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CRITICAL STRESS-INDUCED RELAXATION IN RELATION TO LONG-RANGE ORDERING, IN Au₃Cu, AND SELF-INDUCED ORDERING, IN AuNi SOLID SOLUTIONS

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Summary - This paper reports the results of combined measurements of the resistivity and anelasticity of Au₃Cu and Au₇₀Ni₃₀ alloys. The data show anomalies above the critical temperature for long range order in Au₃Cu and below the spinodal in Au₇₀Ni₃₀. In both cases the anomalies suggest the existence of intermediate states. In Au₃Cu this is a state of pronounced short range order whereas in Au₇₀Ni₃₀ it is an intermediately decomposed state.

Résumé - On présente les résultats de mesures combinées de résistivité et d'anélasticité dans des alliages Au₃Cu et Au₇₀Ni₃₀. Les grandeurs mesurées manifestent des anomalies, au-dessus de la température critique pour l'ordre à longue distance dans Au₃Cu et au-dessous de la spinodale dans Au₇₀Ni₃₀. Dans les deux cas, ces anomalies suggèrent l'existence d'états intermédiaires. Dans Au₃Cu, c'est un état d'ordre à courte distance prononcé, tandis que dans Au₇₀Ni₃₀, il s'agit d'une forme intermédiaire de décomposition.

1. INTRODUCTION

Critical phenomena in the vicinity of second and first order phase transformations are well known (1). These include the premonitory effects observed in first order solid state phase transformations (2). Since both classical and positional ordering is accompanied by microscopic dimensional changes, critical anelastic effects must be expected in the vicinity of both types of transformations (3). For diffusion controlled transformations however, critical anelasticity has not received much attention (4), in contrast to martensitic transformations.

In this paper we present the results of anelastic studies of Au₃Cu and Au₇₀Ni₃₀ alloys. These experiments combined with resistivity studies show that in Au₃Cu strong deviations of the Curie-Weiss behaviour of the anelasticity above the critical temperatures of classical order are caused by the increase in short range order. The critical anelasticity in Au₇₀Ni₃₀ is less well understood. The result of this work seems to indicate a tendency towards ordering as well.

2. THE NATURE OF AuCu AND AuNi SOLID SOLUTIONS

The nature of AuCu and AuNi solid solutions has been the subject of a large number of investigations (5). The two alloys differ in that the former shows short and long range chemical order while the latter shows clustering or decomposition. The critical temperatures for the two alloys under consideration are : 473 K for the order-disorder transformation A2-L1₂[I] in Au₃Cu and 950 K and 500 K for the lower limit of the solute solubility and the spinodal respectively in Au₇₀Ni₃₀ (6).

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All these temperatures are quite low. The solid state reactions of interest are thus controlled by diffusivities ranging from $10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$ to $10^{-26} \text{ m}^2 \cdot \text{s}^{-1}$ (7) and hence very sluggish.

The dissimilarity of the nature of AuCu and AuNi solid solutions occurs in spite of the similar size difference of both solutes, Cu and Ni, which have 13 % and 16 % smaller atomic radii than the Au host. This considerable size difference gives rise to large anelastic effects in the homogenous solid solutions well above the critical temperatures (4,8,9). It will be seen, however, that in the vicinity of the critical temperatures the behaviour of the anelasticity of the two alloys is different.

3. EXPERIMENTAL DETAILS

In general, the reader is referred to reference (10) for information on the experimental procedures. The following details are relevant to this study: the ingots were prepared from high purity starting materials and samples were prepared by rolling and subsequent homogenization and recrystallization anneals of two days at 873 K for Au₃Cu and two weeks at 1050 K for Au₇₀Ni₃₀. Both survey type isochronal and detailed isothermal resistivity measurements were performed as well as isothermal strain relaxation experiments. For the latter the 1.6 cm long sample was mounted vertically in a balance system so that it could be strained by placing small weights on the balancing arm. The resulting length changes were detected with a microwave system with a sensitivity of 2 nm.

