and the particle volume is given by

$$V = (5kT/I_s H)(H_A/H_A^{SP}) \quad (4)$$

where $H_A = -15\,000$ G and $H_A^{SP}$ is the experimental value, $-39.18$ G. We have also $T = 300$ K, $I_s = 3.1$ erg cm$^{-3}$ G$^{-1}$ [8], and $H = 3300$ G. Substituting these values into Equation 4, we get $V = 2.56 \times 10^{-20}$ cm$^3$ or $a = V^{1/3} = 37.5$ Å. This is somewhat smaller than the size estimated by Kalyamin *et al.* [2] using the Mössbauer effect (50 to 100 Å).

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## *Phase decomposition in liquid-quenched eutectic Au–Ge alloy*

Liquid-quenched (LQ) Au–Ge alloys have been observed to contain a number of metastable phases which depend on quenching condition and rate, as well as alloy content [1–4]. Scott [4] recently investigated the formation and stability of the metastable phases in LQ eutectic Au–27% Ge (all compositions are given in atomic percent) by X-ray diffraction and thermal analysis techniques. He found that LQ from the temperature range 500 to 1300° C yields a three-phase microstructure: Au-rich f c c phase, $\alpha$; metastable h c p-phase, $\beta$; and a second metastable phase, $\gamma$, with a b c t structure. Samples quenched at a slower rate from 500° C contained only the $\alpha$ and the $\gamma$ phases. Furthermore, on the basis of the DTA results during isochronal annealing, Scott [4] concluded that the LQ eutectic Au–Ge decomposes in two single stages: (i) decomposition of the $\beta$-phase into equilibrium $\alpha$ and Ge in the temperature range 70 to 100° C; (ii) decomposition of the b c t-$\gamma$ into $\alpha$ and Ge at about 125° C.

X-ray diffraction was used mainly for identifying the metastable phases in Scott's study. Because of the coexistence of a number of constituent phases with widely different volume fractions, and in view of the fact that the mass absorption coefficient of Au is very high as compared to that of Ge, any Ge-rich phase which may be present as a minor constituent can easily go undetected.

In the present work the Au–27% Ge eutectic alloy was prepared by inert-gas induction melting of appropriate amounts of high-purity materials. The homogeneity of the alloy was ensured by repeated melting and quenching into water. Small samples of this alloy were then LQ from 800° C using the gun-technique, yielding typical cooling rates in excess of $10^{6\circ}$ C sec$^{-1}$. Samples from the bulk of the gun-quenched foils (~60 to 70 $\mu$m thick) were used for isochronal and isothermal resistivity measurements. The resistivity measurements were made employing a standard four-probe potentiometric technique. Ageing of the resistivity samples was carried out in appropriate baths controlled to ±0.5° C. The resistivity measurements were made in acetone at 21° C. X-ray diffraction measurements on the central bulk samples were carried out on a diffractometer. A Debye–Scherrer camera was used for obtaining powder patterns from the LQ thin edge flakes. It was ensured that the bulk samples and the flakes used in X-ray analysis contained the same phases in the as-LQ condition. Small flakes from the edges of the gun-quenched samples were also used for TEM. Ageing of the TEM specimens was done *in situ* in the microscope hot stage.

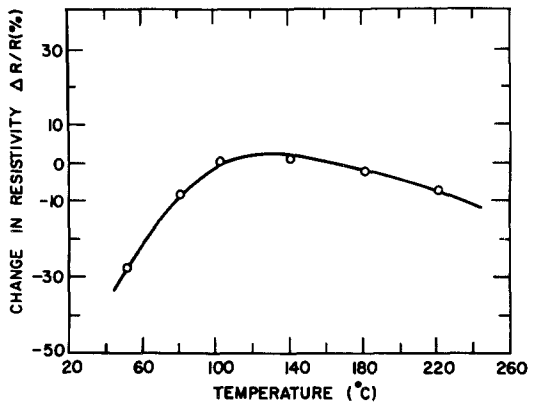


*Figure 1* Isochronal annealing curve for LQ Au–27% Ge. (5 min at each temperature).

From the X-ray patterns of the as-LQ specimens the following three phases were detected: Au-rich equilibrium f c c-phase, $\alpha$; metastable b c t-phase, $\gamma$; very weak relections from the equilibrium Ge-phase. The lattice parameter of the as-LQ f c c $\alpha$ was found to be 4.082 Å, which is in good agreement with values reported by other authors [1–4]. It should be noted that the existence of the Ge-phase in as-LQ eutectic Au–Ge has not previously been reported. The presence of the Ge-phase was also confirmed by TEM.

