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A MEASUREMENT OF THE VACANCY SINK EFFICIENCY OF STACKING-FAULT TETRAHEDRA IN QUENCHED GOLD

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R.W.Siegel[†], K.C.Jain[†], T.Schober[**], R.W.Balluffi[**] and L.E.Thomas[††]

ABSTRACT

The efficiency of stacking-fault tetrahedra as sinks for supersaturated vacancies in quenched gold was measured using stereo electron microscopy. A uniform distribution of partially grown tetrahedra, embedded in a uniform concentration of supersaturated vacancy defects in the vicinity of a free surface, was first established. Upon subsequent annealing, the vacancy defects then annealed to either the partially grown tetrahedra or the free surface. The competition between the surface and tetrahedron sinks near the surface caused a decrease in the final tetrahedron size toward the surface after complete annealing.

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[†] Department of Materials Science, State University of New York at Stony Brook, Stony Brook, L.I., New York.

[**] Department of Materials Science and Engineering, Cornell University, Ithaca, New York.

[††] Now at: Edgar C. Bain Laboratory for Fundamental Research, United States Steel Corporation Research Center, Monroeville, Pennsylvania.

The tetrahedron size as a function of distance from the surface was measured by stereo electron microscopy, and these data, in conjunction with the solution of the appropriate diffusion problem for this situation, allowed a determination of the average sink efficiency $\bar{\epsilon}$. A value $\bar{\epsilon} \simeq 0.7$ at 60°C was obtained indicating that the tetrahedra were relatively good vacancy sinks under the prevailing experimental conditions. This value is in good agreement with a previous determination under similar conditions using a more laborious sectioning technique.

1. INTRODUCTION

Supersaturated vacancy defects in quenched gold precipitate in the form of stacking-fault tetrahedra[1,2] under certain conditions. The tetrahedra apparently are nucleated at impurities[3] and then grow by the absorption of vacancy defects.[4,5] In a number of experiments efforts have been made to measure the migration properties of quenched-in vacancy defects under conditions where the annealing occurred to tetrahedra.[6,7] The tacit assumption in these experiments was that the rates of vacancy annealing were diffusion limited, and that the tetrahedron sinks acted with an absorption efficiency of unity*, since the driving force tending towards equilibrium was large because of the high

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* An absorption or sink efficiency of unity is taken to correspond to a condition under which the vacancy concentration is maintained essentially at the equilibrium value over the entire surface of the sink.

vacancy supersaturations present ($\sim 10^8$ to 10^{10}). However, work by Siegel[3] indicated that this assumption may not be justified, since a comparison of isothermal annealing rates at constant effective migration energy showed that tetrahedra in the size range 344-942 Å were approximately ten times less efficient as sinks than "black-spot defects" at vacancy concentrations in the range of $1.11\text{x}10^{-5} \geq c_v \geq 0.67\text{x}10^{-5}$ at 60°C. It could be concluded, therefore, that the average tetrahedron sink efficiency, $\bar{\epsilon}$, was ~ 0.1 under those conditions, if one assumed that the "black-spot defects" had an efficiency of unity.

Subsequently, Siegel et al.[8] measured $\bar{\epsilon}$ directly using an electron metallography technique. Tetrahedron growth as a function of distance from a free surface was measured after annealing by a rather laborious sectioning technique. Since both the tetrahedra and the surface acted as sinks, the competition between the surface and the tetrahedra for migrating vacancies caused the tetrahedron growth to be reduced near the surface (see Fig. 1). The appropriate competitive diffusion problem was solved, and a value of $\bar{\epsilon} \simeq 0.6$ at 60°C was deduced from a comparison of the theoretically and experimentally determined variation of tetrahedron size as a function of distance from the surface.[8] This value, obtained for vacancy concentrations essentially an order of magnitude higher than in the previous work of Siegel,[3] was not necessarily inconsistent with the earlier result, since it might be qualitatively expected that the sink efficiency would decrease with decreasing vacancy supersaturation as the associated driving force decreases.

