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PRECIPITATION OF VACANCIES IN QUENCHED ALUMINUM

Jean-Loup Bernard Strudel

(Ph. D. Thesis)

August 1968

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PRECIPITATION OF VACANCIES IN QUENCHED ALUMINUM

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ABSTRACT

The major goal of this work was to study the influence of the quenching temperature and the aging temperature on the nucleation and growth of Frank loops and octahedral voids and to determine the conditions favoring the nucleation of voids over loops.

High purity aluminum single crystals were grown and shaped so as to facilitate resistivity measurements, high heating rates and direct observation by electron transmission microscopy on the same specimen.

The samples were quenched from 425°C, 475°C, 525°C or 575°C to -110°C and then pulsed to aging temperatures ranging from -40°C to +100°C. Isothermal annealing curves were obtained by resistivity measurements at liquid helium temperature.

The apparent activation energy for the annealing was found to be $E_2^m = 0.27$ eV at low T_a , and $E_1^m = 0.48$ eV for $T_a > 20^\circ\text{C}$. Voids and dislocation loops were present in every case in different proportions with sizes ranging from 40 Å to 500 Å for the voids and 100 Å to 6000 Å for loops. The use of (110) single crystals facilitated the observation of very small voids.

The results suggest that precipitation of supersaturated vacancies in secondary defects proceeds by a coarsening mechanism. A qualitative interpretation of these results and others is presented and suggestions

are made for a more quantitative model.

The present results indicate that a high initial concentration of divacancies favors the formation of loops over that of voids. The growth rate of loops seems to be higher than that of voids only when defects are distant by less than a hundred interatomic distances.

Details on the performance and design considerations of the up-quenching device are presented in Appendix I.

Some estimates of lattice relaxations and expected width of electron microscopy pictures associated with the voids are reported in Appendix II.

I. INTRODUCTION

Point defects can be introduced in pure metals by three methods:

(1) quenching the metal from high temperature where applicable concentrations of vacancies are present at equilibrium, (2) irradiation by particles or ions able to knock atoms out of their equilibrium sites, thus creating usually both interstitial and vacancy type defects, and (3) plastic deformation at low temperature which also produces both kinds of defects.

The presence of point defects in a lattice in excess of their equilibrium concentration c at the absolute temperature T , increases the free energy of the crystal. If S^f is the formation entropy and E^f the formation energy of the type of point defect considered, its equilibrium concentration is given by the expression:

$$c = \exp (S^f/k) \exp (-E^f/kT)$$

After the quench, in order to lower its free energy, the crystal will tend to eliminate any supersaturation in point defects. If the temperature is high enough, diffusion will take place and isolated defects will migrate and reach surfaces, grain boundaries, and dislocations, or recombine and annihilate when possible.

However, in cases where the supersaturation is large and the density of fixed sinks is low, the migration distances for the defects may become incompatible with the sink density and the temperature. In that case, new sinks are created by clustering of elementary point defects and grow into planar or three-dimensional secondary defects.

The kinetics of precipitation of point defects and the mechanism of nucleation and growth of defect clusters such as loops, stacking fault

tetrahedra, voids and black spots are not yet fully understood.

The quenching technique, because of its obvious simplicity, has been most widely used. Since the first observation of vacancy loops made by Hirsch¹ in 1958 on aluminum specimens, considerable work has been done on the nucleation and growth process of vacancy clusters in quenched metals and especially in aluminum. A comprehensive introduction to this topic and a presentation of the various helpful methods used to investigate this field has been written by Damask and Dienes.² The Proceedings of the Argonne Conference published in 1965³ offer a detailed description of the more recent results.

Barnes and Mazey⁴ on aluminum and more recently Hesketh and Richards⁵ on copper have used the irradiation technique.

A powerful approach is to compare results obtained from quenching a pure material and some of its alloys and from deforming and irradiation at low temperature as in the experimental work of Federighi⁶ on aluminum.

Another approach to the precipitation mechanism consists in studying the role of impurities and of vacancy-impurity complexes as migrating elements.⁷

Comparative studies on silver, gold, copper, and aluminum have also yielded interesting results⁸ despite some very drastic differences between the behavior of vacancies in each of these metals.

Resistivity methods have been used for the determination of the values of the formation energy⁹ of single vacancies E_{1v}^f and divacancies E_{2v}^f and of the corresponding migration energies E_{1v}^m , E_{2v}^m . Flynn et al.¹⁰ and Bass¹¹ recently pointed out that these results have to be combined with diffusion data in order to be correctly interpreted.

Direct observation by transmission electron microscopy has revealed a great variety of secondary defects: voids, Frank sessile loops, perfect loops, double¹² and triple layer loops¹³ have been observed in aluminum alone. The conditions favoring the formation of each of these kinds of defects are not yet completely known.

The main advantage of the method used for the present investigation is that it permits resistivity measurements and electron microscopy observations on the same sample. Due to the low value of the migration energy in aluminum, quenching must take place in an environment kept below room temperature or even below -70°C for elevated values of the quenching temperature T_Q . This was also achieved in the present experimental method. Therefore, aging temperatures T_a were reached from below rather than from above as has usually been the case when electron microscopy specimens have been obtained. A fast up-quenching rate was necessary for aging temperature between 0° and $+100^{\circ}\text{C}$ in order to avoid partial precipitation while the specimen was brought to T_a . An appropriate up-quenching technique enabled exploration of a wider area of the $T_a \times T_Q$ space, keeping the quenching profile $T(t)$ constant. The use of single clusters since the crystallographic orientation giving the best possible contrast could be achieved systematically during electron microscopy investigation.

In the present work, the specimen preparation and the quenching techniques, although unusual and quite delicate, yielded reproducible results. The precise experimental conditions and the details of specimen handling can influence the results and their interpretation. Experimenters in this field are certainly aware of this fact but, with some exceptions,¹⁴

rarely admit the disturbing influence of minor changes in procedure. It is the purpose of Section II to present a detailed description of the experimental procedure and thereby lay the ground for a correct interpretation of the results.

The combined application of resistivity and electron microscopy techniques on single crystal specimens quenched under reproducible conditions and brought to various aging temperatures by reliable methods yielded some new results whose interpretation led to the development of a nucleation model. Many data and complementary evidence are needed before an exact formulation of the present model can be achieved.

II. EXPERIMENTAL PROCEDURE

The high purity Cominco 99.999% aluminum and zone-refined Cominco 99.9999% aluminum was obtained in strips 12 in. x 1 in. x .008 in. and 12 in. x 1 in. x .016 in.

A. Growth of Single Crystals

Single crystal strips 8 in. x 1 in. x .008 in. were grown under 25 μ Hg pressure of helium in a graphite mold packed with 99.9999% pure graphite powder. The tube furnace was inclined 15° from the horizontal position and care was taken to keep the normal to the surface of the sheet in a vertical plane. Under such conditions the oxide film and the thickness of the crystal after growth were found to be uniform. Since the specimen was to be heated by resistance in the subsequent treatments, a constant cross-section was a stringent condition. Chemical or electrochemical thinning have to be reduced to a minimum since they tend to remove edges preferentially. The growth of thin single crystals was thus a necessity. Two different techniques were used to weld the thin strip onto the seed crystals; arc welding under argon atmosphere and spot welding. The first technique was less clean than the second and often yielded erratic results for the resistivity ratios $R_{273^\circ K} / R_{4^\circ K}$. Contamination coming from the tungsten electrode is difficult to avoid. The second technique seemed to be most appropriate to the welding of such thin strips.

Extensive etching of the weld before growth ensures the removal of surface contamination by the copper electrodes of the welding machine.

Neutron activation analysis for various elements has been performed on several specimens by the GCA Corporation. The carbon analysis by

combustion methods has been done by the Ledoux Company. Results of these analyses are presented in Table I.

Table I

B	C	Na	Mg	Si	Ca	K	Fe	Cu	H	N	O
3	18	2	<0.3	<20	10	<1	4	<4	2	30	15

B. Specimen Preparation

After growth, the single crystals were etched in order to remove the oxide layer. The following solution was used at room temperature:

Hydrochloric acid	45 cm ³
Distilled water	30 cm ³
Nitric acid	15 cm ³
Hydrofluoric acid	10 cm ³

All acids were in concentrated commercial solution. Portions 1-1/2 in. x 1 in. in size were cut by shearing from the single crystal strips and thinned down to .005 in. by a chemical polish at 93°C in the following solution:

Phosphoric acid (86%)	240 cm ³
Sulfuric acid (96%)	40 cm ³
Nitric acid (70%)	20 cm ³
Alumina powder	5 gm

Nitric acid must be regularly added in order to maintain these proportions reasonably constant.

The specimen was then mounted on a tray between two brass plates 1-1/2 in. x 1-1/2 in. x .010 in. in order to avoid deformation during

machining on the spark cutter. The side of the upper brass plate facing the specimen had to be properly coated with insulating plastic lacquer in order to avoid undesirable spark erosion and local stress concentrations. The specimen carrying tray was then mounted with precision on the spark cutting machine and a 14-blade jig cut the specimen through the brass plate into a high resistance shape as shown on Fig. 1.

Finally the specimen was thinned down to $.003 \text{ in.} \pm .0003 \text{ in.}$ by chemical polishing and the local damage due to spark erosion machining was thus removed.

C. Experimental Chamber

The specimen holder of the experimental chamber is described in Figs. 2a and 2b. The smaller of the two flanges was made of brass and constitutes the bottom of the quenching dewar described in the next paragraph, while the larger one can be tightened onto a copper container equipped with the matching stainless steel flange. A flat indium ring is used as a gasket.

Because of the great softness of the specimen, considerable care had to be taken during mounting and welding of the leads since mechanical damage was to be avoided. No direct handling of the specimen would take place after this point until it was unmounted to be electropolished and thin foils were to be prepared for electron microscopy.

The specimen chamber was then sealed and connected to a vacuum pump and a helium gas supply. A first value of the specimen resistance at 0°C was measured after leaving the chamber under $500\mu \text{ Hg}$ of helium pressure immersed in a melting ice bath. A measuring current of 100 mA

did not create any detectable disturbance in the temperature equilibrium.

Then the specimen was brought to 580°C by resistance heating and pulsed to 650°C in order to eliminate specimens of irregular cross-section. This thermal pulsing was done with a device described in Appendix I.

As described in Fig. 1, the first legs from each end of the specimen have a different width from the others. They were made thinner in order to balance heat losses from the specimen to the specimen holder by conduction. The sizes finally adopted were determined experimentally and specimens of reasonably regular cross-section brought slowly to within less than 5°C from the melting point showed uniform red color and exhibited uniform melting when 661°C was approached slowly.

After twenty heating and cooling cycles about 575°C, the specimen was slowly cooled down to room temperature (100°/min). After introducing helium gas into the chamber and waiting for temperature equilibration, a second reference value of the resistance was taken at 0°C.

Finally the chamber was cooled down to liquid nitrogen and then to liquid helium and a reference value of the resistance at 4°K was taken. Resistivity ratios were thus established and their values were

$$\frac{R_{273^{\circ}\text{K}}}{R_{4^{\circ}\text{K}}} = 1000 \pm 200 .$$

The geometry of the specimens is responsible for such low values since the surface scattering of electrons becomes dominant at liquid helium temperature. The electron mean free path in aluminum at 4°K is of the same order of magnitude as the thickness of the specimen, i.e. 100μ. Resistivity ratios measured on .016 in. thick samples made of the same material were in excess of 2000.

D. Quenching Technique

Because of the mechanical characteristics of the specimen used, a quenching method minimizing any movement of either the specimen itself or any mass of liquid had to be designed. Thus the specimen had to be heated to the quenching temperature T_Q in the center of the quenching medium kept at low temperature. A rectangular glass capsule open at the bottom end and connected at the top end to a capillary glass tube was lowered into the glass dewar and guided down, so as to fit over the specimen (Fig. 3). The quenching bath, 200 proof ethyl alcohol cooled down to -115°C , was then poured into the dewar, precooled also with liquid nitrogen.

The specimen could then be brought to T_Q by resistance heating. A well regulated DC power supply was operated in the constant voltage mode. The potential drop across the gage length of the specimen and across a standard resistor was measured and the temperature of the specimen was deduced from the resistance versus temperature data established for pure aluminum by Baluffi and Simmons.¹⁵

The quenching bath was slowly stirred while the specimen was heated and the temperature was usually around -110°C when quenching took place.

Quenching was realized by triggering the spring-loaded extraction device connected to the glass capsule covering the specimen. The heating current was turned off milliseconds before and replaced by a constant current of 100 mA. The switching system which permitted this operation is described in Appendix I. The millivolt signal coming from the potential leads was recorded on an oscilloscope equipped with a Polaroid camera. Quenching profiles were thus obtained (Fig. 4). The oscilloscope

was equipped with a highly sensitive differential D.C. input stage and the output of this amplifier to the power stages of the oscilloscope was limited by a set of appropriate Zener diodes in order to avoid saturation of the latter stages while heavy heating current is passing through the specimen; otherwise, the recovery curves of the power tubes would have been superimposed on the quenching curves.

E. Specimen Transfer

After quenching, the alcohol was removed and the specimen, cooled by cold nitrogen gas, was transferred to the experimental chamber. The latter was sealed at liquid nitrogen temperature. The temperature of the specimen could be monitored and constantly kept below -100°C . Finally the chamber, still immersed in liquid nitrogen was connected to a vacuum pump and the specimen kept for a few minutes at -100°C by resistance heating in order to allow the alcohol to evaporate.

F. Resistivity Measurements

Resistivity measurements were carried out by 4°K by potentiometric methods. Two Honeywell Rubicon 6-dial potentiometers were used to measure simultaneously the potential drop across the gage length of the specimen and a standard resistor placed in series. Thermal e.m.f. compensators were placed in the input and output loops of the potentiometer so that no current reversal was necessary. The temperature of the room was controlled to $\pm 0.5^{\circ}\text{C}$. The sensitivity of this resistometric equipment was estimated at $10^{-12} \Omega \times \text{cm}$.

G. Thermal Pulsing Technique

In order to avoid handling of the specimen and repeated transfers from the aging bath to the measuring bath, a thermal pulsing unit involving resistance heating was built and is described in detail in Appendix I.

If local variations in the cross sectional area do not alter appreciably the temperature of the specimen in a steady state, they definitely constitute "hot points" during a rapid temperature rise. If uniform temperature control is to be maintained, the heating rate provided by this method has a limit which depends on physical and geometrical properties of the sample.

In the present case, where heating rates greater than 800°C/s were needed, a method involving both resistance heating and an aging bath was employed.

After completion of the desired resistivity measurements and aging cycles, one leg of the specimen was cut, mounted on a polishing jig and electropolished without being heated above -60°C . Electropolishing could be performed at -60°C in a gently stirred bath of an 80-20 methyl alcohol-perchloric acid solution.

Specimens were finally examined in transmission with an electron microscope Siemens Elmiskop IA operated at 100 kV. The double tilting stage was used at room temperature.

Single crystals with a $[110]$ direction parallel to the electron beam were mostly used since this orientation provided enhanced contrast on very small voids. See Appendix II. Also the use of $\langle 110 \rangle$ single

crystals facilitated accurate comparison of various areas of the same specimen because all defects could be viewed in (110) projection under similar contrast conditions, i.e., with a $\langle 111 \rangle$ beam operating, so that all defects of interest were visible.

III. RESULTS

The quenching profile, followed by some results obtained by various up-quenching methods will be presented first because of their influence on the subsequent resistivity measurements and electron microscopy observations.

A. Down Quenching Profiles

Quenching conditions were easily reproducible and quenching profiles as recorded by the oscilloscope traces (Fig. 4) were similar for all experiments. No attempt was made to change any of the quenching parameters. Slight variations in specimen thickness (from .0028 in. to .0034 in.) resulted in slightly faster or slightly slower quenching rates but the following features of the quenching curves remained unaltered:

1. After a sharp drop of about 100°C , a linear quenching rate ranging from $7 \times 10^3^{\circ}\text{C/s}$ to $1 \times 10^4^{\circ}\text{C/s}$ was maintained down to $+50^{\circ}\text{C}$.
2. An exponential tail followed this linear quenching rate and the temperature fell from $+50^{\circ}\text{C}$ to 0°C in .05s, thus corresponding to an average quenching rate of 10^3°C/s .
3. Finally, the specimen reached the temperature of the quenching bath, i.e. -110°C , within the following .5s (average quenching rate: 200°C/s).

B. Initial Excess Resistivity

Initial excess resistivity values obtained for quenching temperatures as low as 210°C are plotted on a logarithmic scale (Fig. 5) as a function of $1/T_Q$. Within experimental error, the value of the formation energy of lv found in the present work:

$$E^f = 0.76 \text{ eV} \pm 0.04 \text{ eV}$$

is in good agreement with the results obtained by Doyama and Koehler⁹ on zone refined aluminum. The ideally quenched-in resistivity is given by the expression:

$$\Delta\rho_{id} = 1,300 \text{ } \mu\Omega \text{ cm} \exp\left(\frac{-0.76 \text{ eV}}{kT}\right) \quad (1)$$

For quenching temperatures above 425°C, the departure from the straight line becomes important, due to a high supersaturation of the lattice in vacancies and to the rather slow quenching rate obtained with the present method.

For $T_Q > 500^\circ\text{C}$ it is well known that the initial excess resistivity measured experimentally is always lower than could be expected from expression (1) even for quenching rates as high as 10^5°C/s . In the present work the ratios of those two quantities corresponding to four different quenching temperatures is given in Table II

Table II

T_Q	$\Delta\rho_m/\Delta\rho_{id}$
425°C	80%
475°C	60%
525°C	40%
575°C	22%

Several interpretations of this discrepancy have been proposed. Doyama and Koehler¹⁶⁻¹⁷ originated the theory of annealing of mobile vacancy complexes to fixed sinks.

Flynn¹⁸ has developed a kinematical theory of point defects

diffusion to spherical sinks. Bass et al.¹⁰ applied it to the case of gold and Bass¹¹ more recently extended it to the annealing of vacancies in quenched aluminum.

On the other hand, emphasis has been placed recently on the formation of di-, tri-, quadri-vacancies and higher complexes during the quench.¹⁹ Such clusters can be regarded as possible nuclei for further precipitation of mobile vacancies.

The first model is applicable to a material whose density of fixed sinks is very high. It is the case for the gold specimens described by the authors,¹⁰ very small wires with very small grain size.

In the present case, in view of the results obtained by direct observation, this first model does not apply since annealing of the vacancies to secondary defects predominates over annealing at dislocations and other fixed sinks.