Fig. 1 shows the temperature dependence of the percent change in resistivity during isochronal annealing. The annealing time at each temperature was 5 min. Table I lists the various phases detected at each temperature and their relative X-ray intensities. The lattice parameter of the f c c $\alpha$-phase was found to decrease on annealing in the temperature range 60 to 100° C. It is to be noted that

TABLE I X-ray intensities of the phases detected during the isochronal annealing of LQ Au–27 at% Ge. The alloy was held for 5 min at each temperature.

| Annealing temperature (° C) | Phases detected (X-ray intensities) |
|---|---|
| As-LQ | f c c $\alpha$ (weak) + metastable b c t $\gamma$ (strong) + Ge (very weak) |
| 50 | f c c $\alpha$ (medium strong) + b c t $\gamma$ (strong) + Ge (very weak) |
| 80 | f c c $\alpha$ (strong) + b c t $\gamma$ (medium) + Ge (weak) |
| 100 | f c c $\alpha$ (strong) + b c t $\gamma$ (weak) + Ge (weak) |
| 120, 140 | f c c $\alpha$ (strong) + Ge (weak) |
| above 140 | f c c $\alpha$ (very strong) + Ge (weak) |

Scott [4] detected a broad peak in his DTA work in this temperature range and attributed it to the transformation of the metastable h c p $\beta$-phase into the equilibrium $\alpha$ and Ge phases. Although we did not detect the presence of the h c p $\beta$-phase from the X-ray patterns, TEM examination of the LQ foils (Fig. 2a) did show some faulting in the matrix, indicating that the h c p-phase is present as a minor constituent. Thus, the observed annealing behaviour in the temperature interval 60 to 100° C is probably due to the transformation of the h c p $\beta$ into the equilibrium components $\alpha$ and Ge. The micrograph in Fig. 2a also shows that the Ge-phase, exhibiting a lighter contrast, forms a thin, generally interconnected network around grains which contain the Au-rich phases. This seems surprising because in the temperature regime 60 to 100° C, where the lattice parameter of the $\alpha$-phase shows a decrease, the isochronal resistivity (Fig. 1) increases gradually to a maximum at about 100° C. It would seem that the Ge rejected from the $\beta$-phase is absorbed by the Ge-rich phase present at the grain peripheries. Since the Ge-rich phase is a poor conductor, compared with Au, its continuity gives an increase in resistivity in the temperature range 60 to 100° C, where one would normally expect to see a decrease due to the rejection of Ge by the $\beta$-phase. Above 100° C, the Ge-phase begins to lose its connectivity (Fig. 2b) and both the resistivity and the lattice parameter of the Au-rich $\alpha$-phase decrease with increasing temperature. The isochronal resistivity curve displays a broad maximum at 120° C, after which the resistivity decreases. Scott [4] also observed a sharp peak at 125° C in DTA measurements, which he attributed to the transformation of the metastable $\gamma$-phase into $\alpha$ and Ge. This seems to be the case in the present case as well.

Isothermal resistivity experiments, Figs. 3a and b, were carried out at several temperatures. At 65° C (Fig. 3a), only single stage annealing is seen, which is attributed to the decomposition of the metastable $\beta$-phase. At 100° C (Fig. 3a), however, annealing results in two stages: The first stage at early times corresponds to the decomposition of the h c p $\beta$-phase, described above; the second stage at later times represents the decomposition of the metastable b c t $\gamma$-phase. As shown in Fig. 3b, isothermal annealing at 120, 140, and 180° C is marked by a single stage, which is due to the trans-