In the present work we have repeated the earlier experiment[8] using an improved technique in which stereo electron microscopy was used to measure in a more direct way the variation of tetrahedron size with distance from the surface. The work was carried out in order to substantiate further the earlier results and to obtain a quantitative comparison between the stereo electron microscopy technique and the electron metallography sectioning technique used previously.[8]

2. EXPERIMENTAL PROCEDURE

The first step was to establish a uniform distribution of partially grown tetrahedra embedded in a uniform concentration of supersaturated vacancy defects in the vicinity of a clean free surface as illustrated in Fig. 1 (initial state). Upon subsequent annealing, the vacancy defects would then anneal to completion by competitive absorption at either the surface or tetrahedron sinks causing a decrease in final tetrahedron size toward the surface as indicated in Fig. 1 (final state).

The samples were prepared from a ribbon shaped polycrystalline foil of COMINCO Grade 59 gold of 99.999 wt. % nominal purity with a gauge section 8.0 cm long, 0.48 cm wide and 0.011 cm thick. The ribbon was shaped into a standard quenching specimen[8] and mounted on a heavy copper frame and resistance heated for 1 h at 930°C in order to both anneal and purify it.[7] The shape of the specimen was such that a uniform temperature could be maintained along the gauge length during resistance heating, quenching strains could be minimized, and the gauge length could enter the quenching medium (distilled water at 25°C) edge-on.

Quenching was accomplished by holding the specimen ~ 0.5 cm directly above the water while heated to the quench temperature of 930°C, holding it for about 2-3 min, and then dropping the entire assembly into the water. The specimen quench temperature was measured with an optical pyrometer, and it was verified that temperature uniformity over the gauge length to within ± 2°C was achieved.

After quenching, the specimen remained at room temperature (~ 25°C) for 3.0 ± 0.5 min while necessary handling operations were performed. The specimen was then aged for 15 min at 60 ± 1°C in order to nucleate completely tetrahedra throughout the bulk. The central portion of the gauge length was subsequently cut into six rectangular samples (0.48 cm by approximately 0.85 cm) to be used for obtaining the tetrahedron size *versus* depth data. Of the two remaining ends, one was used to determine the initial tetrahedron size just after the 15 min anneal at 60°C, and the other was used to determine the final tetrahedron size in the specimen bulk after complete annealing at 60°C.

In order to remove the region near the specimen surface which was perturbed due to vacancy losses during the quench, and to provide a new clean surface in a region of uniform tetrahedra and supersaturated vacancies prior to the final annealing treatment, all six rectangular samples were electro-thinned for 5 min at 63°C in the standard cyanide electrolyte[9] so that a thickness of ~ 16μ was removed from each surface. The thickness removed was determined by weight loss measurements using a calibration of sample weight loss versus sample thickness which was performed independently on identical samples. It was determined in a previous investigation[8] that this thickness decrease was sufficient to remove any perturbed region entirely. All of the samples, except those to be used for the determination of the initial tetrahedron size, were then annealed at 60 ± 1°C for 24 h in order to produce complete vacancy annealing.

The initial tetrahedron size was determined from the sample taken from the end of the gauge length which had only the post-quench 15 min anneal at 60°C. Subsequent to this aging treatment, the sample was stored for about 2 h at -15°C and then electrothinned for microscopic examination at 0°C for about 30 min and examined immediately. As such, it was possible to observe the sample under conditions of no appreciable additional annealing. The final bulk tetrahedron size was measured in the sample taken from the other end of the gauge length after the completion of vacancy annealing. The tetrahedron size distributions and densities in these samples were determined in the standard fashion.

The tetrahedron size versus distance away from the surface was directly measured using stereo electron microscopy on the remaining six rectangular samples which were prepared for stereo microscopy as follows. One surface was masked off, and the specimen was electro polished from the opposite surface by a selective perforation technique[8] until perforation just occurred. This procedure produced a thin wedge-shaped region around the periphery of the perforation which was suitable for transmission microscopy and which was bounded on one surface by the original masked surface. The masking was removed from the original surface, and a small amount of tin was then evaporated on this surface. This step provided a background of circular tin islands about 100 Å in diameter (and of negligible thickness) on this surface which provided a reference plane for the parallax measurements associated with the stereo microscopy technique. Stereo micrograph pairs at approximately normal incidence to the original surface (see below) were obtained by tilting the specimens around the operating reflection vector $\vec{g}$ (here $\vec{g}$ = (200)) and photographing the same areas under similar kinematical diffraction conditions at different tilt angles. The magnification was 40,000X, and total tilt angles of 10-25° were used. The parallax values were measured directly from the original micrographs using a Hilger-Watts Mirror Stereoscope with a 4X binocular and a floating spot measuring device. The uncertainty in the depth positions of the tetrahedra was estimated to be ± 25 Å.