The second model, in its present form, although predicting an initiation of precipitation during the quench, seems unable to account for the discrepancy in the value of the initial quenched-in resistivity mentioned in Table II. Estimates of the resistivity per lv of a group of clustered vacancies²⁰ indicate that a resistivity change due to clustering would have a marked effect on resistivity measurements only in case high order clusters are actually formed. Indeed the resistivity of a divacancy is expected to be only at most 10% smaller than the resistivity of two isolated vacancies^{21,22} and a significant decrease in resistivity is expected to take place only when clusters contain more than ten vacancies.

These considerations therefore point to the necessity of developing

It is interesting to note that increasing the up-quenching rate beyond the value of the down-quenching rate in the region $0^{\circ}\text{C} \rightarrow 50^{\circ}\text{C}$ did not affect the final structure of the aged specimen. Note also that the average sizes of the secondary defects reported in this paper are below those obtained by direct quenching from T_Q to T_a . This is to be expected since the nucleation takes place within the milliseconds following the quench. With the present experimental procedure T_a is reached from below, whereas in former experiments it was reached from above.

D. Isothermal Resistivity Curves

Figures 8 through 11 present various isothermal resistivity curves corresponding to quenching temperatures 575°C , 525°C , 475°C and 425°C .

The S shape of these curves for low values of T_a has already been pointed out and interpreted by Kimura et al.¹⁷ and by Doyama and Koehler.²³ For $T_a > 0^{\circ}\text{C}$ and more markedly for larger values of T_Q , the initial curvature tends to disappear and the linear part of the curve expands further on both sides of $\tau_{1/2}$, the annealing half time.

Figure 12 is a plot of the various annealing half-times corresponding to various values of T_Q and T_a . The values of the migration energies provided by the cross-cut method are known to be too low and would be in this case:

$$E_{1v}^m = 0.48 \text{ eV}$$

$$E_{2v}^m = 0.27 \text{ eV}$$

The group of specimens quenched from $T_Q = 525^{\circ}\text{C}$ contained a higher impurity content ($R_{273^{\circ}\text{K}}/R_{4^{\circ}\text{K}}$ ranging from 600 to 700).

It can be noticed that the presence of impurities tends to decrease $\tau_{1/2}$ regardless of T_Q and T_a and also to lower the migration energies of mobile complexes:

$$E_a^m = 0.42 \text{ eV for low values of } T_a.$$

$$E_b^m = 0.19 \text{ eV for high values of } T_a.$$

E. Isochronal Resistivity Curves

The influence of the heating rate on the shape of isochronal aging curves is obvious. Thus, only qualitative results can be expected from such curves and their interpretation is still ambiguous in some cases.

Curves corresponding to various heating rates are plotted on Fig. 13. As expected, the slower the heating rate, the lower are the transformation temperatures and the more complete the transformations. An infinitely slow heating rate can be considered when different specimens, quenched from the same temperature, here $T_Q = 575^\circ\text{C}$ for instance, are aged for a long time at temperatures T_a spaced between -100°C and $+100^\circ\text{C}$. Federighi³ and Doyama and Koehler⁹ using up-quenching techniques involving liquid baths found curves of type c (Fig. 13). If on the contrary, the specimens are brought to the aging temperature with the appropriately fast heating rate, as in the present experiments, a simple decay curve is found as shown on Fig. 13, type d.

F. Electron Micrographs

Most experiments were carried out on $\langle 110 \rangle$ single crystals, some on $\langle 211 \rangle$, and a few on $\langle 111 \rangle$. When the specimen was properly treated,

no recrystallization was observed and its initial orientation was preserved in the thin foil. Several foils were prepared from various sections of a specimen in order to make sure that the arrangement of clusters and dislocations was uniform along the specimen.

As shown in Fig. 14 the distribution of secondary defects was quite uniform and dislocations were mainly confined in cell walls. A few isolated and heavily jogged dislocations were sometimes observed.

The sizes of the secondary defects observed after quench and complete aging are represented schematically in Fig. 15 as a function of T_a and T_Q .

Leaving aside the density of the defects observed in each case we see that under the experimental conditions described above:

1. Both voids and loops were present in all cases although some doubts remain in a few limited cases when the methods of observation become inappropriate.
2. The size of both defects increased with increasing aging temperature and decreasing quenching temperatures.

Estimates of absolute density of defects necessarily involve measurements of foil thickness across large areas. Since the latter is very difficult to do, any results would be highly unreliable. Table III presents average ratios of densities of defects and other quantities connected with the relative efficiencies of voids and loops when acting as sinks under various conditions of supersaturation and mobility of point defects. The series of experiments corresponding to $T_Q = 425^\circ\text{C}$ does not appear in Table III because the absolute densities of both defects were too small to be reliably estimated by electron microscopy observation.

The series of specimens quenched from 525°C had a higher content than the other three series. Increasing the concentration in impurities enhanced the precipitation, reducing proportionately the size of the defects. Impurities also favored the nucleation of voids over loops.

In most cases the presence of voids in the foil was easy to determine and the now well-established black-white contrast change across thickness fringes can be seen on Fig. 16. When the voids were smaller than $80\text{\AA}$, their presence was more difficult to detect. But if their density was large enough, they could always be seen in very thin regions of the foil, i.e., between the first and second $\langle 111 \rangle$ thickness contours, for instance. Voids smaller than $50\text{\AA}$ can be observed but the size of the image observed is expected to be much larger than the actual size of the defect. A $[110]$ foil presents a definite advantage over all other orientations; $\langle 111 \rangle$ diffraction beams can be used and correspond to the shortest extinction distance in FCC metals, and the lattice distortions resulting from the relaxation of the $\langle 111 \rangle$ facets of the octahedra ensure additional contrast effects as explained in Appendix II.

If large voids are formed, a detailed contrast can be observed. Figure 1 through 5 of Appendix II show voids observed along the $\langle 110 \rangle$ direction under several diffraction conditions. For low aging temperatures the voids appeared as regular octahedra with peculiar contrast effects along the two vertical edges. For temperatures higher than 80°C they often appeared slightly truncated either by $\langle 111 \rangle$ planes or more commonly by $\langle 100 \rangle$, although the latter truncation resembled more

a rounding off of the $\langle 100 \rangle$ apex than a strict truncation by $\langle 100 \rangle$ planes.

Table III

T_a	T_Q	475°C			525°C			575°C		
		$\frac{C_{Vd}}{C_{Lp}}$	$\frac{v/Vd}{v/Lp}$	$\frac{v \rightarrow Vd}{v \rightarrow Lp}$	$\frac{C_{Vd}}{C_{Lp}}$	$\frac{v/Vd}{v/Lp}$	$\frac{v \rightarrow Vd}{v \rightarrow Lp}$	$\frac{C_{Vd}}{C_{Lp}}$	$\frac{v/Vd}{v/Lp}$	$\frac{v \rightarrow Vd}{v \rightarrow Lp}$
+80°C								10	1.5	18
+60°C		20	0.6 ?	20				8	1.2	13
+40°C		15	0.7	11	30	0.3	9	8	1.0	9
+20°C		10	1	13	15	0.25	4	3.7	0.7	3
0°C					10	0.2	2	3	0.5	1.5
-20°C		8	1.5	16	6	0.15	1	2	0.3	0.6
-40°C								1	0.1	0.1

C_{Vd} : atomic concentration in voids
 C_{Lp} : atomic concentration in loops
 v/Vd : number of vacancies contained in a void of average size
 v/Lp : number of vacancies contained in a loop of average size
 $v \rightarrow Vd$: total number of vacancies going to voids
 $v \rightarrow Lp$: total number of vacancies going to loops

IV. DISCUSSION

A consistent account of the results presented here and of experimental data published before can only be found if the gap between the critical radius approach and the chemical reactions rate approach is narrowed. However, the problem of knowing which cluster of vacancies is more stable under a given set of conditions is still open to discussion since neither theoretical calculations nor experimental evidence have been able so far to give unambiguous answers.

A. The Critical Radius Approach

Considering the free energy change ΔG_n , when n vacancies have gathered in a single cluster, we can write

$$\Delta G_n = n(g^f - g^p) + n\Delta g_s + \alpha n^{2/3} \sigma$$

where g^f and g^p are the free energy associated with an isolated single vacancy and a vacancy bound to a precipitate respectively. The term Δg_s represents the elastic strain energy per atom and the last term takes into account the surface energy and contains a form factor.

The critical radius for growth N_c can be derived from the above expression as the value of n for which $\partial(\Delta G_n)/\partial n = 0$, hence

$$N_c = \left[\frac{2\alpha\sigma}{3(g^f - g^p + \Delta g_s)} \right]^3$$

The critical radius for growth will be a function of the energy per vacancy in a given type of cluster and will thus depend on the nature of the cluster and its internal structure.^{3,24} But it will also depend on external parameters such as the degree of supersaturation, i.e., the

concentration of mobile vacancies C_{mv} and the aging temperature. A vacancy cluster containing less than twenty vacancies, for instance, may be stable and growing under a very high flux of moving vacancies when the loss of vacancies by emission is compensated by the capture of new ones. The same cluster may be subcritical and shrink under conditions where C_{mv} would be very low.

Federighi²⁶ and Doyama and Koehler⁹ have reported independently that specimens quenched from high temperatures and isothermally aged at a sufficiently low temperature to eliminate stage Q-1 of the recovery, i.e., -50° to -70°C , exhibit a small additional recovery stage Q-2 when isochronally annealed at increasing temperatures. During the long low temperature isothermal aging, a high density of small defects have been nucleated and have grown to an equilibrium size. As T_a is increased, so is N_c , the smaller defects become unstable and begin to shrink by emission of mobile vacancies which will be captured by larger defects. A new equilibrium distribution will thus develop around a larger mean size. A similar effect is responsible for the shape of the recovery curve b on Fig. 7 obtained for a specimen heated up to the aging temperature of $+40^{\circ}\text{C}$ with insufficient heating rate.

The same effect is thought to be responsible for the larger loops observed around the edges of colonies. The presence of sinks in an area lowers locally the concentration in mobile defects, thus increasing N_c and leading to the formation of fewer but larger clusters. The strong dependence of N_c on the aging temperature and on the degree of supersaturation seems to be well confirmed by the redistribution in sizes taking place in these experiments.

If we consider the two extreme values of N_c during an isothermal anneal, Table IV summarizes the various limit cases. The initial critical radius N_c^i is strongly dependent on C_{mv} and therefore on T_Q and T_a , whereas the final critical radius $N_c^f > N_c^i$ depends only on the aging temperature T_a . In this table C_{mv} is the concentration of mobile vacancies as the beginning of the anneal.

Table IV

Conditions	C_{mv}	Growth of N_c during aging	Mobile defects
1. T_Q high, T_a high	very high	N_c^i N_c^f └────────┘	1v mostly
2. T_Q high, T_a low	high	N_c^i N_c^f └────────┘	2v
3. T_Q low, T_a high	low	N_c^i N_c^f └────────┘	1v and 2v
4. T_Q low, T_a low	very low	N_c^i N_c^f └────────┘	1v and 2v

In the first case we can expect an easy nucleation followed by rapid dissolution of small clusters as N_c increases. An incubation period is not detectable on the resistivity curves (Fig. 8). In the second case, on the contrary, an incubation period is necessary, as in the fourth case, but the clusters observed after full anneal will be larger in the latter case than in the former.

B. The Reaction Rate Approach

The mechanism of precipitation can be envisaged as the evolution of a vacancy distribution inherited from the quench (Fig. 10).

The values of the initial excess resistivity just after the quench (Fig. 5) suggest that either a large fraction of the vacancies in equilibrium at T_Q has been lost at sinks and surfaces during the quench, or have already gathered into clusters of four to ten vacancies. These clusters are then present in the lattice at appreciable concentration just after the quench as suggested by the computer curves obtained by Cotterill.⁷

Let N be the number of vacancies contained in a cluster and C_{nv} the atomic concentration in clusters of that type. The initial distribution $C_{nv}(n)$ just after the quench will be determined by T_Q and the quenching profile (Fig. 18).

As in the case of gold,²⁵ the comparison of isothermal resistivity curves for various T_a and T_Q 's suggests that a single process is responsible for the precipitation and leads to S-shaped resistivity curves.

The first stage of the precipitation mechanism can be considered as an initiation period for the precipitation. The spreading of the C_{nv} distribution towards larger cluster sizes, (Fig. 19) already initiated during the quench is now pursued and leads to the formation of a very high density of small multivacancy clusters invisible by direct observation, involving up to perhaps twenty vacancies. The high value of their electrical resistivity²⁰ combined with a still large supersaturation in mono- and di-vacancies will not lower very much the excess

resistivity. This stage corresponds to the first almost horizontal part of the S-shaped curve. During this stage C_{mv} is much larger than in the following stages and the critical radius is thus extremely small. Any small cluster can act as a nucleus for precipitation.

As the first stage impoverishes the lattice in mobile vacancies, the critical radius N_c becomes larger and many clusters formed during the first stage now become unstable with respect to the new conditions. They dissociate progressively by emitting single or divacancies and contribute therefore to the growth of clusters having sizes larger than N_c .

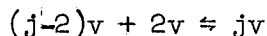
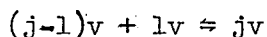
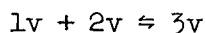
This second stage of precipitation corresponds to a coarsening process. The critical radius for growth which depends strongly on T_a , is now of the same order of magnitude as the vacancy clusters visible by direct observation in electron microscopy.

A hump on the C_{mv} distribution tends to form as the critical radius increases (Fig. 19b). The stable group located on the right of N_c will keep growing and move away from N_c , thus becoming thermally more stable.

The first stage has a storage effect for vacancies, whereas the second stage amounts to an overall steady state transport of vacancies from subcritical storage clusters towards stable, growing clusters. This stage corresponds to the linear part of the resistivity decay curve. The evaluation of activation energies for annealing suggests that the diffusion of monovacancies in one case, divacancies in the other case, is the limiting process in the precipitation sequences (Fig. 12).

This second approach to the precipitation mechanism will find its detailed justification when the set of equations corresponding to the

following set of equilibrium reactions will be solved:



Dienes and Damask² have obtained solutions for irreversible reactions up to $j = 8$; but such an approach necessarily leads to rapid exhaustion of the supersaturated vacancies in the lattice. The set of reaction rate equations corresponding to the reversible reactions written above would be:

$$\begin{aligned} \frac{dC_{lv}}{dt} = & -A_{11}C_{lv}^2 \exp\left(\frac{-E_{lv}^m}{kT}\right) + B_{11}C_{2v} \exp\left(\frac{-E_{lv}^m - E_{lv-1v}^B}{kT}\right) \\ & -A_{12}C_{lv}C_{2v} \exp\left(\frac{-E_{lv}^m}{kT}\right) + B_{12}C_{3v} \exp\left(\frac{-E_{lv}^m - E_{lv-2v}^B}{kT}\right) \\ & -A_{13}C_{lv}C_{3v} \exp\left(\frac{-E_{lv}^m}{kT}\right) + B_{13}C_{4v} \exp\left(\frac{-E_{lv}^m - E_{lv-3v}^B}{kT}\right) \\ & \dots\dots\dots \\ & -A_{1j}C_{lv}C_{jv} \exp\left(\frac{-E_{lv}^m}{kT}\right) + B_{1(j+1)} \exp\left(\frac{-E_{lv}^m - E_{-v(j+1)v}^B}{kT}\right) \\ & \dots\dots\dots \end{aligned}$$

and

$$\begin{aligned} \frac{dC_{jv}}{dt} = & +A_{(j-1)1}C_{lv}C_{(j-1)v} \exp\left(\frac{-E_{lv}^m}{kT}\right) - B_{1j}C_{jv} \exp\left(\frac{-E_{lv}^m - E_{lv-(j-1)v}^B}{kT}\right) \\ & +A_{(j-2)2}C_{2v}C_{(j-2)v} \exp\left(\frac{-E_{2v}^m}{kT}\right) - B_{2j}C_{jv} \exp\left(\frac{-E_{2v}^m - E_{2v-(j-2)v}^B}{kT}\right) \\ & -A_{j1}C_{jv}C_{lv} \exp\left(\frac{-E_{lv}^m}{kT}\right) + B_{1(j+1)}C_{(j+1)v} \exp\left(\frac{-E_{lv}^m - E_{lv-(j+1)v}^B}{kT}\right) \end{aligned}$$

$$-A_{j2} C_{jv} C_{2v} \exp\left(\frac{-E_{2v}^m}{kT}\right) + B_{2(j+2)} C_{(j+2)v} \exp\left(\frac{-E_{2v}^m - E_{2v(j+2)v}^B}{kT}\right)$$

If no loss of the total number of vacancies is assumed, then the following equation can be added:

$$\sum_j j C_{jv} = C_{\text{total}}$$

and the initial distribution of $C_{jv}(j)$ just after quench would be given as the initial condition.

If, on the contrary, the diffusion of mobile vacancies to fixed sinks is taken into account, the first two equations should be modified and written:

$$\begin{aligned} \frac{\partial C_{1v}}{\partial t} = D_{1v} \nabla^2 C_{1v} - \sum_j A_{1j} C_{1v} C_{jv} \exp\left(\frac{-E_{1v}^m}{kT}\right) + \\ + \sum_j B_{1j} \exp\left(\frac{-E_{1v}^m - E_{1v-jv}^B}{kT}\right) \end{aligned}$$

$$\begin{aligned} \frac{\partial C_{2v}}{\partial t} = D_{2v} \nabla^2 C_{2v} + 1/2 A_{11} C_{1v}^2 \exp\left(\frac{-E_{1v}^m}{kT}\right) - \\ - 1/2 B_{11} C_{2v} \exp\left(\frac{-E_{1v}^m - E_{1v-1v}^B}{kT}\right) - \sum_j A_{2j} C_{2v} C_{jv} \exp\left(\frac{-E_{2v}^m}{kT}\right) + \\ + \sum_j B_{2j} \exp\left(\frac{-E_{2v}^m - E_{2v-(j-2)v}^B}{kT}\right) \end{aligned}$$

where D_{1v} and D_{2v} are the diffusion coefficients for single and di-vacancies, respectively. And some assumptions should be made about the

initial density and distribution of fixed sinks.

The difficulty in solving these equations is the absence of reliable data concerning the various coefficients. Although E_{1v}^m and E_{2v}^m are now fairly well known for noble metals and aluminum, reports on the estimates of the binding energies E_{1v-jv}^B and E_{2v-jv}^B are still widely conflicting even for values of j such as 3, 4, or 5. The atomic structure of tri-, tetra-, and penta-vacancies and the relative energies of various configurations is still being discussed and plays a determining role on the stability of these clusters and their ability to retain or emit single or divacancies.

It is not certain at the moment whether or not the binding energy increases monotonically with the number of vacancies contained in the cluster and this point is most important in order to elucidate the first stages of growth. For large values of j , the binding energy will progressively increase towards the value of the energy of formation.