4. EXPERIMENTAL RESULTS

4.1. Pretransitional ordering in Au₃Cu

The isochronal resistivity data shown in Fig. 1 show in which temperature ranges marked changes occur within 10 min. Included in this figure are results of longer anneals which are indicated by the respective annealing times. This figure demonstrates that after a quench from a temperature in which the short range order is relatively low but well pronounced, 612 K, the resistivity and hence the short range order increases until a 10 min anneal is sufficient to achieve the equilibrium value of the short range order at around 500 K. Thereafter, the equilibrium short range order decreases as expected (10). The resistivity and its changes of a sample quenched nominally from 1050 K are significantly different in three respects. First, due to the accelerated kinetics during the quench, the initial resistivity is higher than the one in the sample quenched from 612 K. Second, only a small increase in resistivity and hence local order is observed at low annealing temperatures. The third and most pronounced difference is the steep decrease and subsequent increase of the resistivity in the temperature interval between about 350 K and 500 K. These changes reflect the establishment of the long range order and the subsequent decrease of its equilibrium value as the critical order-disorder temperature of 473 K is reached. The rising branch of the isochronal resistivity between about 430 K and 473 K reflects the equilibrium character of the equilibrium long range order.

A portion of Fig. 1 and Fig. 2 contains information on the evolution of the short range order upon extended isothermal annealing. In all cases it is seen that the values of the measured parameters, the resistivity shown in Fig. 1 and the anelasticity shown in Fig. 2, indicate deviations from the values expected from an extrapolation from high temperature. It is qualitatively clear that the long time increase of the resistivity shown in Fig. 1 reflects an increase of the degree of the short range order (10). In the discussion it will be shown that the anelastic data lead to the same conclusion.

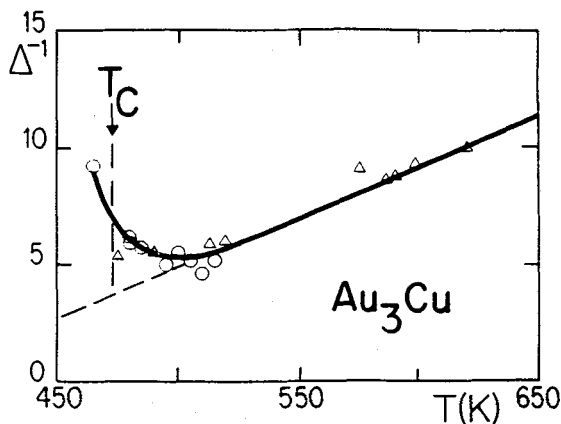
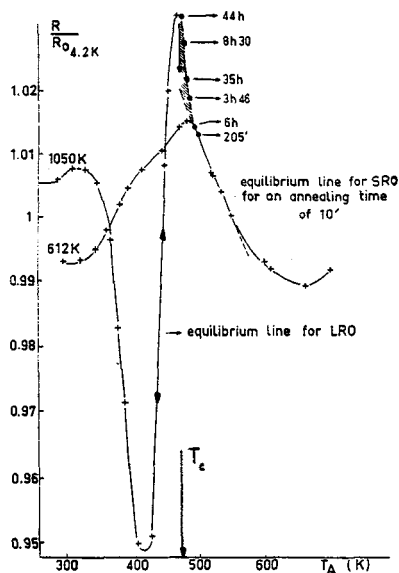


Fig. 1 (left). The isochronal (10 min) annealing of the resistivity ratio R/R_0 of Au_3Cu measured at 4.2 K; R_0 is the equilibrium resistivity measured after a quench from 550 K. The results of the anneals after two quenches from 612 K and 1050 K respectively are shown. The data points identified with a time indicate the equilibrium resistivity reached after these long times. The quantity T_c represents the critical temperature of long-range ordering in Au_3Cu .

Fig. 2 (right). The reciprocal relaxation strength Δ^{-1} of Au_3Cu as a function of the temperature T . The critical temperature of long range ordering, T_c , is indicated in the figure.

4.2. Clustering in $Au_{70}Ni_{30}$

The isochronal resistivity measurements made on $Au_{70}Ni_{30}$ alloys quenched from two different temperatures shown in Fig. 3 display formally the same trends as the one seen in Fig. 1. A sample quenched from a low temperature, 630 K, reaches monotonously the equilibrium short range order at about 510 K. The sample quenched from the higher temperature, 1050 K, and containing a higher vacancy supersaturation, however, develops a higher degree of short range order first until the resistivity drops because of the kinetic onset of the spinodal decomposition. Thereafter, the resistivity rises until the spinodal temperature of about 500 K is reached. It should be emphasized that the rising branch between about 430 K and 500 K in Fig. 3 is reversible as is also indicated by the arrows. The nature of this state will be discussed below.