3. RESULTS

The results are presented in Fig. 2. The tetrahedron density in all of the regions observed was found to be essentially the same, with an average value of $N_s = (1.31 \pm 0.21) \times 10^{15}$ cm^{-3}, verifying that during the 15 min post quench aging treatment at 60°C nucleation had been completed and that the subsequent experiment was performed under conditions of growth only. The stereo electron microscopy data are denoted by solid (●) points. Each of these points represents an average of ten individual measurements and, therefore, has the same statistical weight. The root mean square (RMS) edge lengths for the initial and final bulk tetrahedron distributions obtained by the standard technique, are denoted by the cross-open (⊗) points at $x = 0$ and $x = \infty$, respectively. The error bars represent mean deviations. The initial RMS edge length was found to be $L_o = 268 \pm 17$ Å, as determined by observations of seven different specimen areas and the measuring of 1594 tetrahedra. The final RMS edge length in the specimen bulk was $L_b = 472 \pm 14$ Å, as determined by observations of ten different specimen areas and the measuring of 2160 tetrahedra.

Using $L_b = 472$ Å, and $N_s = 1.31 \times 10^{15}$ cm^{-3}, the total fractional vacancy concentration stored in the tetrahedra in the unperturbed volume was found to be $c_v = 2.95 \times 10^{-4}$.[10] This value agrees very well with the expected total vacancy concentration at 930°C in gold.[11]

The theoretical curves presented in Fig. 2 were calculated from the solution of the appropriate diffusion equation for the annealing of an initially uniform average concentration, $c_o = c(x,0)$, of mobile vacancy defects, with diffusion coefficient D, to a flat surface at $x = 0$ and a uniform density of stacking-fault tetrahedra which act as competitive sinks, in the form:[8]

$$\frac{\partial c(x,t)}{\partial t} = D \left\{ \frac{\partial^2 c(x,t)}{\partial x^2} - 2\pi N_s \bar{\Gamma}\bar{\epsilon} L(x,t) c(x,t) \right\}, \qquad (1)$$

where the first term (RHS) is the divergence of the diffusion current in the volume, and the second term (RHS) describes the sink action of the tetrahedra. The factor $\bar{\Gamma}$ in the second term (RHS) takes into account the growth of a tetrahedron relative to its sphere of influence, is a function of $(LN_s^{1/3})$, and increases monotonically from its value of unity at $L = 0$.* The steady state solution to Eq. (1), under the assumption that $\bar{\epsilon}$, $\bar{\Gamma}$ and D could be taken as averaged constant values, was found in our previous work[8] to be

$$x = \left[\frac{3}{2\pi N_s \bar{\Gamma}\bar{\epsilon} L_b} \right]^{\frac{1}{2}} \int_{w_o}^{w} \frac{dw}{(w^3 - 3w + 2)^{1/2}}, \qquad (2)$$

where $w = \dfrac{L(x,t)}{L_b}$, the fractional tetrahedron size, with an initial value of $w_o = w(x,0) = L_o/L_b$.