C. The Relative Stability and Growth Rate of Frank Loops and Octahedral Voids

In aluminum, three different types of vacancy clusters have been observed on electron transmission micrographs: octahedral voids with and without truncations, single and multiple stacking fault loops, and perfect dislocation loops. The first two types of defect predominate when quenching and handling stresses are minimized.^{27,28}

Jackson,²⁹ Silcox and Whelan,³⁰ and Cotterill,³ using the continuum approach have compared energies of clusters of various types and sizes. Vineyard,³¹ Dienes and Damask,² Doyama and Cotterill,^{3,32} and more recently Johnson,²⁴ using the atomistic approach have estimated the

relative energy of various multivacancy clusters.

This latter approach is preferred for clusters of near atomic dimensions, perhaps a few tens of Ångströms in diameter since the elastic continuum theory is expected to fail. The surface curvature of such a defect can no longer be ignored and experimental values of surface energies cannot be used since they are determined for flat surfaces. At present the continuum and atomistic calculations do not overlap.

Even within the atomistic approach, the use of different types of potential functions yields different results. The planar structure of the trivacancy is estimated as the most stable by some authors³² using a Morse potential, whereas the filled tetrahedron is preferred when a Born-Mayer potential is used.^{2,31} The role of impurities in stabilizing one defect or the other cannot be ignored but leads to complex configurations which quickly become unmanageable by computer calculations for larger clusters.³³

Doyama and Cotterill³² suggested that the configuration of multiple vacancy clusters such as the tri or quadrivacancy, could determine at an early stage of precipitation whether a vacancy cluster would grow as a three dimensional aggregate or a collapsed vacancy disk. The figures given in the first column of Table III, show that loops become relatively more numerous than voids under conditions where higher values of the divacancy concentration are expected at the start of aging, i.e., for high T_Q and low T_a . This suggests that when nucleation of vacancy aggregates takes place primarily by addition of divacancies, there is a greater change of development of a planar cluster than when it takes place by the addition of single vacancies. Conversely for high T_a or

slow quenching rate,^{12,34} divacancies are expected to dissociate rapidly and more three dimensional clusters are observed.

If we consider now the growth rate of voids as compared to loops, the second columns of Table III are of interest. They show that under conditions where the concentration of secondary defects is low, the trapping efficiency of voids is comparable to that of loops. On the contrary, when the nucleation rate is high, as for instance, in the more impure series of specimens or for low aging temperatures after quench from a high temperature, the growth ability is much higher for loops than for voids.

In these cases a significant fraction of the total number of vacancies that eventually go to each defect come from short distances within which the greater stress fields associated with loops should be effective. Therefore, the loops might be expected to attract greater total numbers of vacancies than voids. When defects are far apart, loops should still grow faster during the very early stages, but most of the growth would occur by random walk of vacancies from greater distances where the stress field of the defect is unimportant. Under these conditions the total number of vacancies reaching a loop should not be greatly different from that reaching a void.

D. The Role of Impurities in the Nucleation of Secondary Clusters

The atomic concentration of loops and voids commonly observed by electron microscopy techniques being in the range 10^{-6} to 10^{-11} , it is quite clear that nucleation is very likely to be heterogeneous even in zone refined metals. This point is confirmed by the recent calculations

of Davis and Hirth³⁵ showing that the rate for homogeneous nucleation of vacancy clusters is incompatible with experimental results. The binding energy between impurity atoms and single vacancies or divacancies favors the formation of nuclei and probably alters its internal configuration and lowers its energy of formation.

The series of specimens quenched from 525°C which contains a higher concentration of impurities shows a faster annealing rate (Fig. 12) and a higher nucleation rate than other samples.

During the first stage of precipitation, the influence of certain specific impurities may be one of the factors favoring the formation of one type of cluster over the other. Yoshida and Shimomura³⁶ have found some evidence of the influence of hydrogen on void formation in aluminum. The presence of hydrogen under pressure inside very small clusters may prevent their collapse. Lally and Partridge³⁷ in magnesium and Clareborough and Loretto³⁴ on copper, aluminum and gold quenched from hydrogen atmosphere have shown evidence of the role of this element in the formation of voids. The refining effects produced by the repeated quench-annealing cycles reported by Cotterill and Segall,³⁸ support the heterogeneous nucleation of numerous clusters of short lifetime involved in the present model.

During the initiation period of the precipitation process, many unstable clusters have formed which will be completely dissolved in the following stages. Since they are likely to have formed around some impurity, the repeated departure of mobile defects from this shrinking cluster will increase the probability of mobile vacancy-impurity complex

formation. Therefore, impurities are expected to be drained towards growing clusters. Repeated quenching and aging cycles will thus create local concentrations of impurities at the sites of stable clusters.

V. CONCLUSIONS

The experimental results presented and discussed here can be summarized as follows:

1. Quench-annealing experiments involving up-quenching of the specimen to the aging temperature yield results tending towards those obtained by down-quenching from T_Q to T_a when the up-quenching rate is adequate, i.e., 800°C/s in the present case.

2. Values of the apparent activation energy for the annealing of supersaturated vacancies were found to be:

$$E_{1v}^m = 0.48 \text{ eV}$$

$$E_{2v}^m = 0.27 \text{ eV}$$

3. The presence of higher concentrations of impurities lowered those values to:

$$E_1^m = 0.42 \text{ eV for } T_a < 20^\circ\text{C}$$

$$E_2^m = 0.19 \text{ eV for } T_a \geq 20^\circ\text{C}$$

The role of impurities in the nucleation process was confirmed and the nucleation rate was enhanced in more impure specimens.

4. Keeping the quenching method and the quenching profile identical in all cases and varying only T_Q and T_a showed that Frank loops and octahedral voids were present in all cases with various sizes and density.

5. The size of secondary defects observed after complete isothermal annealing continuously increased with lower T_Q 's and higher T_a 's. The size and density of defects observable by transmission electron

microscopy of thin foils appeared to be the only limit to further investigation of the T_Q , T_a space.

6. Higher concentrations of divacancies at the start of aging favored the formation of loops over voids.

7. The larger stress fields surrounding loops were found to favor their growth as compared to the growth of voids when very high densities of secondary defects were present. When defects were far apart, the annealing of excess vacancies seemed to take place only by random walk to the sinks; the stress fields of the loops appeared to be ineffective within most of the volume from which vacancies were drawn.

More experimental data and theoretical calculations are needed in order to understand the detailed mechanism of nucleation and growth of vacancy aggregates in quenched metals.

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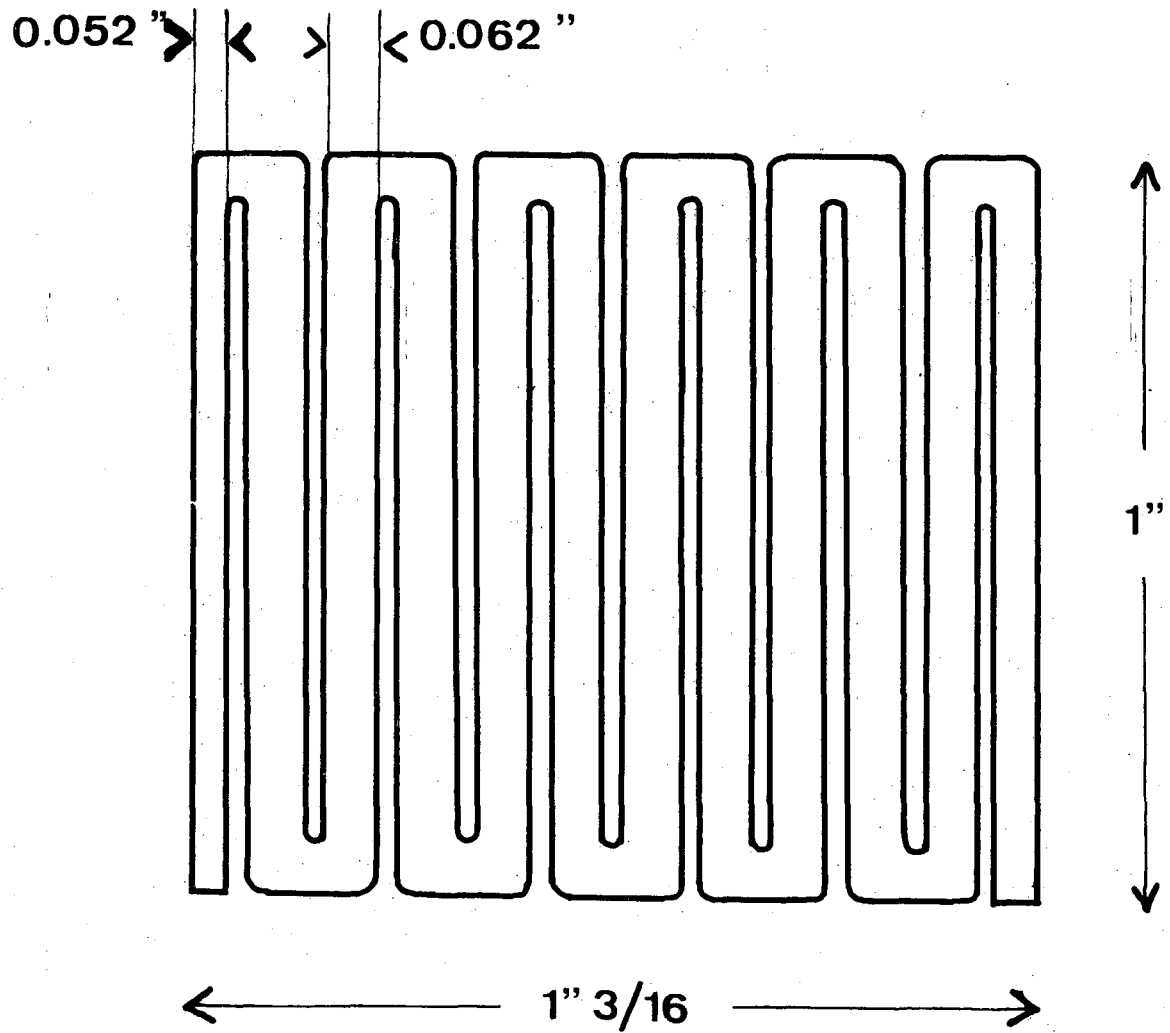
FIGURE CAPTIONS

- Fig. 1 Shape of the aluminum single crystal specimen after spark-cutting.
- Fig. 2 a- Photograph of the specimen holder used for liquid helium resistivity measurements. b- Sketch of the specimen holder: A-Specimen; B-Insulating surface tension breaker for the quenching liquid and guide for the potential leads; C-Current lead; D-Glass dewar; E-Small flange used during the quench; F-Auxiliary clamp; G-Potential leads made of 0.002 in. wire of Cominco 99.999% pure aluminum; H-Main specimen clamps used as current leads; K-Main flange used with an indium gasket as the top of the experimental chamber.
- Fig. 3 Sketch of the quenching device: A-Spring loaded device for extraction of the quenching capsule; B-Capillary tube facilitating level adjustment of the liquid inside the capsule; C-Quenching bath; D-Rectangular heating capsule made of glass; E-Glass dewar; F-Teflon guide for the capsule; G-Aluminum specimen; H-Opening for removal of the quenching liquid; J-Small flange used for quenching; K-Large flange closing the experimental chamber.
- Fig. 4 Oscilloscope trace of the down quenching profile from $T_Q = 525^\circ\text{C}$ to -110°C .
- Fig. 5 Initial excess resistivity $\Delta\rho_0$ as a function of $1/T_Q$.

- Fig. 6 Up-quenching profiles recorded by oscilloscope:
A-Heating by Joule's effect alone $400^{\circ}\text{C}/\text{s}$.
B-Heating by immersion in a liquid bath kept at the aging temperature $T_a = 40^{\circ}\text{C}$.
C-Heating by combining both methods $1000^{\circ}\text{C}/\text{s}$.
- Fig. 7 Isothermal annealing curves for $T_Q = 525^{\circ}\text{C}$, $T_a = +40^{\circ}\text{C}$.
Curve A. Up-quenching in an oil bath at $+40^{\circ}\text{C}$
Curve B. Fast up-quenching by combined heating
- Fig. 8 Set of isothermal annealing curves after quenching from 575°C .
- Fig. 9 Set of isothermal annealing curves after quenching from 525°C . These specimens are more impure than for the other series.
- Fig. 10 Set of isothermal annealing curves after quenching from 475°C .
- Fig. 11 Set of isothermal annealing curves after quenching from 425°C .
- Fig. 12 Calculation of the activation energy by plotting the times to reach 50% of the recovery versus the reciprocal of the aging temperature.
- Fig. 13 Isochronal annealing curves for various heating rates:
Curve A: Heating rate $10^{\circ}/\text{mn}$
Curve B: Heating rate $25^{\circ}/\text{mn}$
Curve C: Infinitely slow. Obtained by plotting the final excess resistivity for the various aging temperatures (results obtained by Doyama and Koehler⁹)

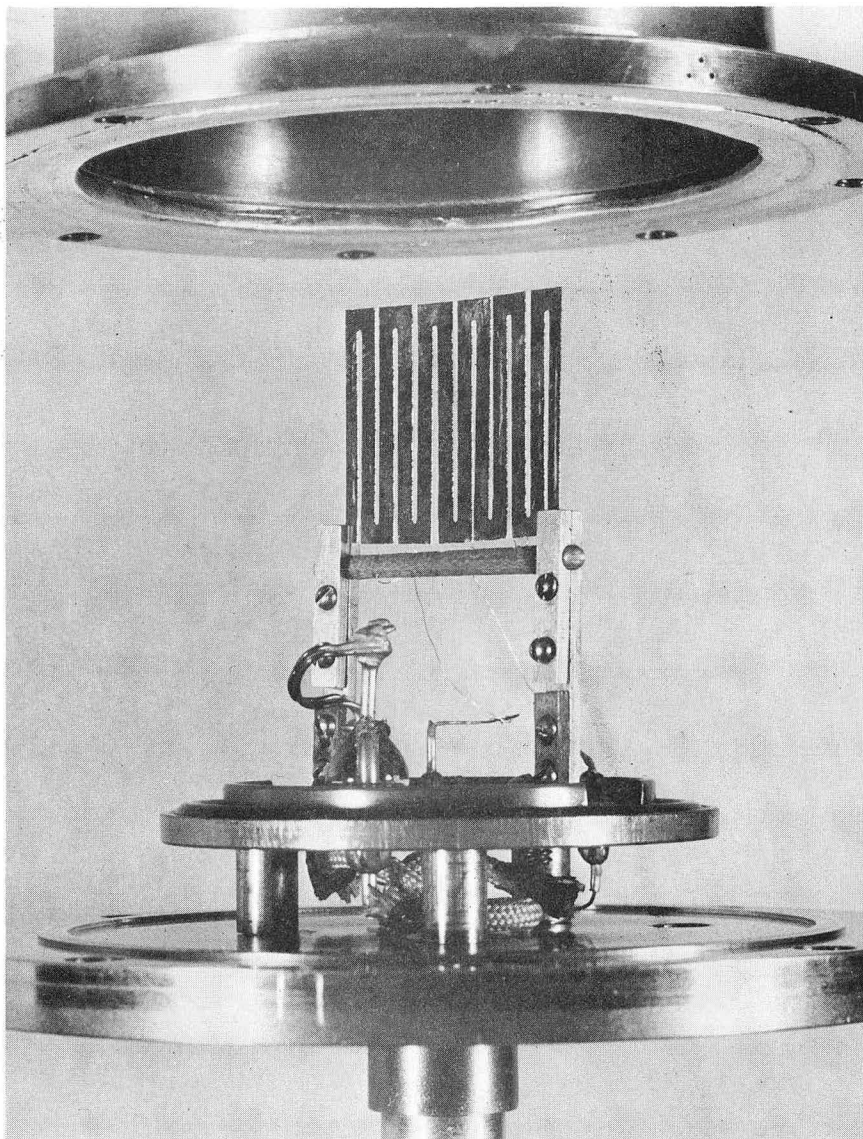
Curve D: Infinitely slow = present work

- Fig. 14 Low magnification electronmicrograph.
- Fig. 15 Summary of the results in a T_a , T_Q diagram.
- Fig. 16 Thickness contrast on voids.
- Fig. 17 Electron micrographs of specimens quenched from the same temperature $T_Q = 575^\circ\text{C}$ and aged at: a - $T_a = -40^\circ\text{C}$; b - $T_a = 0^\circ\text{C}$; c - $T_a = +40^\circ\text{C}$; d - $T_a = +60^\circ\text{C}$
- Fig. 18 Initial distribution of clusters after quench $C_{nv}(n)$. Full lines to slow quenching rate (i.e., $< 10^4^\circ\text{C/s}$). Upper curves correspond to high values of T_Q , 600°C for instance.
- Fig. 19 Evolution of the C_{nv} distribution during aging.



