$R - R_e = Af(t) + B e^{-t/\tau}, \quad (1)$$

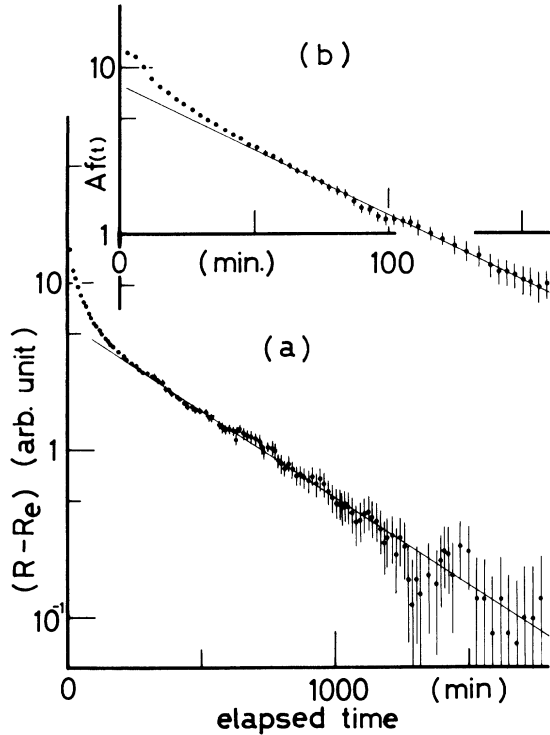


FIG. 1. (a) Electrical resistance ( $R - R_e$ ) of the quenched specimen from 673 to 653 K plotted against elapsed time  $t$  on a semilog scale. The oblique straight line is calculated by using the second term of Eq. (1). (b) The first term in Eq. (1),  $Af(t)$ , plotted against elapsed time  $t$  on a semilog scale. The oblique straight line is drawn by assuming that  $Af(t)$  is described by a single exponential function of  $(-t/\tau)$ .

where  $A$  and  $B$  are constants and  $\tau$  is the relaxation time. Figure 1(b) shows the logarithm of  $Af(t)$  plotted against the elapsed time  $t$ . The first steep decrement of  $R - R_e$  may be thought to be caused by the rapid change of the lattice parameter, nucleation of domains, and so on. Therefore, the time dependence of  $Af(t)$  is not expected to be described by a single exponential function of  $t$ . At each temperature below  $T_i$ , the time dependence of  $R - R_e$  is similar to the examples shown in Figs. 1(a) and 1(b). From the time dependence of the electrical resistance after 300 min the relaxation time  $\tau$  was obtained. Figure 2 shows the relaxation time plotted as a function of temperature. The relaxation time  $\tau$  in Fig. 2 becomes longer as the temperature approaches  $T_i$  and this seems to be a critical slowing-down phenomenon.

#### IV. DISCUSSION

First, we discuss the resistivity due to deviations in the average periodic potential in a binary alloy.

Fisher and Langer<sup>4</sup> have shown that the dominant

contribution to the magnetic resistivity  $\rho_{\text{mag}}$  of metal is due to short-range spin fluctuations. Simons and Salamon<sup>5</sup> measured simultaneously the specific heat and the temperature derivative of the resistivity of  $\beta$ -brass near its order-disorder transition point and an extension of the Fisher-Langer theory for magnetic transitions is used to explain their results. As described by Simons and Salamon, the contribution of the short-range order in  $\beta$ -brass to the energy density may be expressed in the Ising-model form

$$U_c = -J \sum_{ij} \langle \sigma_i \sigma_j \rangle, \quad (2)$$

where the sum is taken over nearest-neighbor ion pairs, and the convenient notation  $\sigma_i = \pm 1$  is used for the occupation of the  $i$ th lattice site by an atom of Cu or Zn, respectively. They conclude that  $\rho_c(T) \propto U_c(T)$ , where  $\rho_c$  is the resistivity due to deviations in the average periodic potential, since the temperature dependence of both  $\rho_c(T)$  and  $U_c(T)$  is determined by the nearest-neighbor correlations.

In view of the relation  $\rho_c \propto U_c(T)$ , the theoretical conclusions for the Ising spin system may be applicable to explain the experimental result on  $\rho_c$ . Therefore, the relaxation time determined from the time dependence of the transient electrical resistivity may correspond to the correlation time between adjacent spins in the Ising spin system. As the temperature approaches the phase-transition temperature, the spin correlation time becomes longer; hence the temperature dependence of the relaxation time obtained from  $\rho_c$  is expected to show

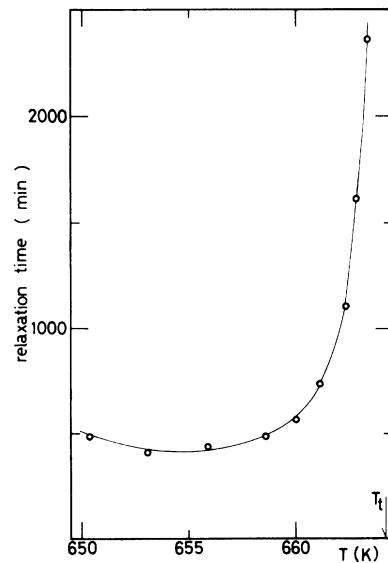


FIG. 2. Relaxation time  $\tau$  plotted as a function of temperature. The phase-transition temperature of the first order is shown as  $T_i$ .