In carrying out the integration to obtain Eq. (2), we employed the boundary condition $w = w_o$ at $x = 0$ for all t: i.e., we assumed no tetrahedron growth at the surface. According to the present model, this assumption should be true if the surface

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* The quantity $\bar{\epsilon}$ is the absolute tetrahedron sink efficiency which is defined as the actual current of vacancies to a tetrahedron divided by the current which would reach the tetrahedron if it acted as a perfect sink. In our previous work[8] we erroneously described $\bar{\epsilon}$ in this equation as the tetrahedron efficiency relative to that of the free surface.

acts as a perfect sink, since no growth should be expected if the vacancy concentration in the vicinity of the tetrahedra at the surface is maintained essentially at equilibrium (see Eq. (1)). (We are, of course, neglecting small differences between the equilibrium concentrations at a tetrahedron and a flat surface.) It should be noted, however, that some tetrahedron growth at the surface is actually to be expected even if the surface is an efficient sink, and that this growth is not predicted by the present model because of its relative coarseness. An estimate of the actual tetrahedron growth at the surface under conditions where both the surface and the tetrahedra act as perfect sinks may be made by using the result of Venables and Balluffi[12] that the flux received by such a tetrahedron (treated as a hemispherical dimple on the surface) should be about three times the unperturbed flux which would have reached the same area of the surface in the absence of the tetrahedron. Applying this result to the present data we estimate a tetrahedron growth increment of about 20 Å. This increment is relatively small and indicates that our present model (represented by Eqs. (1) and (2)) should be adequate despite its comparative coarseness provided that the surface acts as a perfect sink.

In our previous work,[8] theoretical curves of L versus x were determined numerically from Eq. (2). However, Eq. (2) can be integrated, and the solution may be written as

$$x = [2\pi N_s \bar{\Gamma}\bar{\epsilon} L_b]^{-1/2} \ln\left(\frac{\sqrt{3}+\sqrt{w+2}}{\sqrt{3}-\sqrt{w+2}} \cdot \frac{\sqrt{3}-\sqrt{w_o+2}}{\sqrt{3}+\sqrt{w_o+2}}\right) . \quad (3)$$

The theoretical curves presented in Fig. 2 were, therefore, calculated using Eq. (3) for $\bar{\epsilon} = 1.0, 0.6, 0.3$, and 0.1 using the values of $L_o = 268$ Å, $L_b = 472$ Å, $N_s = 1.31\mathrm{x}10^{15}$ cm^{-3} and $\bar{\Gamma} = 2.16$ determined in the present experiment. The value of $\bar{\Gamma}$ used was taken as the arithmetic average of the initial and final values of $\bar{\Gamma}$ found directly from the experimental values of L_o, L_b, and N_s.

From a comparison of the experimental data points with the theoretical curves in Fig. 2, it may be concluded that the sink efficiency of the stacking-fault tetrahedra averaged over the major portion of their gorwth was $\bar{\epsilon} \simeq 0.7$ at 60°C, and that the tetrahedra therefore acted as quite good sinks over most of their growth. It is noted that the data appear to be consistent with little tetrahedron growth at the surface, and that our assumption of an efficient surface sink therefore seems justified. This latter result is apparent from the data shown in Fig. 2 of reference 8 and also from further as yet unpublished measurements.[13]

4. DISCUSSION

The present result is seen to be in good agreement with $\bar{\epsilon} \simeq 0.6$ found in our previous determination[8] under essentially the same conditions. The major difference between the two electron metallography methods which we have used is that in the stereo technique employed here, the distances of the individual tetrahedra from the surface sink are measured directly, whereas, in the sectioning technique used earlier[8] these distances were obtained for large ensembles of tetrahedra by taking the mean distances of these ensembles from the competitive surface. Thus, the two techniques appear interchangeable if sufficient statistical data are taken. The apparent scatter in the individually measured tetrahedron sizes at a given value of x in Fig. 2 is due to the fact that the tetrahedra have essentially a normal size distribution. It is interesting to note that an extrapolation of the mean of the stereo electron microscopy data to the limits $x = 0$ and ∞ gives good agreement with the values found for L_o and L_b even though the two types of electron microscopy data were obtained independently in two different laboratories.