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Fig. 1



XBB 674-1905

Fig. 2a

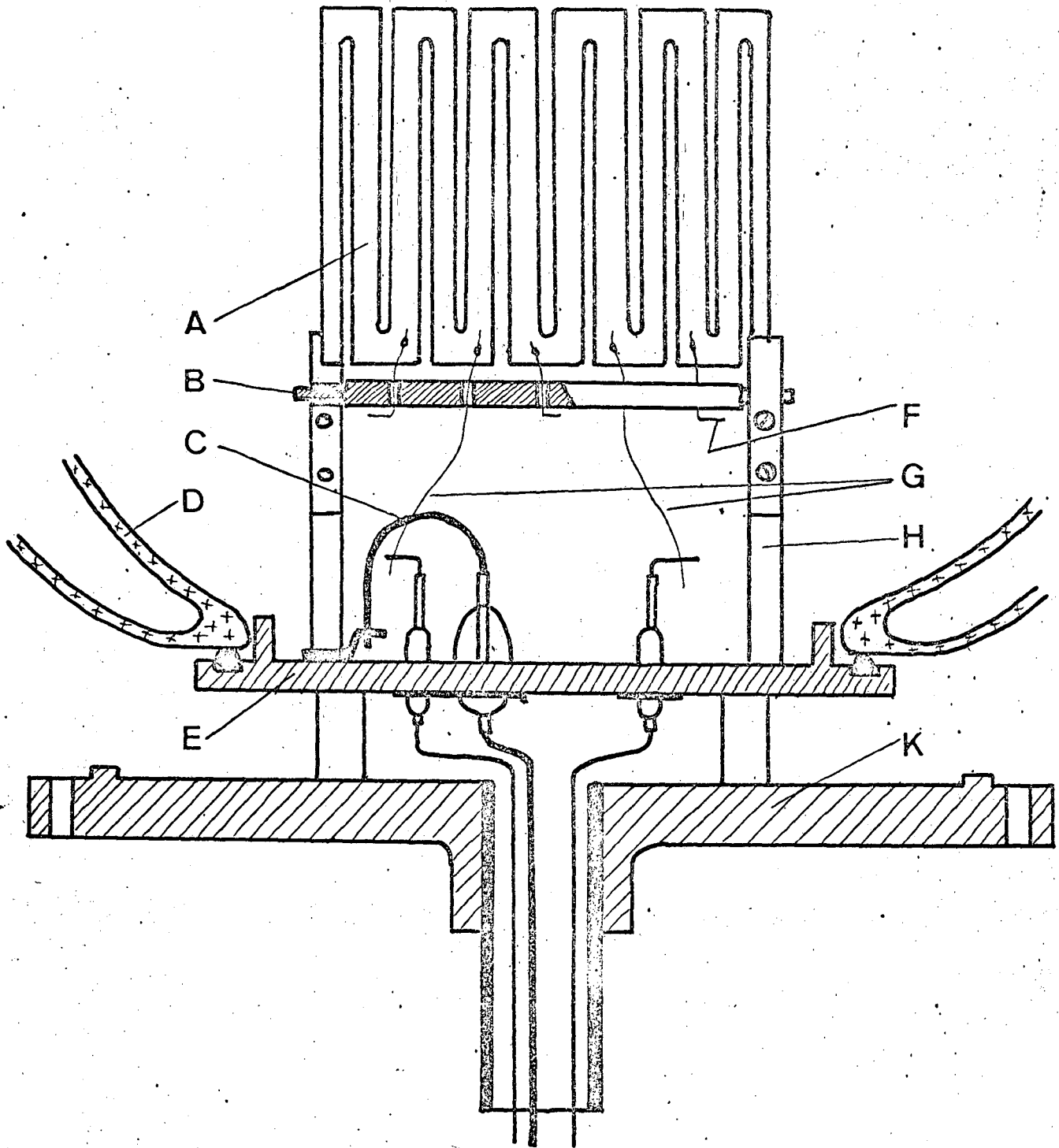


FIG. 2- b

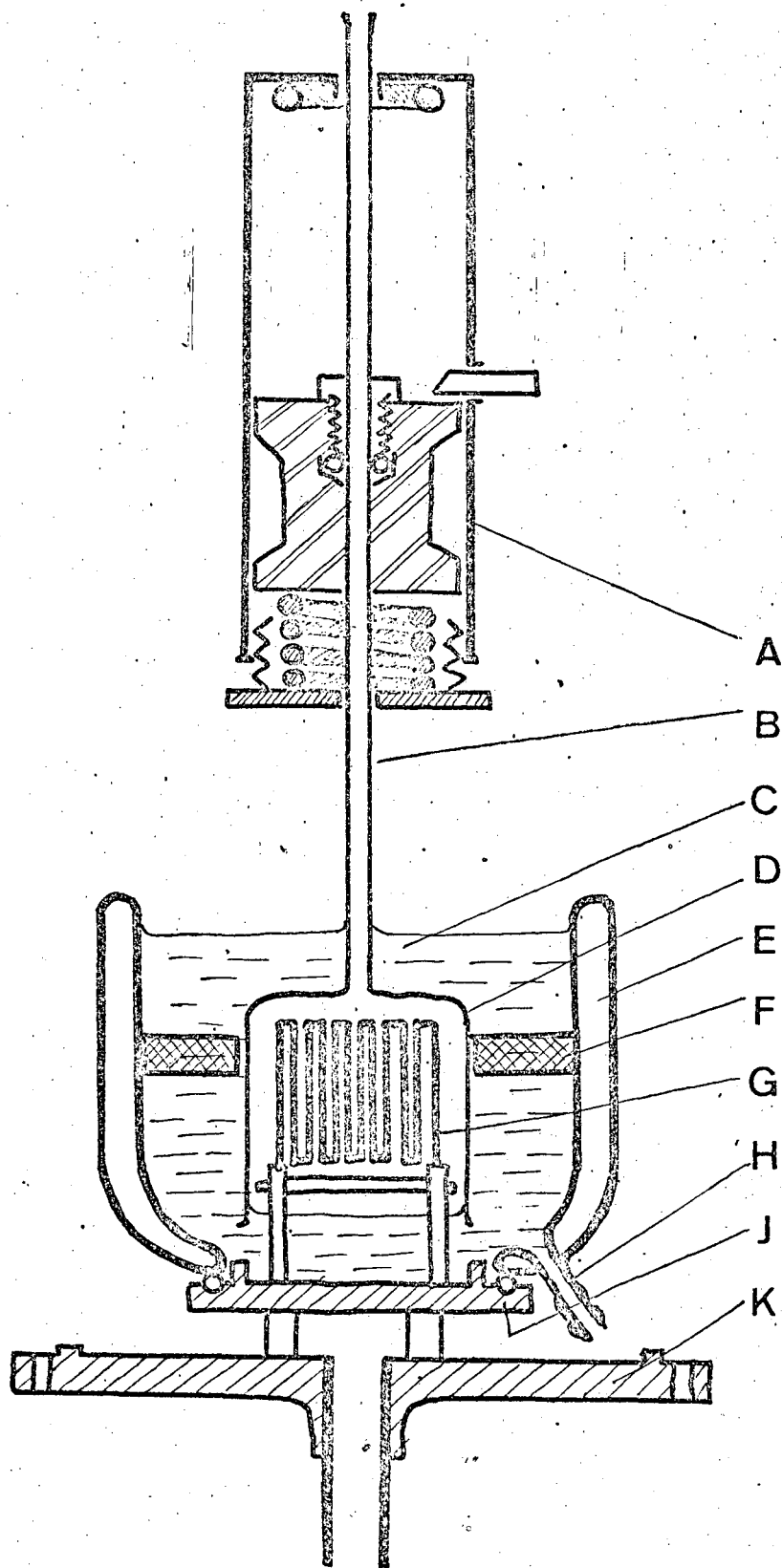


FIG. 3

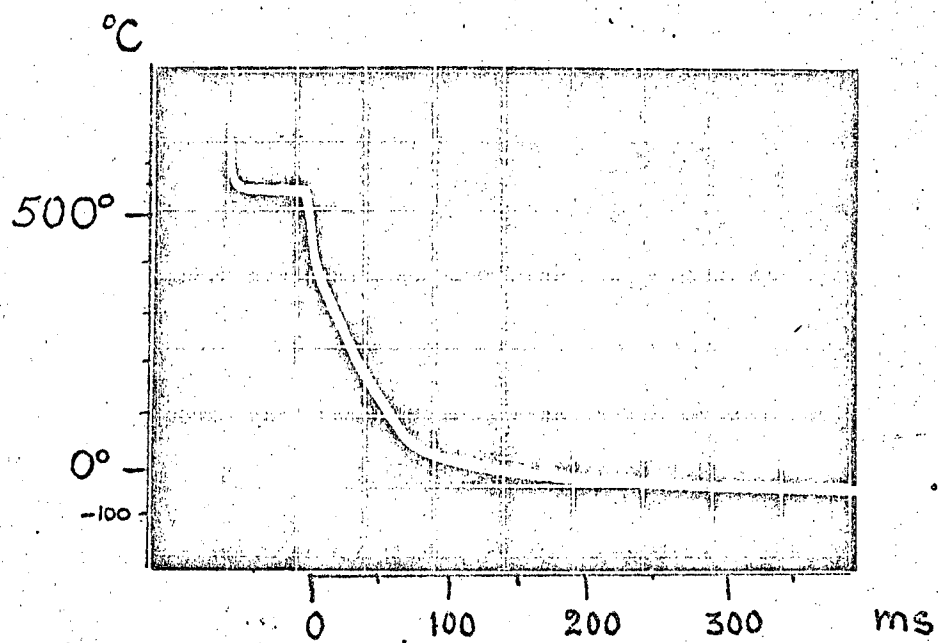


FIG. 4

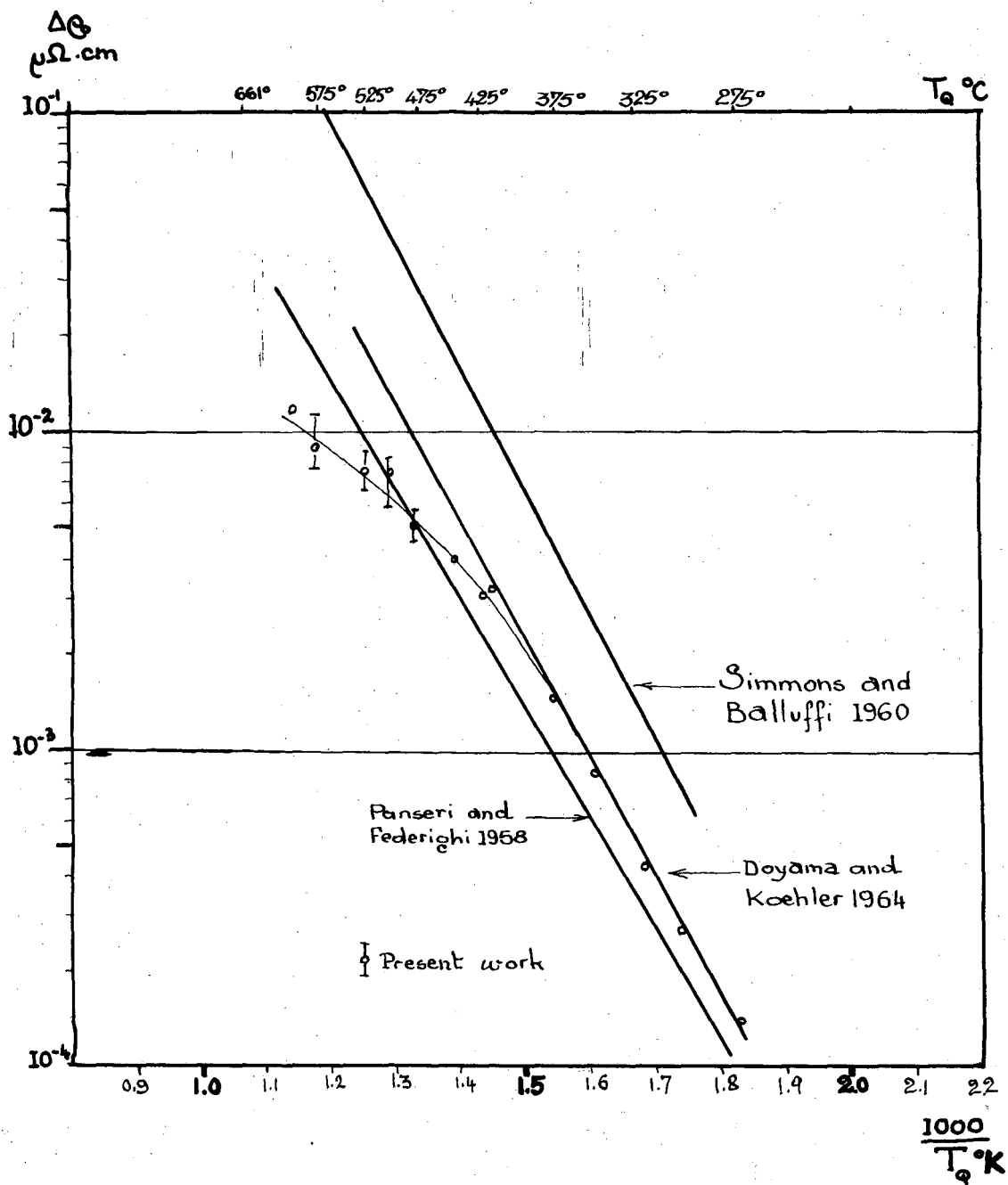
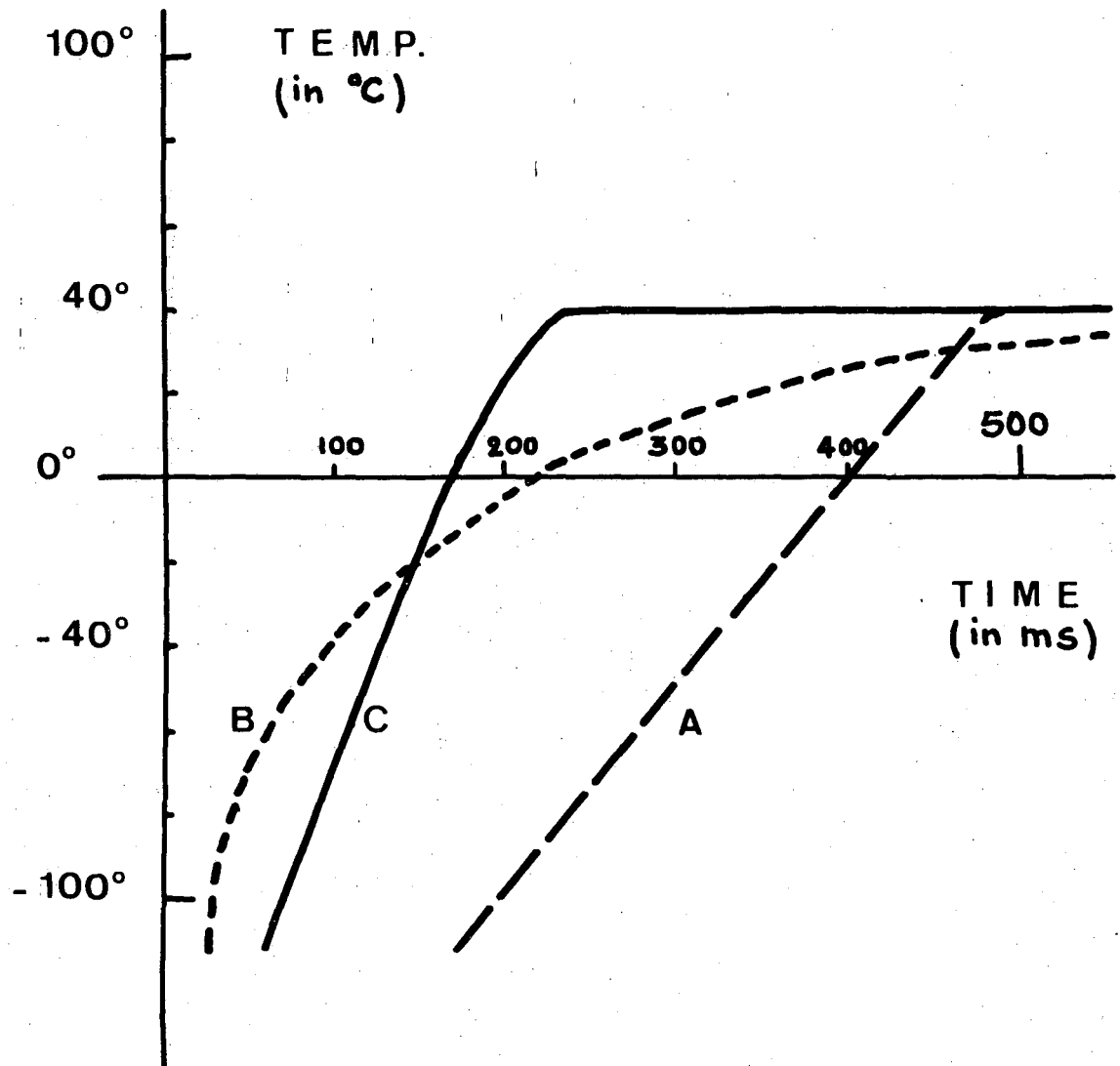