The reproduction of prior elastic after effect measurements confirmed the Curie-Weiss type behaviour also in $Au_{70}Ni_{30}$ as can be seen in Fig. 4. This figure shows that the relaxation strength reaches 160 % ! Another remarkable feature of this relaxation process is the wide distribution of the relaxation times characterized by Gaussian half width between 2 and 3, as can be seen in Fig. 5.

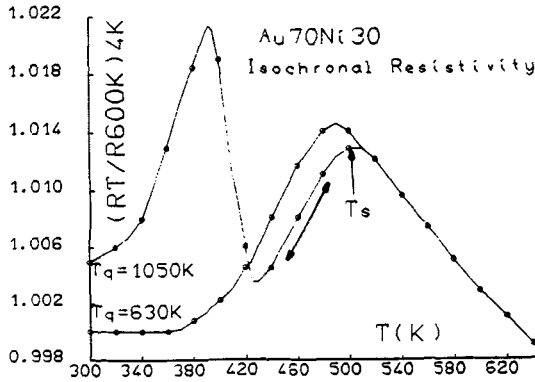


Fig. 3. The isochronal (10 min) annealing of the resistivity ratio R/R_0 of $Au_{70}Ni_{30}$ measured at 4.2 K ; R_0 is the equilibrium resistivity measured after a quench from 630 K. The results of the anneals after quenches from 630 K and 1050 K respectively are shown. The quantity T_s represents the coherent spinodal.

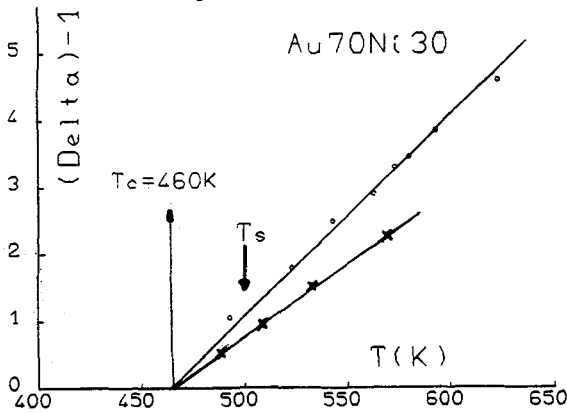


Fig. 4. Reciprocal relaxation strength Δ^{-1} of slowly cooled $Au_{70}Ni_{30}$ as a function of temperature T : (●) after (5), (+) present data. The critical temperature T_c is interpreted to represent a phase transformation.

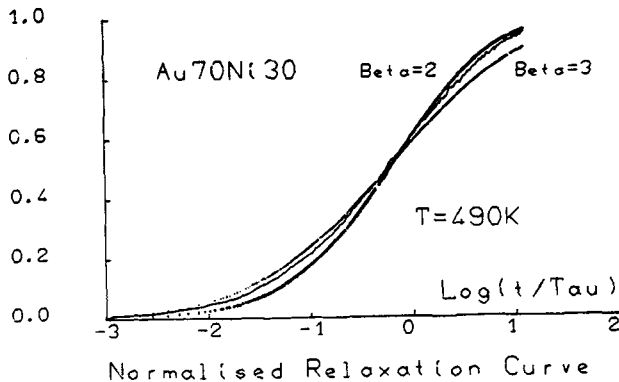


Fig. 5. Normalized isothermal strain relaxation of $Au_{70}Ni_{30}$ measured at 490 K.

The critical temperature determined from these experiments, 460 K, does not, however, coincide with any known critical temperature in $Au_{70}Ni_{30}$. It was noticed that a slowly quenched sample deforms spontaneously upon annealing below 460 K. Simultaneously the resistivity drops by about 20 %. Both phenomena are reversed by heating to a temperature higher than 460 K. It is suggested that a hitherto unknown phase transformation occurs at this temperature.