The necessity of having more information regarding the sink efficiency of vacancy precipitates is clear if one looks at the second term (RHS) in Eq. (1) which describes the rate of annealing of vacancies to the tetrahedron sinks. Since the efficiency, $\bar{\epsilon}$, enters as a linear factor, as does the diffusion coefficient, D, if one assumes that the annealing is solely diffusion limited, as has been the general assumption in the past,[6,7] then the rate controlling <u>effective</u> diffusion coefficient is the product $(\bar{\epsilon}D)$. Thus, if it is desired to obtain mobile vacancy defect parameters, such as their diffusion coefficient or effective migration energy, from experiments in which vacancy loss to sinks is taking place, a knowledge of $\bar{\epsilon}$ is necessary. For example, if the efficiency is temperature dependent the effective migration energy would, in fact, contain a sink contribution in addition to the vacancy defect migration energy being sought. Further work concerning the temperature dependence of $\bar{\epsilon}$ of tetrahedra in quenched gold is currently in progress.[13]

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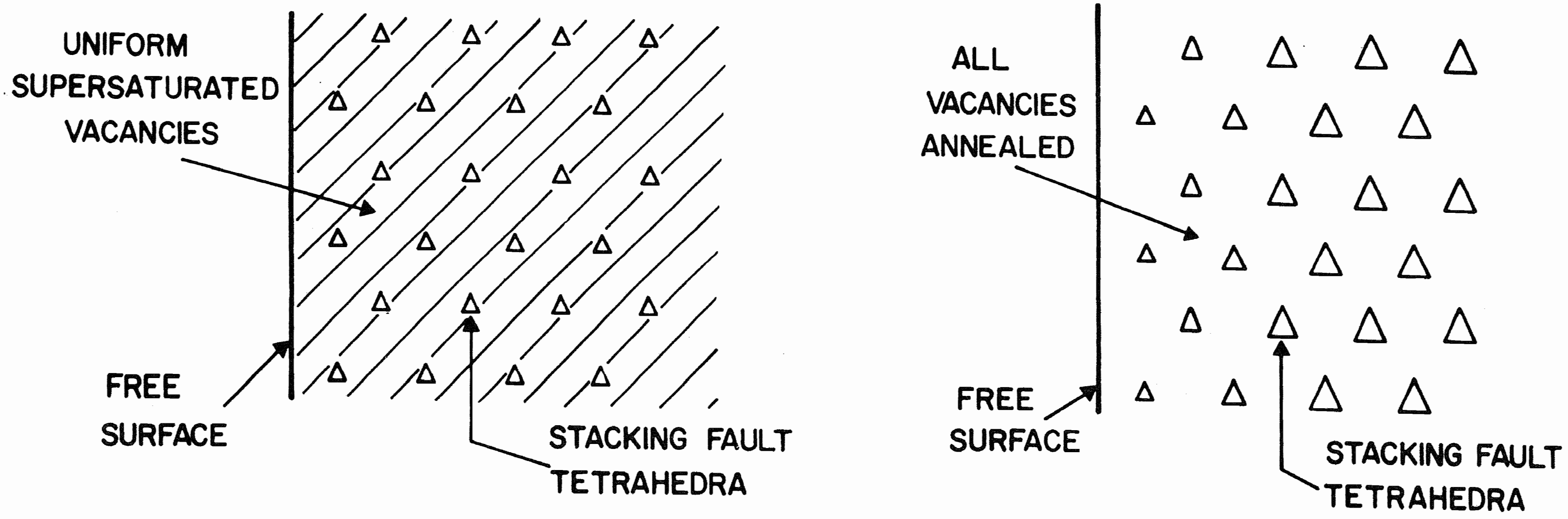
FIGURE CAPTIONS

Figure 1. An idealized representation of the initial and final states of the samples in the present experiment. The triangles represent schematically the distribution of tetrahedron average size and density in the samples.

Figure 2. The tetrahedron edge length, L, as a function of distance, x, from the competitive surface sink. The experimental data points are compared with the solution to the theoretical diffusion problem for various values of the average tetrahedron sink efficiency, $\bar{\epsilon}$. The solid (●) experimental data points represent stereo microscopy data, and the crossed-open (⊗) points represent conventional statistical electron microscopy data of the initial and final tetrahedron sizes in bulk.