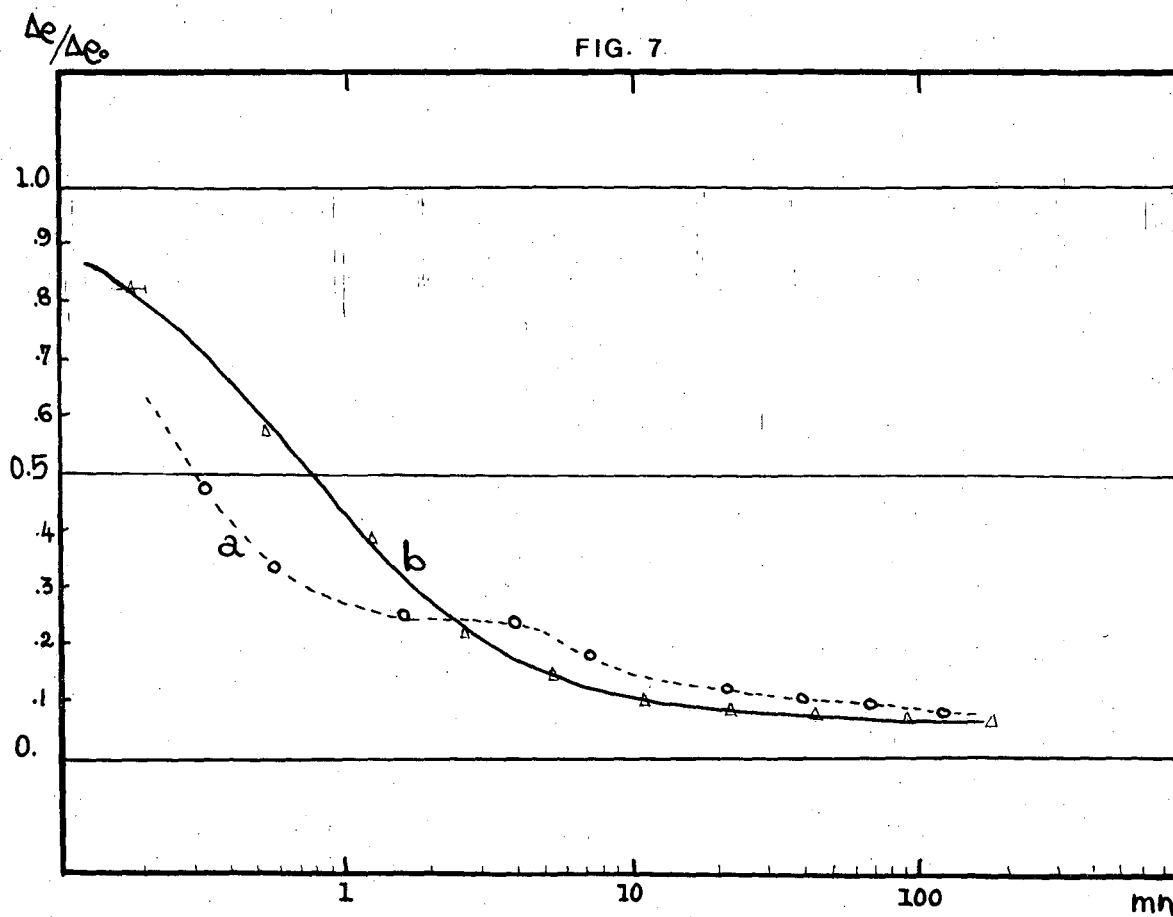
Fig. 5

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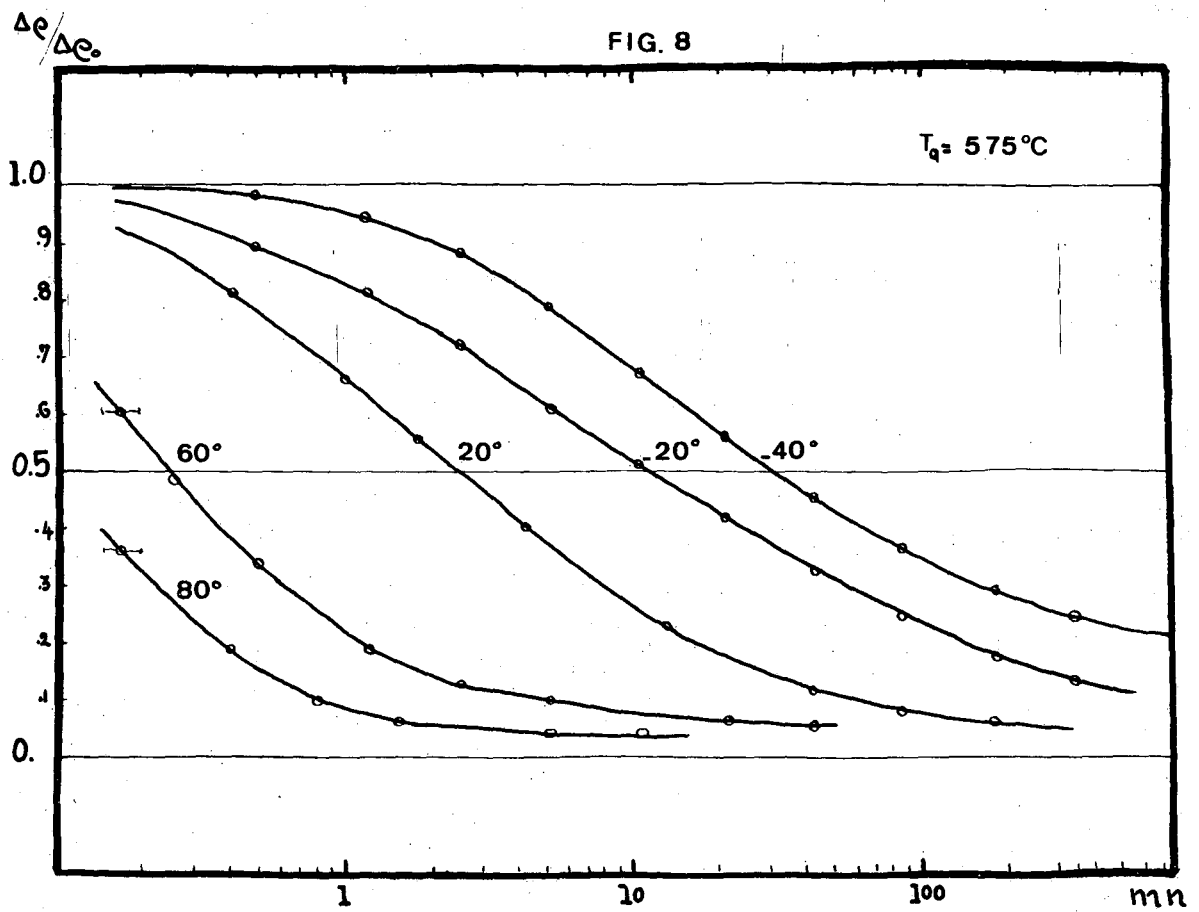
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Fig. 6



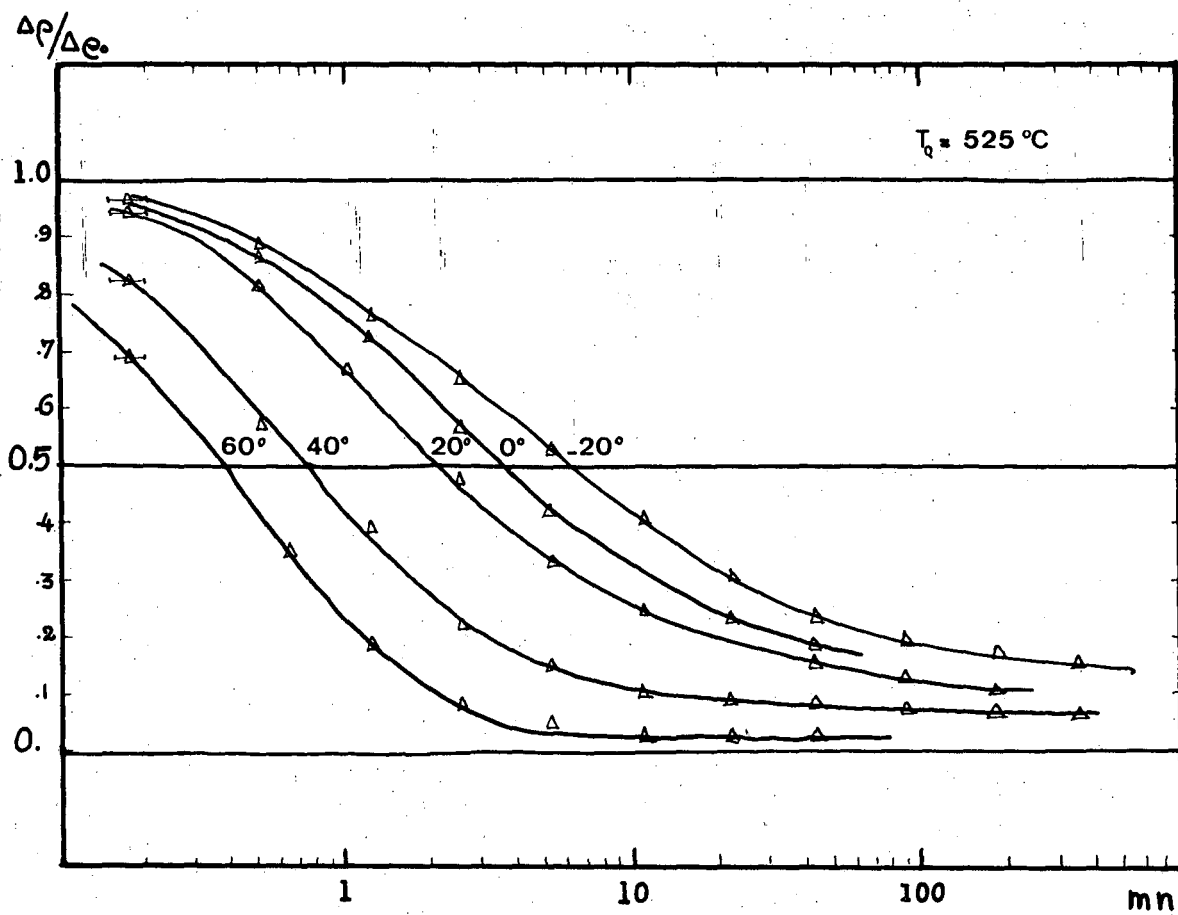
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Fig. 7



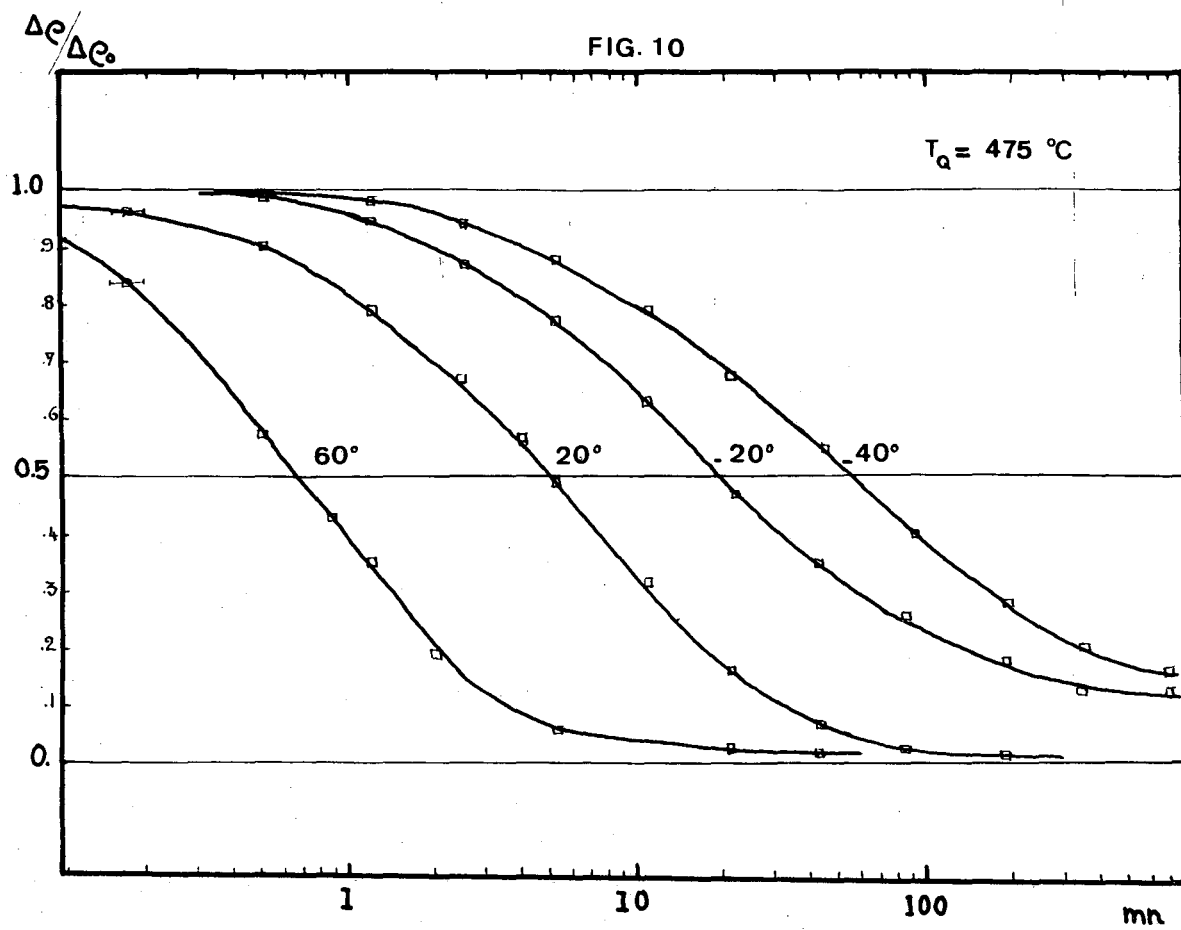
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Fig. 8



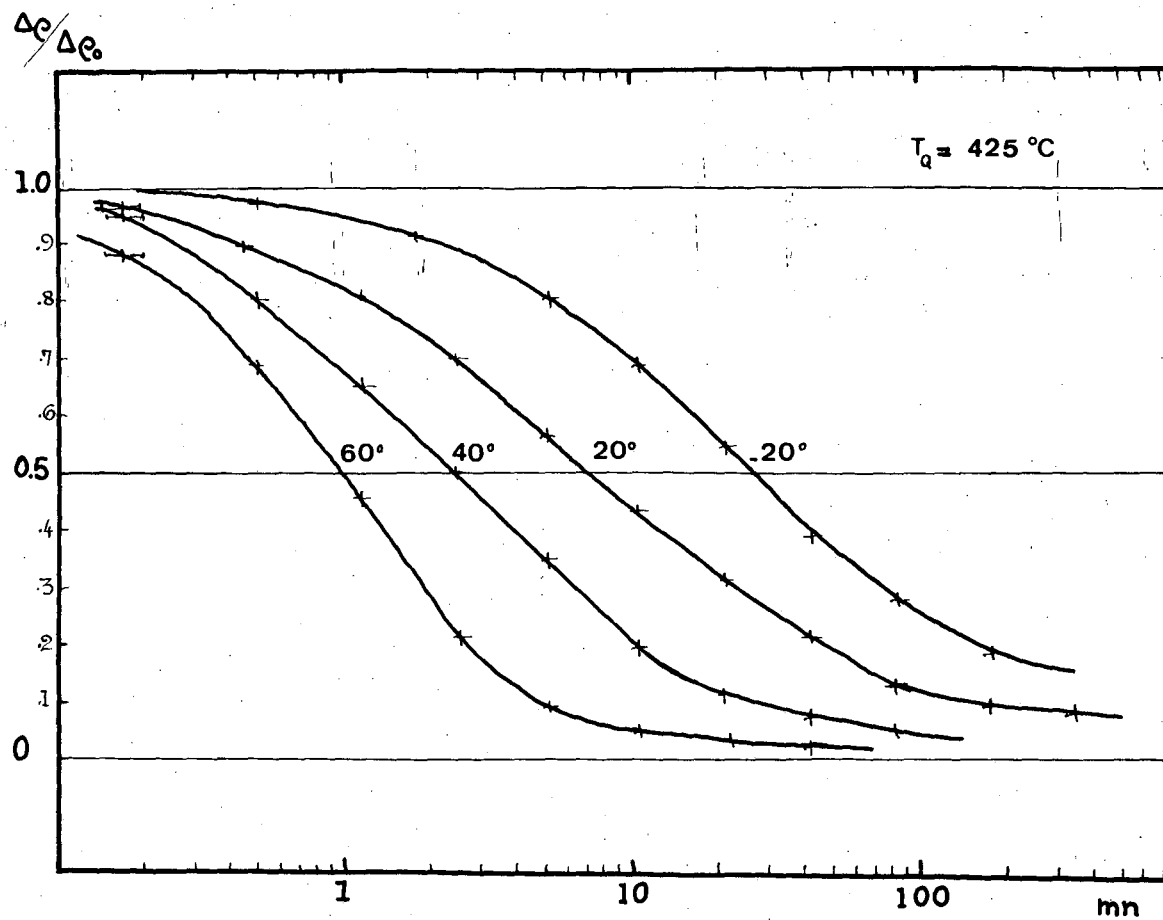
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Fig. 9