5. DISCUSSION

While it is true that the ground states of Au_3Cu and $Au_{70}Ni_{30}$ are long range ordered and decomposed respectively, the evolution of these states depends critically on the initial condition and intermediately ordered or decomposed states appear to be interspersed between the solid solution and ground states. The experimental results presented in the previous section contribute to an understanding of the subtleties of the situation in both alloy systems. The deviations of the Curie-Weiss behaviour of the reciprocal relaxation strength evident in Fig. 2 can be readily understood in terms of the increase in the short range order in the vicinity of the critical temperature of long range order. A Curie-Weiss law holds only if both the total number and the moment of the elastic dipoles giving rise to the relaxation remain constant (11). Neither is true if it is recalled that the anisotropy of the Zener relaxation must be interpreted in terms of second nearest neighbour interactions and a full set of short range order parameters (12). Using the theory of Welch and Leclaire the leading terms of the polynomial representing the relaxation strength Δ_{WLC} may be written as

$$\Delta_{WLC} \approx \Delta_{LCL} (1 - 2\alpha_1 + 2\alpha_2 - 2\alpha_3 + \alpha_4) \quad (1)$$

where Δ_{LCL} represents the relaxation strength due to the stress induced change of the local order in the first shell around a reference atom only (13). The parameters α_i denote the short range order parameters for the i 'th shell. Using the values α_i obtained by Monte-Carlo simulations at the critical temperature, 473 K (7), Eq. (1) yields $\Delta_{WLC} \approx 2\Delta_{LCL}$. The factor two is close to the greatest deviation of the relaxation strength from a Curie-Weiss behaviour at the critical temperature seen in Fig. 3.

The reversibility of the resistivity below the spinodal is somewhat unexpected as it might be thought that the decomposition process in $Au_{70}Ni_{30}$ is irreversible. There are, however, already indications of quasi-stationary states in this alloy below the spinodal (14): it has been observed that only fluctuations of a particular wavelength around 10 Å develop. In particular, the expected coarsening, i.e. the growth of fluctuations with increasing wavelengths could not be detected. The observed reversibility of the resistivity agrees qualitatively with this observation: according to the lattice model of the elastic free energy of solid solutions, one has for the amplification factor R of a Fourier component i of the concentration fluctuation c

$$R(k_i) \propto f'' + K_1 M(k) + K_2 k^2 \quad (2)$$

In this equation, the quantity f'' denotes the second partial derivative of the free energy with respect to the composition, the quantity K_2 represents the combined chemical and elastic gradient energies and K_1 is a measure of the specific coherency strain introduced by a concentration fluctuation. Finally, the function $M(k)$ describes in a simplified way the wavevector dependence of the modulus M . According to Eq. (2) it is possible that a certain concentration fluctuation i for which $M(k_i)$ has a minimum grows while all others do not. The reversibility of the resistivity shown in Fig. 3 now suggests that the growth of this concentration fluctuation reaches a limit at a certain stage, i.e. $R(k_i)$ becomes zero again at a finite

amplitude of the fluctuation. Formally, this can be incorporated into Eq. (2) by assuming that $M(k_1) = f[e(c)]$ where e is the coherence strain introduced by the fluctuation c . This implicit strain dependence of the effective modulus is nothing else but the anharmonicity of the solid solution. The stationary concentration fluctuation $c(k_1)$ and hence the resistivity can now vary reversibly as the temperature is changed according to the variation of f . This agrees with the observations shown in Fig. 3.

The critical temperature at 460 K which indicates that a phase transformation occurs under certain quenching conditions, i.e. whenever a composition fluctuation of a certain wave number k_1 has evolved, can also be phenomenologically understood in terms of equation (2). If the effective modulus becomes negative this transformation would be bainitic in nature, i.e. it is at least partially diffusion controlled.

In summary, the combined measurements of the anelasticity and resistivity of Au_3Cu and $Au_{70}Ni_{30}$ alloys indicate that states of intermediate order or disorder exist in the vicinity of first order transformations. In the case of the alloy Au_3Cu tending towards long range order, this is a state where the range of the local order extends to higher and higher order neighbours. In $Au_{70}Ni_{30}$ alloys, tending towards decomposition, the opposite occurs. Here, a composition fluctuation with an intermediate wave number k where $0 < k < k_B$ appears to be at least metastable.

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