INITIAL STATE

FINAL STATE

Figure 1

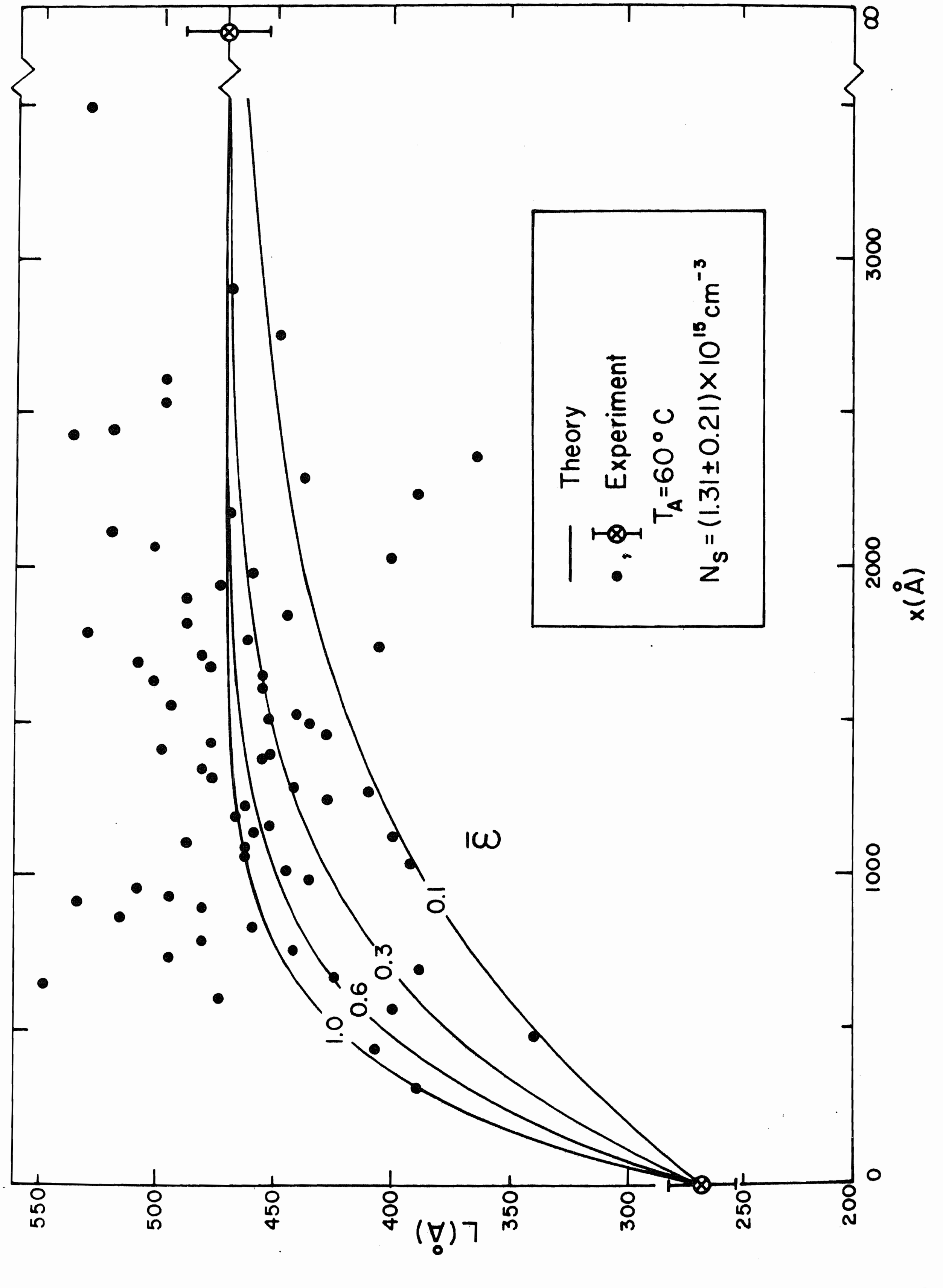

L(Å)
550
500
450
400
350
300
250
200
x(Å)
0
1000
2000
3000
∞
1.0
0.6
0.3
0.1
ω̄
Theory
Experiment
T_A=60°C
N_S = (1.31±0.21)×10^{15}cm^{-3}

Figure 2