XBL 688-5632

Fig. 10



XBL 688-5633

Fig. 11

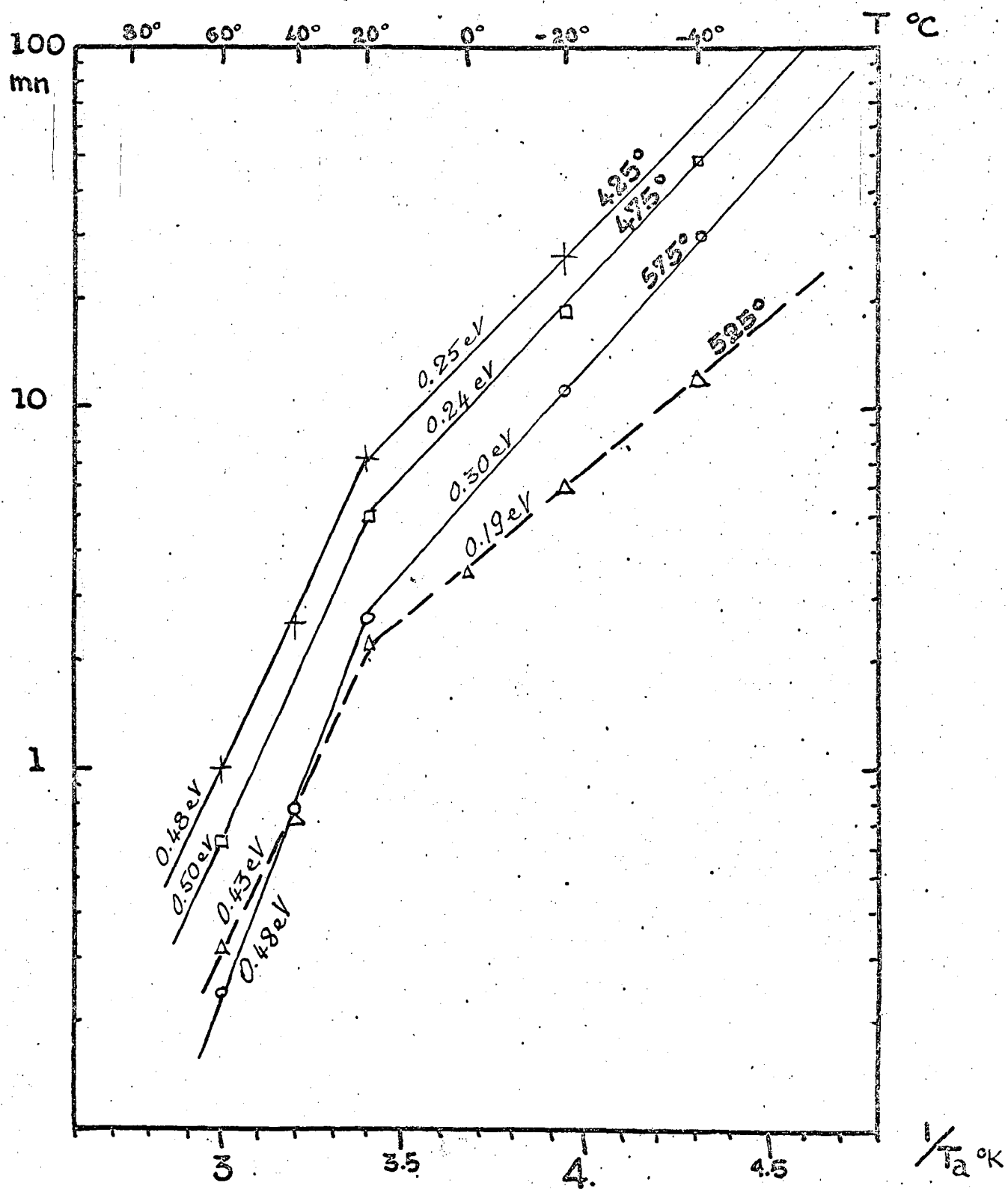
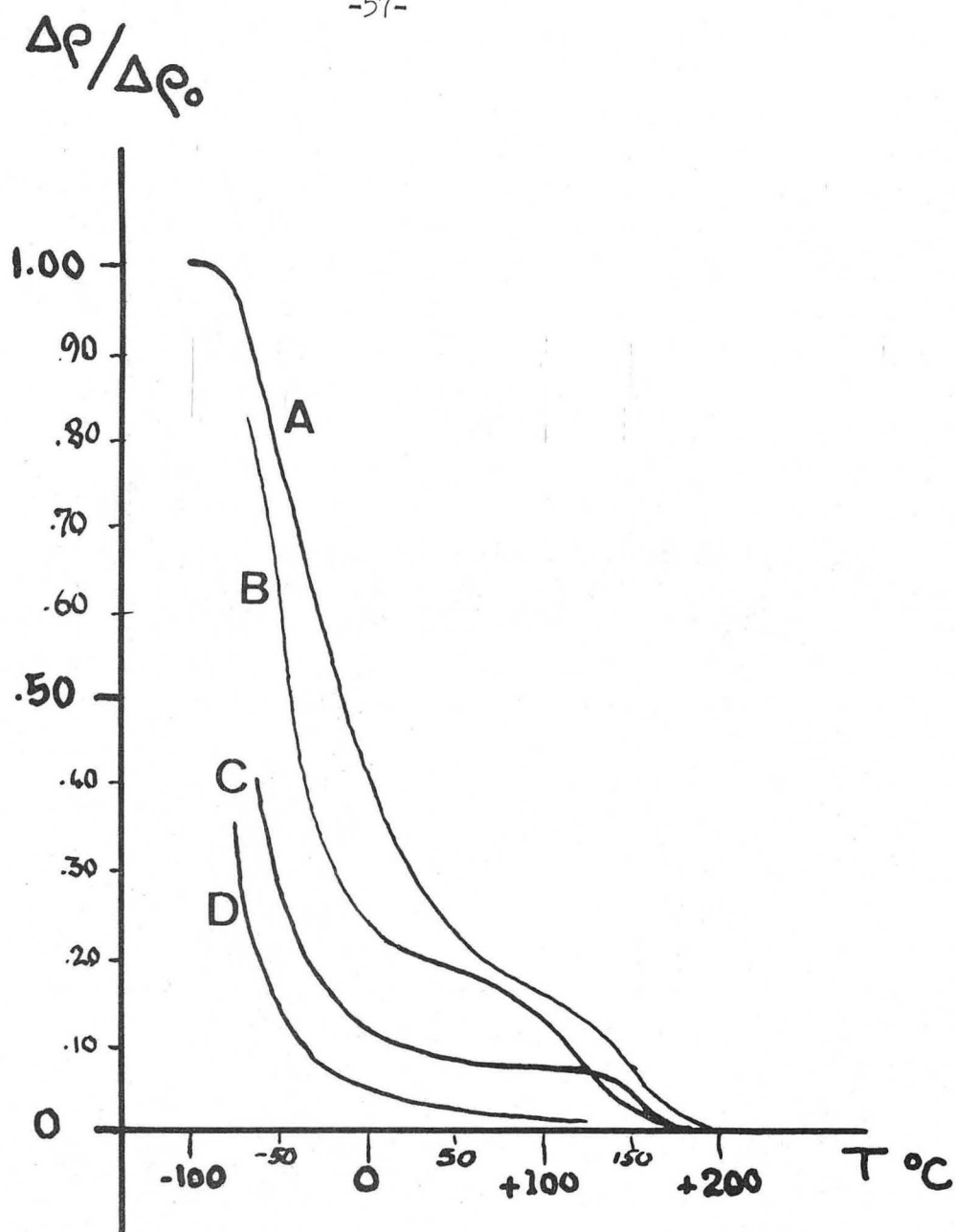
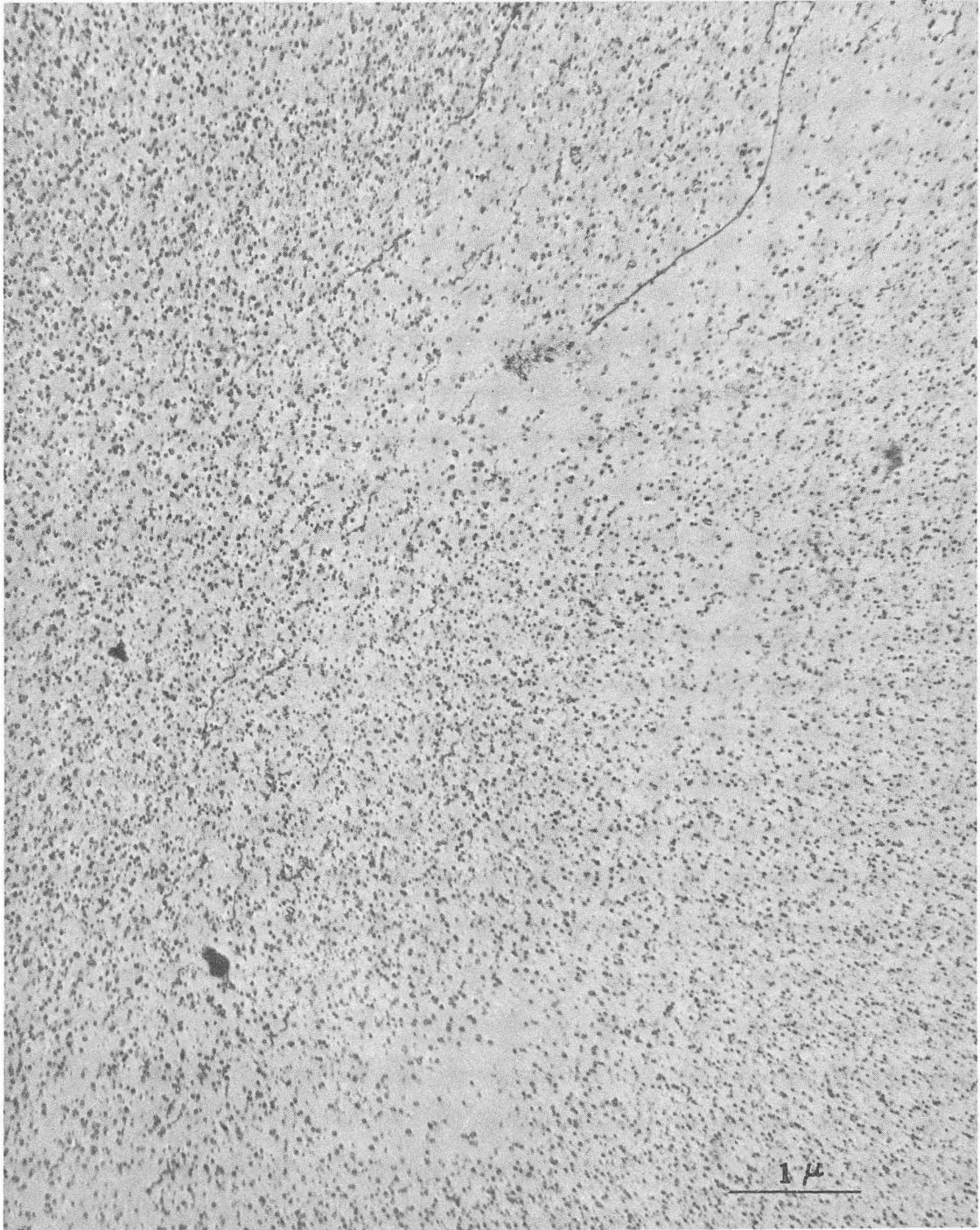


FIG. 12



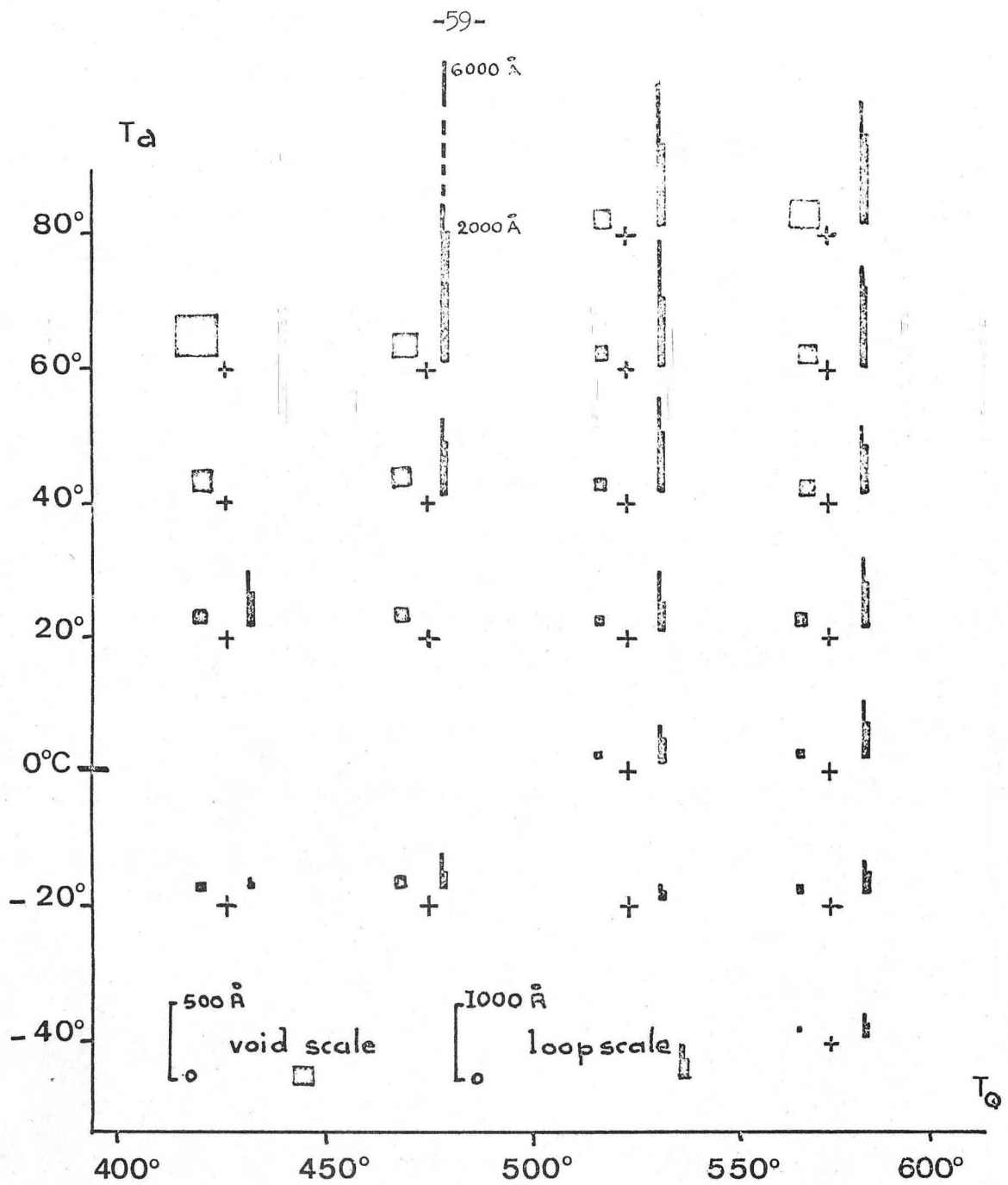
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Fig. 13



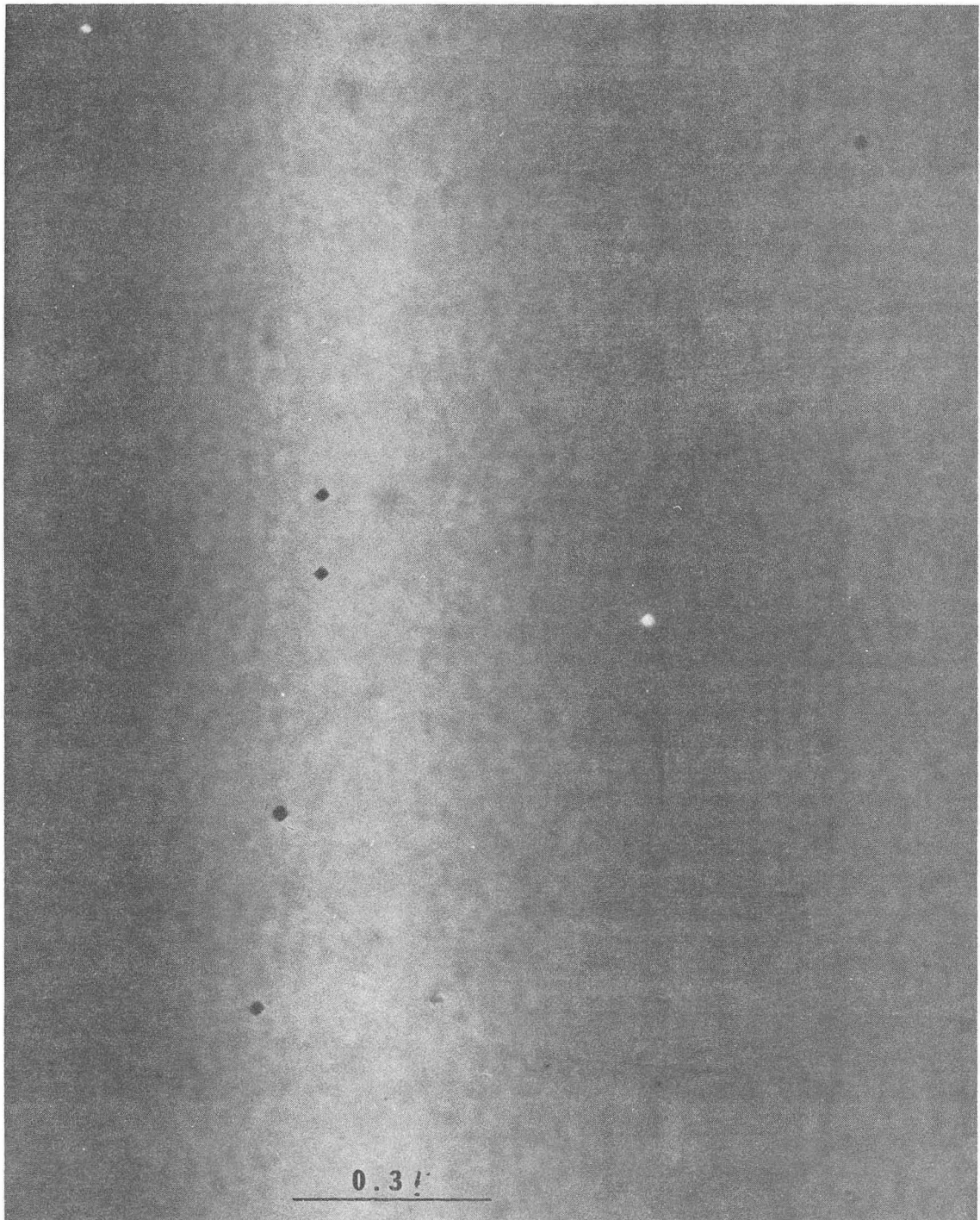
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Fig. 14



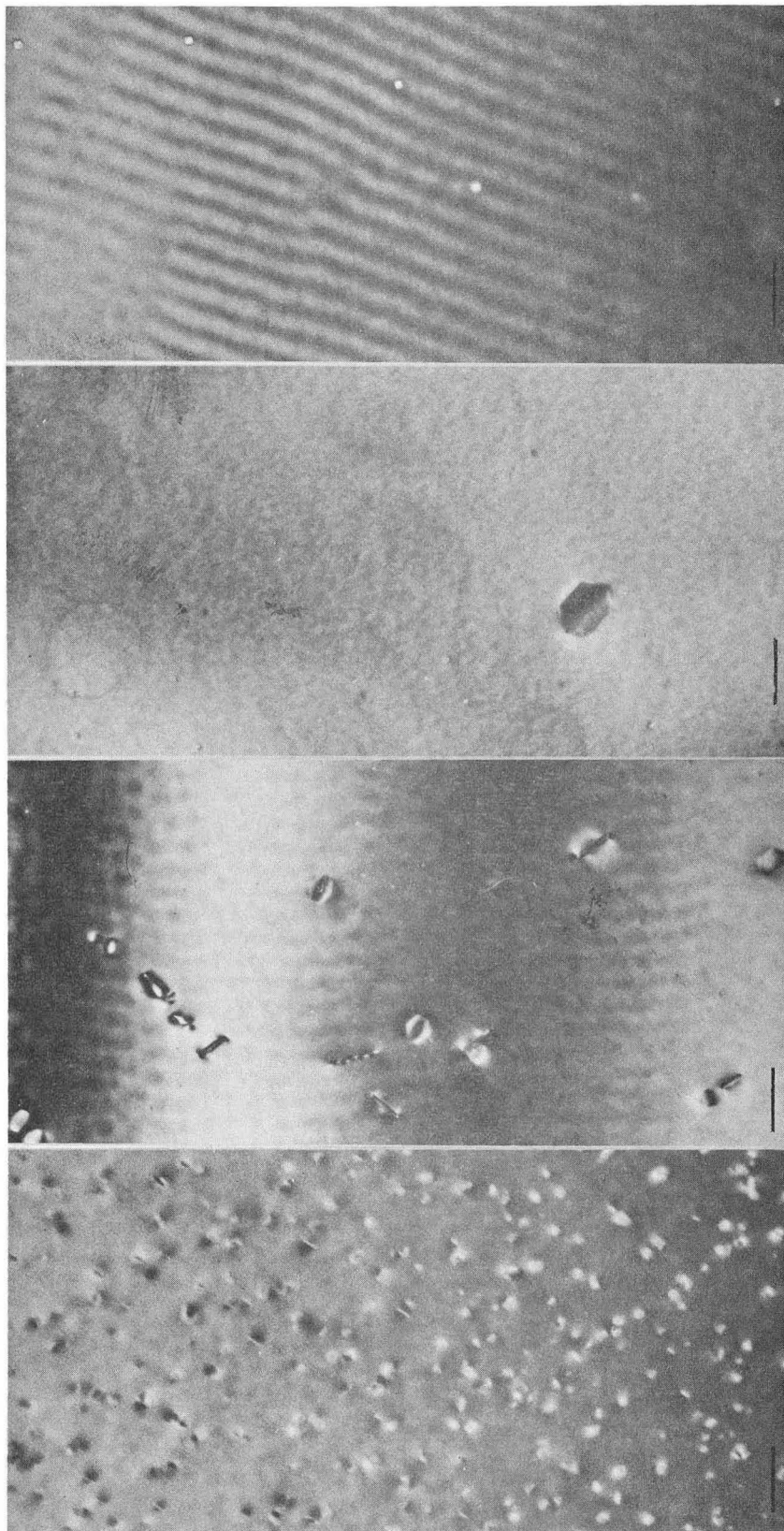
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Fig. 15