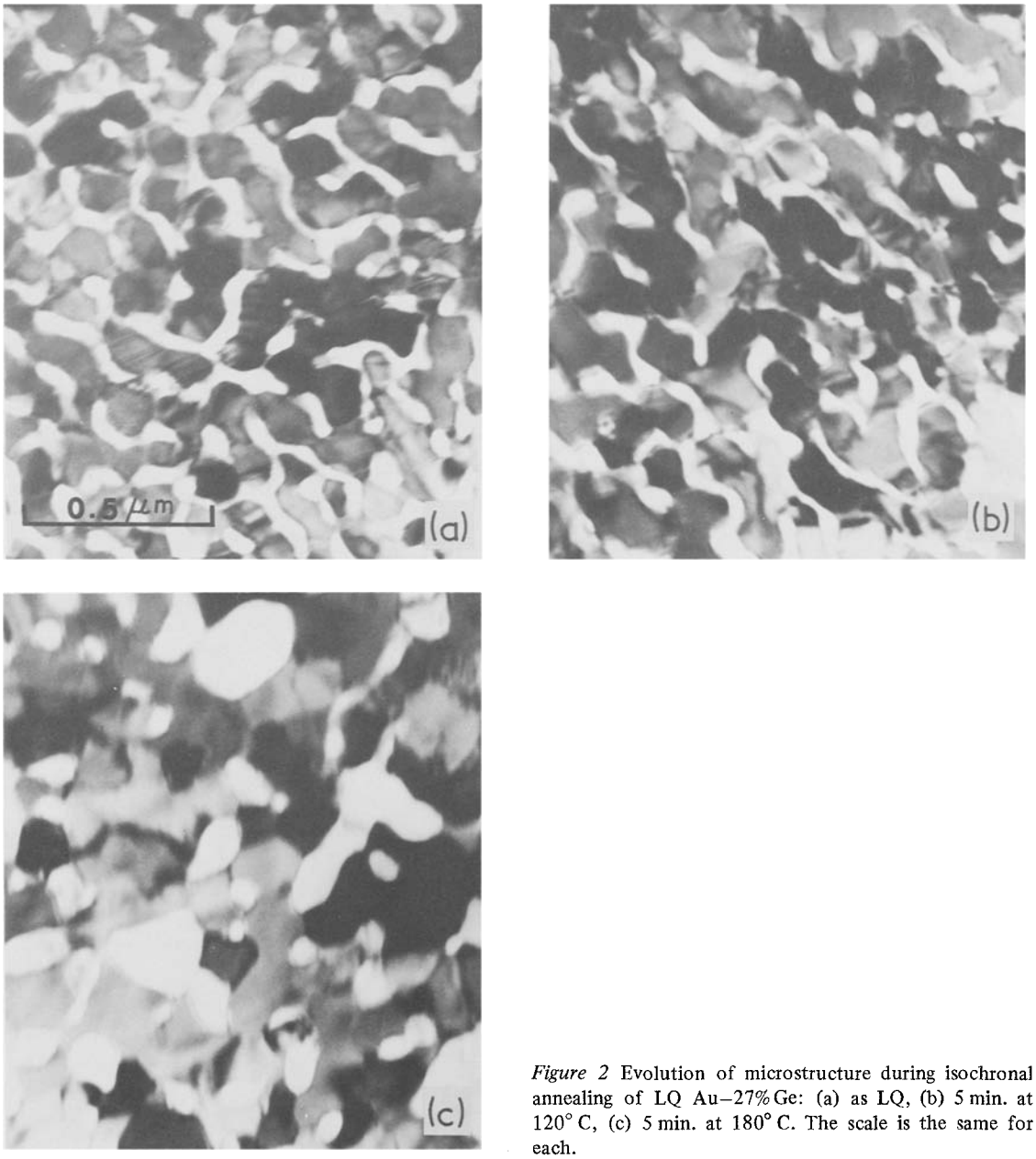


*Figure 2* Evolution of microstructure during isochronal annealing of LQ Au–27% Ge: (a) as LQ, (b) 5 min. at 120° C, (c) 5 min. at 180° C. The scale is the same for each.

formation of metastable $\gamma$-phase into the equilibrium constituents, $\alpha$ and Ge. The annealing stage representing the decomposition of the $\gamma$-phase in Fig. 3b is preceded by an "incubation time", $\tau$. This period decreases with increasing annealing temperature. The microstructure recorded after isochronal annealing for 5 min at 180° C consists of a completely disconnected two-phase structure (Fig. 2c). The volume fraction of the Ge phase seems to have increased as compared with the as-LQ condition (Fig. 2a).

The decomposition stages observed in this investigation are in good agreement with those reported by Scott [4]. As pointed out before, other authors have not reported the presence of the Ge-phase in the as-LQ state. Our as-LQ microstructure (Fig. 2a) has a significant volume fraction of Ge-phase, and its morphology appears to

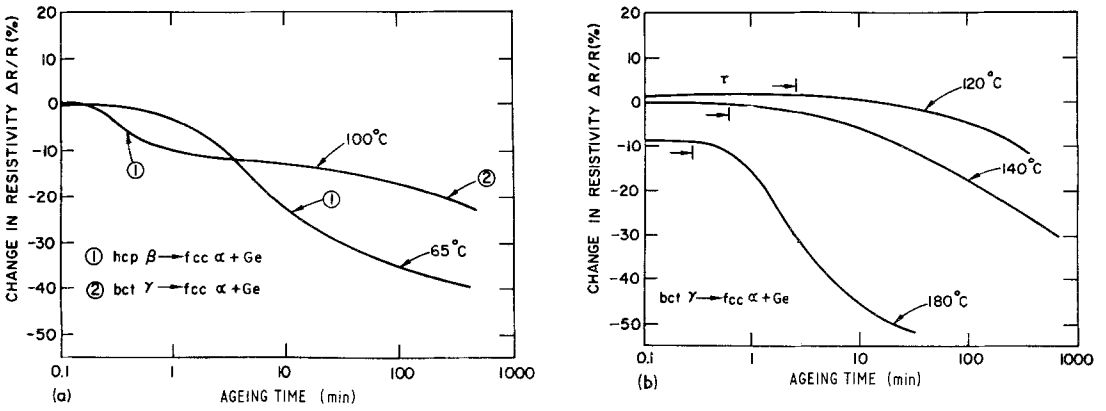


*Figure 3* Isothermal annealing curves for LQ Au–27% Ge. (a) At 65 and 100° C, (b) at 120, 140, and 180° C.

control the course of the resistivity change during isochronal annealing at lower temperatures. The present results indicate that the decomposition of the metastable $\beta$ and $\gamma$ phases into the equilibrium $\alpha$ and Ge phases involves the growth of the equilibrium phases, already present in the as-LQ state, instead of nucleation and growth. X-ray results alone are not sufficient for identifying all of the metastable phases which may be present in varying quantities. TEM and electrical resistivity have aided in establishing the modes of decomposition.

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