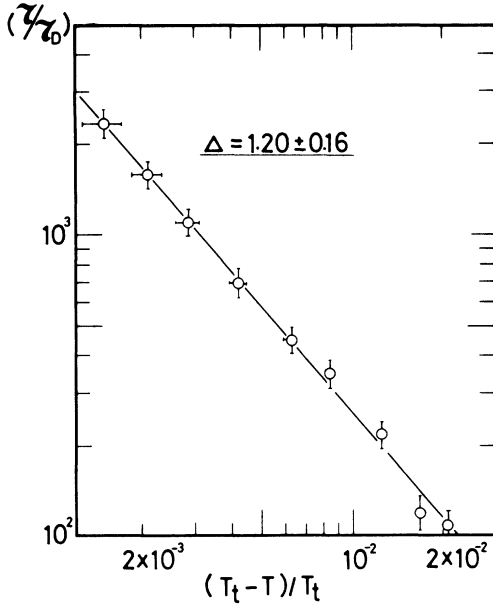


FIG. 3. Ratio of the relaxation time  $\tau$  to the diffusion time  $\tau_D$  plotted against the reduced temperature  $(T_t - T)/T_t$  on a  $\log_{10}$ - $\log_{10}$  scale. The critical exponent  $\Delta$  is  $\Delta = 1.20 \pm 0.16$ . The experimental error is mainly due to the uncertainty in the phase-transition temperatures.

the critical slowing-down phenomenon. Though the phase transition of  $\text{Cu}_3\text{Au}$  is of the first order, the phase-transition point ( $T_t$ ) of the first order is very close to a hypothetical transition point ( $T_c$ ) of the second order. The correlation time between  $\sigma_i$  and  $\sigma_j$  in the  $\text{Cu}_3\text{Au}$  alloy becomes longer as the temperature approaches  $T_c$ . At  $T_t$ , as the disordered state appears suddenly, the increment of the correlation time is cut off. This speculation explains comparatively well our experimental results.

Finally, let us consider the temperature dependence of the relaxation time. After Mason,<sup>6</sup> the spin-relaxation time in the Ising model is given by

$$\tau = \frac{1 + \beta\chi_0}{\cosh(\beta\sigma M/kT)} \tau_0$$

and (3)

$$\tau_0 = (1/2\Gamma)e^{\Delta U/kT},$$

where  $\beta$ ,  $\chi_0$ , and  $M$  are a molecular-field coefficient, the magnetic susceptibility, and the magnetic moment, respectively, and  $\Delta U$  is a potential barrier which prevents the spin rotation. According to Eq. (3) the temperature dependence of the

relaxation time  $\tau$  is determined by the product of  $\chi_0$  and  $\tau_0$  in the vicinity of the Curie temperature.

The relaxation mechanism of the order-disorder transition in a binary alloy may be explained qualitatively by the above model.<sup>7</sup> As shown in Fig. 2, the temperature-dependence curve of the relaxation time  $\tau$  in  $\text{Cu}_3\text{Au}$  shows a clear minimum somewhere around 655 K. The same result is observed by Nagy and Nagy.<sup>8</sup> These results suggest that the observed relaxation time is composed of two kinds of terms depending on temperature in opposite ways: One is the diffusion time of each atom,  $\tau_D$ , and the other is the term corresponding to  $(1 + \beta\chi_0)/\cosh(\beta\sigma M/kT)$  in Eq. (3). Therefore, it has been assumed that the observed relaxation time  $\tau$  is proportional to the product of the above two terms, that is,

$$\tau = C(T) \tau_D. \quad (4)$$

The diffusion time  $\tau_D$  is assumed to be expressed by the following formula with reference to Eq. (3):

$$\tau_D = D e^{E/kT}, \quad (5)$$

where  $k$  is the Boltzmann constant and  $E$  is the activation energy for the dominant diffusion process. The term  $C(T)$  has been assumed to vary with temperature as

$$C(T) \propto (T_t - T)^{-\Delta}. \quad (6)$$

Equations (4)–(6) have been fitted by least squares to the data of Fig. 2. The best fit gives  $E = 1.6$  eV which is consistent with Nagy's result  $E = 0.84$  eV.<sup>8</sup> Figure 3 shows  $\tau/\tau_D$  plotted against  $(T_t - T)/T_t$  on a  $\log_{10}$ - $\log_{10}$  scale. The critical exponent  $\Delta$  is obtained as  $\Delta = 1.20 \pm 0.16$ . The uncertainty in  $\Delta$  is due to the experimental ambiguity of the phase-transition temperature. A theoretical value of  $\Delta$  equal to  $\gamma'$  in three dimensions (1.25) is in accord with our experimental results, though the  $\text{Cu}_3\text{Au}$  alloy phase transition is considered to be of the first order. Our  $\Delta$  value is also consistent with the results for the antiferroelectric substance  $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$  whose phase change is of the first order.<sup>9</sup> A more rigorous theory of the first-order phase change is required for a more precise discussion of the  $\Delta$  value.

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