XBB 689-5658

Fig. 16



D

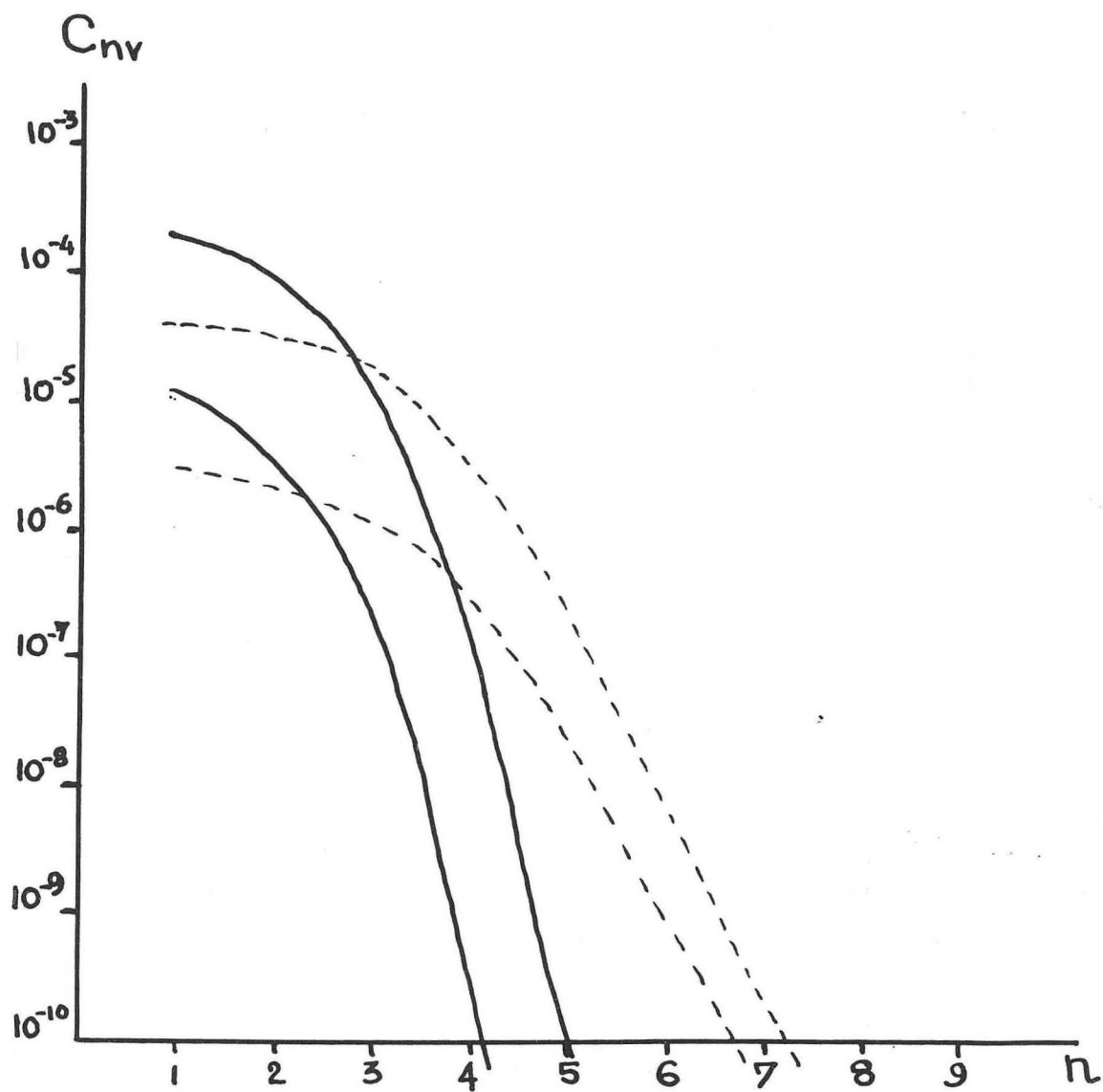
C

B

A

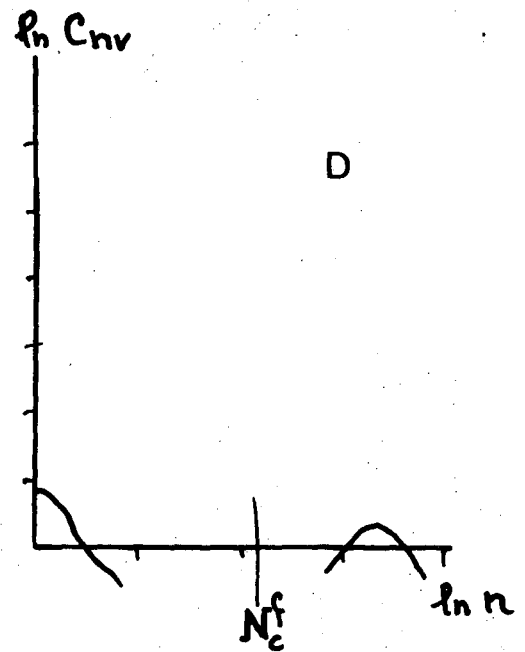
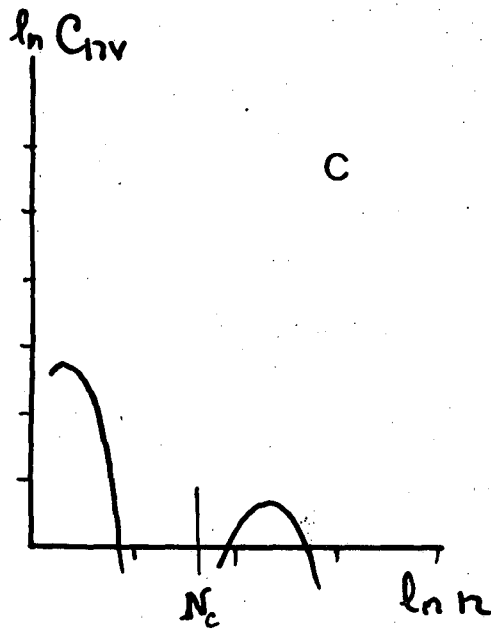
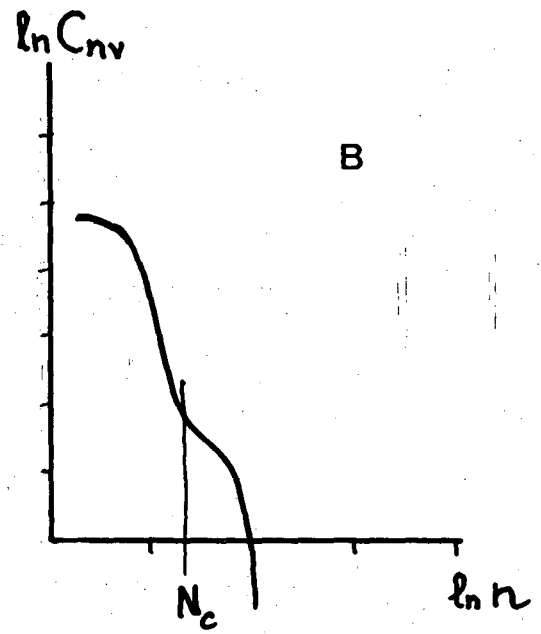
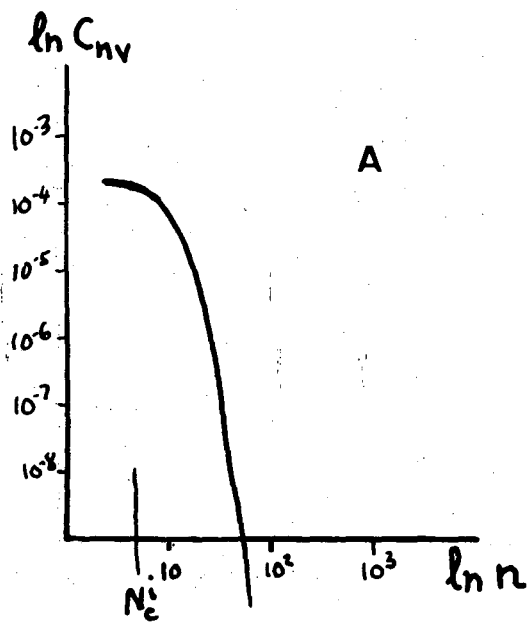
XBB 689-5659

Fig. 17



XBL 688-5636

Fig. 18



XBL 688-5637

Fig. 19

APPENDIX I

TEMPERATURE PULSES OF ALUMINUM SPECIMENS BY RESISTANCE HEATING

A. Introduction

In order to study the annealing kinetics of point defects produced by quenching, irradiation, or cold work, an accurate knowledge of the specimen thermal history is required. In particular when isothermal and isochronal anneals are carried out,¹ the profile of up-quenching sequence and the annealing temperature must be controlled accurately.

Electrical heating by Joule's effect has been employed in a number of investigations involving quenched, face-centered cubic metals, e.g., copper,² silver,^{3,4} gold,⁵ and aluminum.⁶ In those cases the up-quenching pulse and the temperature control were done manually. Recently Emrick⁷ heated gold specimens by means of a shaped electrical current. The advantage of such a technique is a very short rise time at the expense of regulation when the desired temperature is reached.

The experimental device described here has been designed to ensure high heating rates without overshoot and good temperature control and stability.

B. General Description

The components of the control system are shown in block form in Fig. 1. In the present case the aluminum single crystal was located in an experimental chamber (a) which was immersed in liquid helium. The chamber was evacuated and then filled with helium gas to a low pressure. The specimen was introduced as the unknown resistance in a precision Kelvin double bridge (b). The bridge was operated in series with an external

DC transistorized regulator (c). The power was supplied to the current loop by a bank of low internal resistance batteries (d). The resistance of the specimen was raised to the value present on the bridge by a controlled heating current. The current control was obtained by amplifying the bridge output and using it to drive the series regulator. A high-gain DC differential amplifier (e) was used in the control loop. The output of the bridge was also monitored by a null indicator (f), thus allowing the operator to bring the bridge to a fine balance with a zero adjust located in the series regulator circuit. Since a Kelvin double bridge must be used with a yoke and potential leads whose lengths are imposed by the experimental set-up, a potential lead compensator (g) had to be added to the bridge circuit in order to preserve its accuracy.

The annealing time was controlled by a preset digital counter (h). This unit was electronically coupled with a switching circuit (i) which was placed in series with the DC regulator. The timer was actuated coincidentally with the closure of the current loop or at some later time by the operator. At the end of the present time interval, a pulse from the digital counter activated the opening of the current loop by turning off the SCR.

The average temperature of a test specimen was determined from data⁸ published on the temperature dependence of the resistance ratio $R(T)/R(293^\circ\text{K})$. The resistance of a well annealed crystal was determined accurately at 273°K prior to any experiment and the corresponding value of $R(T)$ at the desired annealing temperature, T , was calculated.

C. Design Considerations and Circuits

The basic requirements of the control system are briefly considered before discussing the various components in detail. In the present experiments, the annealing temperatures of interest could be divided into two ranges of importance, i.e., $173^{\circ}\text{K} \leq T < 373^{\circ}\text{K}$ and $373^{\circ}\text{K} \leq T \leq 873^{\circ}\text{K}$. In the former case, regulation of $\pm 0.1^{\circ}$ was sought and in the latter case, regulation of better than $\pm 1^{\circ}$ was considered acceptable. In order to appreciate fully the advantages of 0.1° temperature regulation, the specimen resistance must be measured with an accuracy of at least 0.05%. This comes from the fact that the change of electrical resistivity, with temperature is in the first approximation given by

$$\frac{\Delta e}{e} = \alpha \Delta T \quad (1)$$

where α is of the order of $5 \cdot 10^{-3}$ per degree for aluminum in the temperature range of interest.

In order to obtain the required heating rates of at least 800°C/s (see pp.17-18), a 15A current was needed. This short rise time requirement determines the large transient power the regulator must be able to release and thus the transient current the Kelvin bridge and the current leads must carry without damage or alteration.

The Honeywell portable Kelvin double bridge (Model 1622) was selected. It provided the desired 0.05% accuracy, covered the resistance ranges of interest, and was capable of carrying the necessary transient currents for a few milliseconds. An important feature of the Kelvin bridge, relative to ratio sets, is the bridge's low and reasonably constant output impedance to the galvanometer (i.e., $< 1\text{k}\Omega$). In addition the potential

lead compensation exposed below would not be practical with ratio sets because of the dependence of compensations on the bridge ratio, A/B .

For the purpose of further discussion, it is useful to establish the equations of the bridge. Referring to Fig. 2a, let X be the resistance of the specimen introduced as the unknown; R the reference resistance set on the bridge; and assume a current, I , is flowing from the generator. When I enters the bridge it is divided into a large fraction, i , flowing through the reference resistance and the specimen, and a small fraction, i' , flowing through the arms A and B . When the bridge is unbalanced, a voltage, V_0 , appears at the galvanometer output. If the resistance of the yoke, d , is small, if the resistance of the external potential leads, m and p , can be neglected, and if $a/b = A/B$, then the Kelvin double bridge is equivalent to a Wheatstone bridge. Its equations can then be written as:

$$V = \frac{1}{\frac{1}{A+B} + \frac{1}{R+X}} \quad (2)$$

$$I = i + i' \quad (3)$$

$$V = (A + B)i' = (R + X)i \quad (4)$$

and

$$V_0 = Bi' - Ri \quad (5)$$

Solving this system for V_0 yields

$$V_0 = \frac{BX-AR}{A+B+R+X} \cdot I \quad (6)$$

If X is written as $X = \frac{A}{B}R + \Delta X$ and considering that $R + X \ll A + B$, expression (6) becomes:

$$V_0 = \frac{B}{A+B} \cdot \Delta X \cdot I \quad (7)$$

Thus the error signal in volts, V_0 , is proportional to the error ΔX in the specimen resistance and hence temperature. The sensitivity of the technique depends directly on the bridge ratio, A/B , employed and on the current, I , flowing through the circuit.

Because of the nature of the experimental chamber, the specimen could not be connected to the bridge as recommended. The resistance of the yoke, d , and potential leads, m and p , (see Fig. 2a) will not be negligible with respect to the values of the arms A and B . The resistance reading R on the bridge and the actual resistance of the specimen X will then be related by:

$$A = \frac{A+m}{B} R \quad (8)$$

Since the value of m will certainly exceed the resistance of the potential lead provided by the manufacturer, it becomes necessary to alter the bridge by inserting a fixed resistor of value n in branch B and q in branch b with $n \approx q$ (see Fig. 2b). The potential lead compensation (denoted g in Fig. 1) is then simply a set of wire-wound variable resistors, i.e., m' and p' . If n and q are taken such that $n = m$ and $q = p$, the sums $(m + m')$ and $(p + p')$ can be adjusted so as to verify that

$$\frac{m + m'}{n} = \frac{p + p'}{q} = \frac{A}{B} = \frac{a}{b} \quad (9)$$

R and X are now related by

$$X = \frac{A + (m + m')}{B + n} R = \frac{A}{B} R \quad (10)$$

so that the bridge reading is correct and its accuracy preserved. Note that n and q should be chosen as small as possible in order to minimize the compensation with m' and n' for the cases $\frac{A}{B} = 1$ and 10 .

The circuit diagram of the series regulator is shown in Fig. 3. A 12V, low internal resistance ($< 0.1 \Omega$), DC power supply is connected to the input of the regulator. The bridge error signal is amplified and fed to the regulator at a level determined by a "zero adjust" circuit which employs a 2N1305 transistor whose base voltage is determined by a ten turn, 10Ω potentiometer. While the resistance of the aluminum specimen is still below the preset value, a large error signal appears at the bridge. The amplified bridge output will reach +10V to +30V above C, thus bringing V_{BE} of the 2N1305 to large positive values. The 1N3392 Zener diode prevents V_{BE} from exceeding the breakdown value for that transistor. An adjustable dummy load placed in series with the bridge allows proper adjustment of the power brought to the specimen while the gain adjustment on the DC differential amplifier is set so as to obtain the best possible temperature control with minimal overshoot and with no oscillation when going from temperature rise to temperature regulation. The circuit was designed for two ranges of power, i.e., 0.3 to 6 watts and 2 to 30 watts. For the latter output condition, a $0.1 \mu F$ capacitor is introduced into the feedback loop of the 2N1305 and the dummy load, D, is adjusted in the range 0.1 to 1Ω .

The differential DC amplifier should meet the following specifications: a. high sensitivity and low noise ($\leq 10 \mu V$); b. high common mode rejection ($\geq 300 V$); c. gain of 100 to 1000 at up to 10 kc; and, d. fast recovery time after large input overload ($\leq 1 ms$). The last two

conditions insure a fast heating rate without overshoot. The Dynamics differential DC amplifier (Model 6450) was employed.

For the purpose of monitoring the bridge output, it was found necessary to use an electronic null indicator since overload protection and fast recovery were needed. Its sensitivity should be in the $\mu\text{V}/\text{cm}$ range; its input impedance in the $\text{M}\Omega$ range; and it should have adequate isolation from the line voltage in order to avoid disturbances on the input side of the high gain DC amplifier. The Brown electronic null indicator (Model 104WL-6) was used.

The timer was a Beckman Instruments, Inc. preset digital counter (model 5423) fed with the 60 cps line signal. Its second decade was modified so as to trigger the third decade after 59 pulses instead of 99. The annealing time could then be preset directly in seconds rather than in line cycles. Controlled anneals of 999.9 seconds were possible with this arrangement.

The switching circuit is presented in Fig. 4. It is essentially composed of a power SCR transistor (type C 45) triggered manually at the start of a thermal cycle. It is turned off at the end of the cycle by discharging an RC circuit with reverse polarity across the power transistor. This discharge is triggered by applying to the gate of a 2N2327 SCR transistor a 5 volts signal coming from the preset digital counter. In the present circuit the time constant of the RC circuit and the charging voltage of the capacitor can be chosen so as to be adequate to turn off the power transistor without bringing any additional power to the specimen. This is particularly important as a feature of the switching circuit for the present application.

All potential leads and low signal leads were carefully shielded. The circuit was grounded at one point only in order to avoid ground loops. It seemed most appropriate to ground a current lead as close as possible to the galvanometer output of the bridge.

D. Results

Aluminum crystals, 0.16 cm by 0.0008 cm in cross section and 25 cm long with a 10 cm gauge length, were mounted in a 8 cm diameter stainless steel chamber. For these experiments the chamber was filled with helium gas to 5 μ , Hg pressure and it was embedded in either liquid helium or liquid nitrogen. Typical operating conditions were: amplifier gain 100; dummy load, 0.5 Ω ; and series regulator in the high output power condition (i.e., 2 to 30 W).

From measured variations in the bridge error signal, V_0 , and employing Eqs. (1) and (7), it was concluded that the average temperature of a test specimen could be controlled to within $\pm 0.1^\circ$ in the temperature range 173°K to 373°K. The temperature regulation was estimated to be $\pm 0.5^\circ$ above 373°K.

The principal weakness of the self-heating technique arises from temperature in-homogeneities along the specimen gauge length due to end losses and/or local variations in the cross sectional area. In order to evaluate the importance of a nonuniform temperature distribution, a series of specimens were pulsed to temperatures in the range 650°C to 655°C. If the cross section of a crystal was not sufficiently uniform, local melting would take place. When the cross section was reasonably uniform, no specimen damage was observed after such pulses and melting

between potential leads was induced after brief pulses to 658°C. These results were interpreted as indicating that, for ideal specimen geometry, minimal overshoot was taking place and acceptable local and average temperature control was still possible for annealing temperatures approaching the melting point of an aluminum specimen.

When used alone, resistance heating performed with the present device has several advantages over the classical method using stirred liquid baths: (1) specimen handling is avoided; thin or delicate crystals may be mechanically deformed while being introduced or removed from a liquid bath or by the stirring action of the bath itself; (2) since annealing takes place within an experimental chamber whose environment can be carefully controlled, contamination of highly reactive metals can be minimized; and (3) the specimen alone is brought up to the desired temperature while the supporting elements and chamber wall remain close to the temperature of the cryogenic liquid employed, thus low temperature conditions are re-established quickly after each thermal pulse and subsequent resistance measurements can be made promptly.

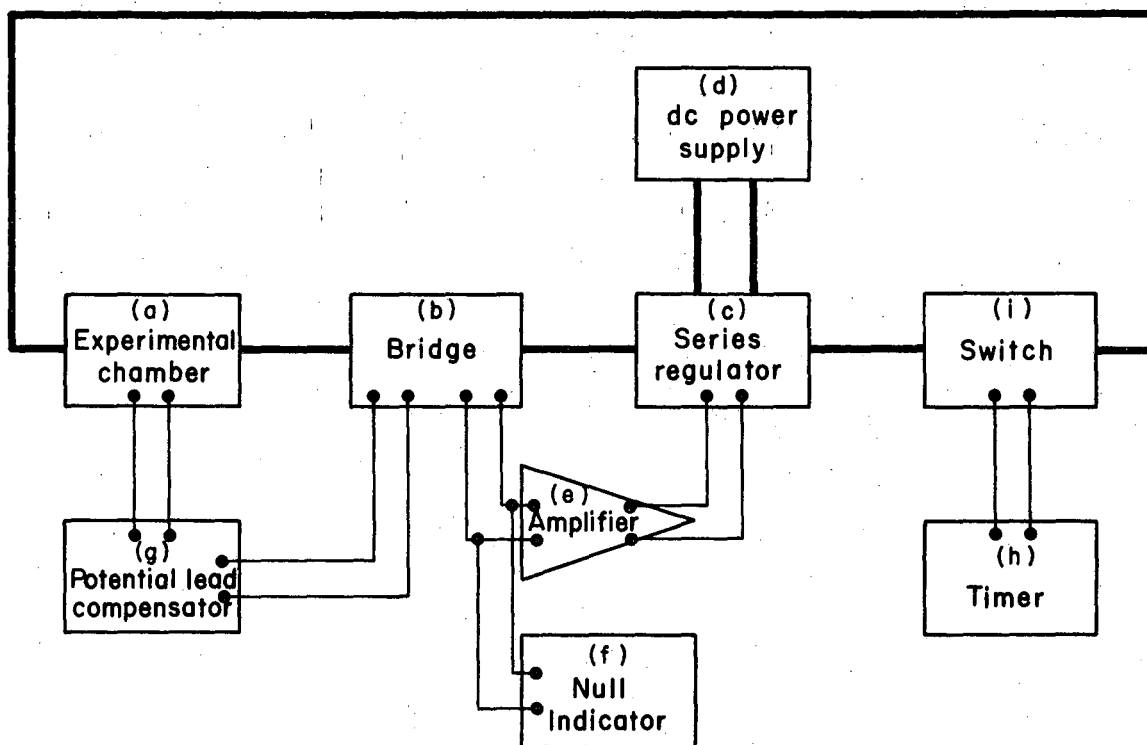
In conclusion it is felt that these results, combined with reproducible data obtained from isochronal and isothermal anneals of quenched copper⁹ and aluminum samples, illustrate the reliability of this up-quenching and aging method.

ACKNOWLEDGMENTS

The author would like to thank Mr. K. Lamers of the Electronic Research and Development Group, Mr. H. Heath of the Electrical Standards Division, and Mr. R. LaPierre of the Electrical Engineering Research and Development Group, Nuclear Chemistry Division for assistance and valuable discussions.

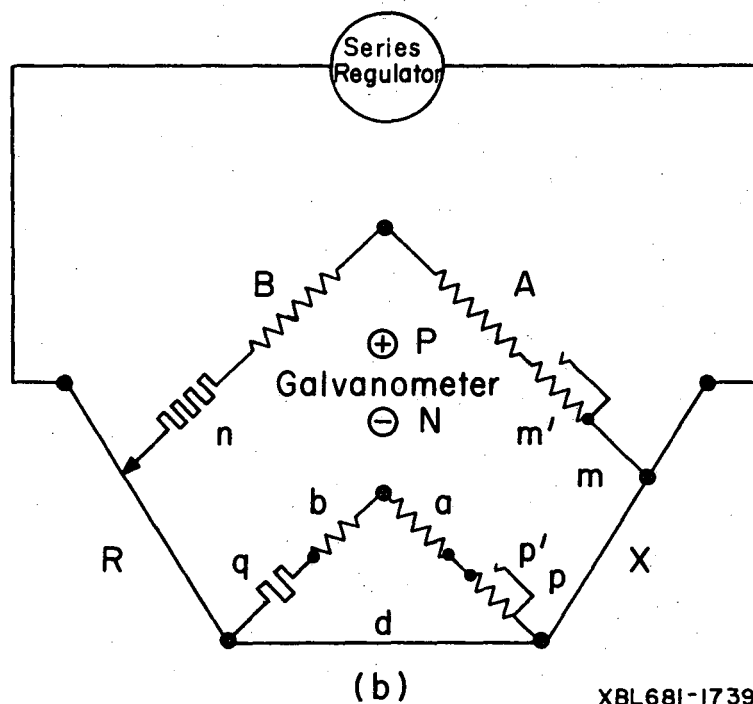
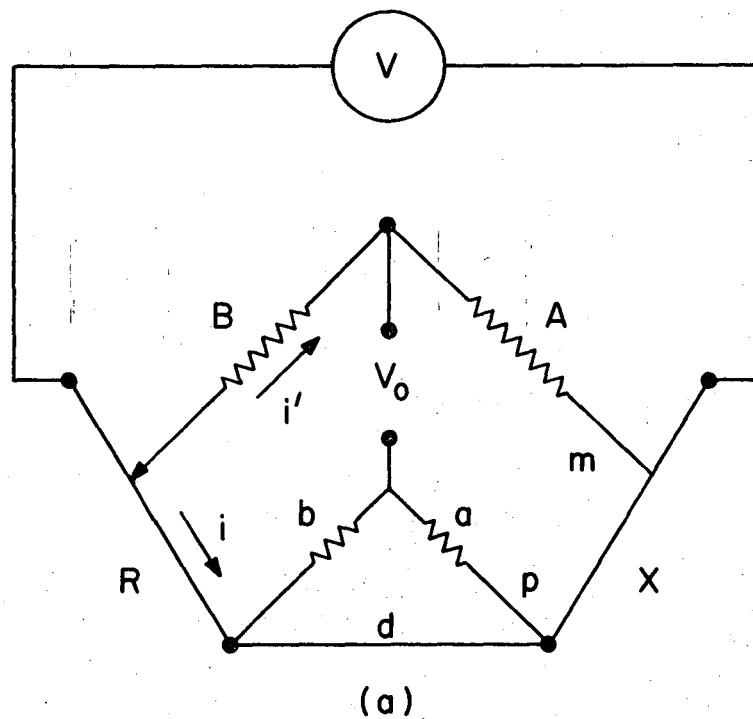
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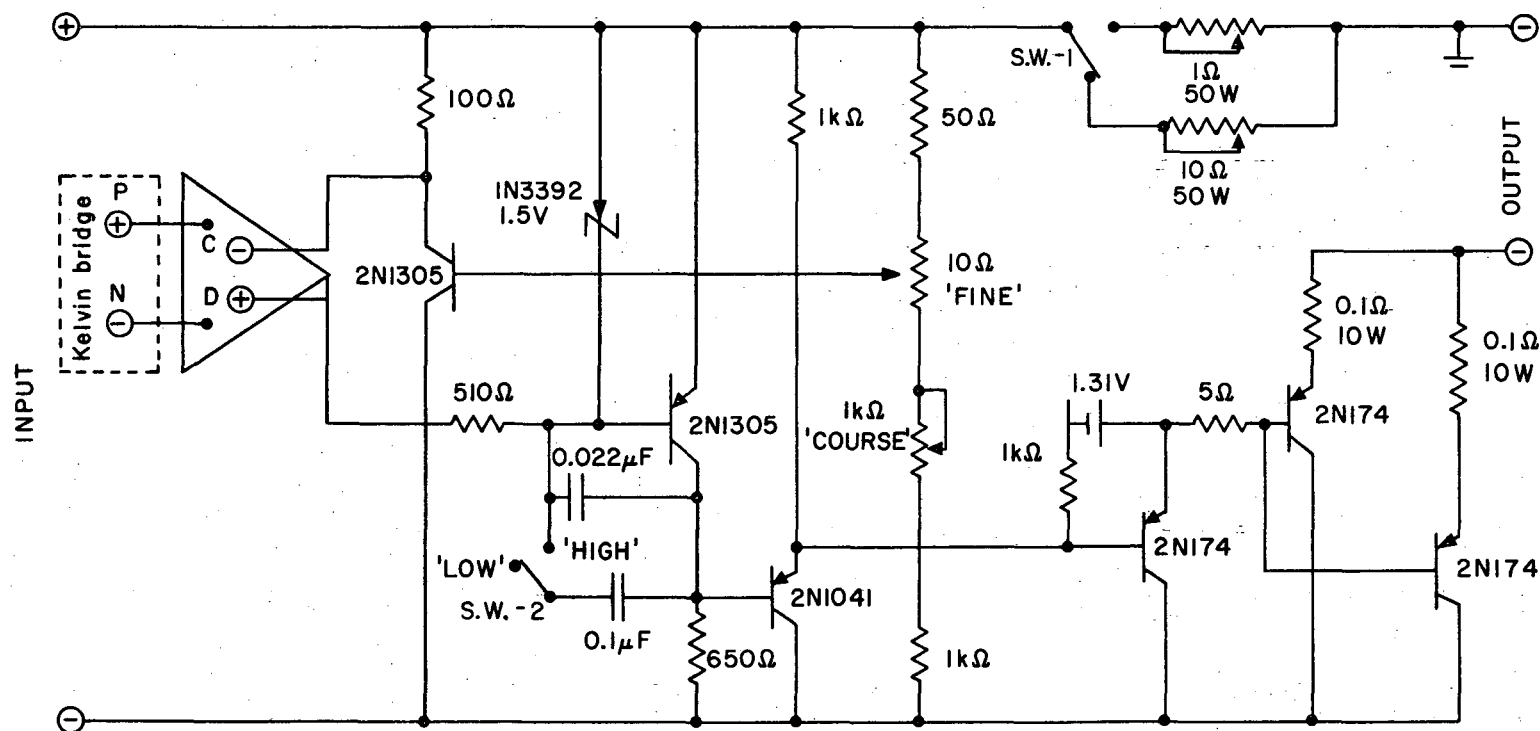
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Fig. AI-1. Block diagram of the components used in carrying out an annealing cycle.



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Fig. A1.2. Bridge circuits: a- Kelvin double bridge; b- Modified Kelvin double bridge with variable potential lead compensation represented by m' and p' .

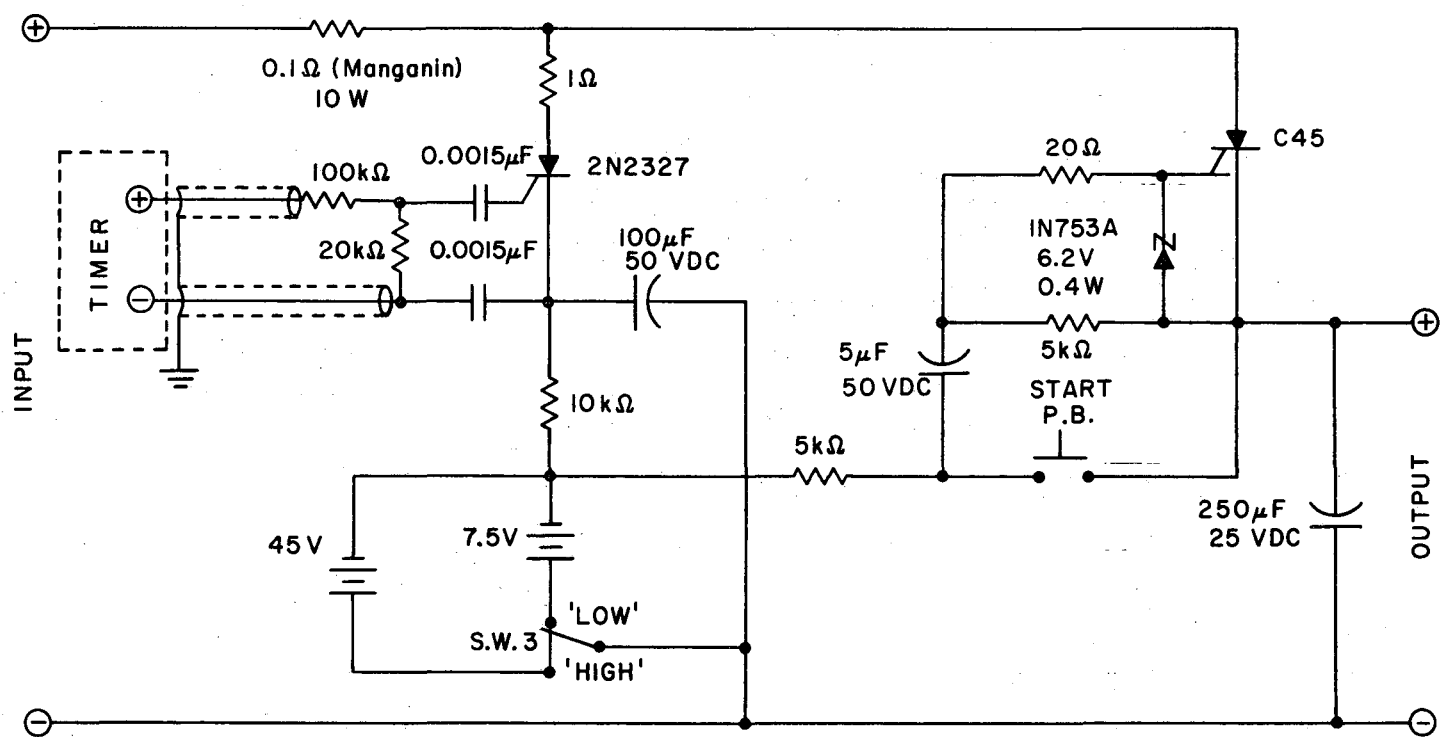


All resistors are 1/2W unless otherwise specified

All 2N174 transistors are heat sunk

XBL681-1740

Fig. AI.3. Circuit diagram of the series regulator; switches s.w. 1 and s.w. 2 are shown in the "low" output power position.



All resistors are 1/2W unless otherwise specified

XBL681-1741

Fig. AI.4. Circuit diagram of the SCR switching unit: switch s.w. 3 is shown in the "low" charging position.

APPENDIX II

ELECTRON MICROSCOPY IMAGES OF VOIDS IN QUENCHED ALUMINUM

A. Introduction

The formation of three dimensional voids by precipitation of vacancies was first observed in aluminum and reported in detail by Kiritani¹ and Kiritani et al.² It was later observed in gold³ and also in silver and copper⁴ under certain quenching conditions.

In aluminum these voids usually have the shape of regular octahedra, limited by (111)-type surfaces.

The purpose of the work presented here was to calculate the lattice relaxations around those defects assuming that their core was empty. This assumption does not deny the possible role of certain gaseous impurities during the nucleation and the initial stages of the growth process but simply neglects the influence of a gas present inside the voids under very low pressure. It excludes the case of a gas captured inside the octahedra under high pressure.

When voids larger than $200 \text{ \AA}$ can be observed under appropriate diffraction conditions, it becomes evident that the simple interpretation of the contrast effects based on the change in thickness of the foil caused by the presence of the void,² cannot account for the finer details observed around the edges of the octahedron. Figure 1 shows a large void in a single crystal of aluminum observed along the [110] direction with a $\langle 111 \rangle$ beam operating in a region of good transmission, i.e., where Δ is slightly positive.

For voids smaller than $200 \text{ \AA}$, a contrast effect different from

those due to a mere change in thickness is also observable along the trace of the two (111) surfaces limiting the octahedra, positioned edge-on and parallel to the operating beam. This effect is visible on Fig. 2b and on the corresponding photometric curve in Fig. 2b.

Truncations are sometimes observed that alter the octahedral shape of the voids. Figure 3 shows an example of a truncation by a (111) plane. On Fig. 4, truncations by (100) planes are visible on two of the six apices of the octahedron. Truncation and imaging effects are visible on the two pictures of the same void (see on Fig. 5a and b under different diffraction conditions).

When the images of voids recorded on the photographic plates fall below $40 \text{ \AA}$ (distance between the two vertical (111) planes limiting the octahedron), their relationship to the actual defects is not well established.

In order to correlate properly the observed image with the size of the actual cluster, it would be interesting to know the strain field around such defects. The equations describing the imaging of a strain field by electron diffraction have been developed by Howie and Whelan.⁵

When only one strong reflection g is operating, the amplitude of the transmitted beam T and that of the diffracted beam S as a function of the depth z in the crystal are given by the expressions:

$$\frac{dT}{dz} = - \frac{\Pi}{\xi'_0} T + \Pi \left(\frac{i}{\xi_g} - \frac{1}{\xi'_g} \right) S$$

$$\frac{dS}{dz} = \Pi \left(\frac{1}{\xi_g} - \frac{1}{\xi'_g} \right) T + \Pi \left[-\frac{1}{\xi'_0} + 2i (\delta_g + \beta') \right] S$$

where $\beta' = \frac{\partial}{\partial z} (\underline{g} \cdot \underline{u})$ and $u(x,y,z)$ is the expression of the strain field.

The contract effects observed around gas bubbles formed in aluminum after irradiation was interpreted in this manner by Levy and Gerl.⁶

Unfortunately, a method of this type cannot yield quantitative results since the dynamical contrast theory in its present form is not applicable to the void configuration. The assumptions contained in the "column approximation" are not fulfilled since strain fields around such defects are varying too rapidly. The column approximation assumes that several rows of atoms are located inside the column. It assumes also that the deformation is uniform in the column and that the column can be regarded as surrounded by columns having similar properties. Here the strain field will be found changing rapidly over interatomic distances and the columns passing next to the surfaces of the voids will be the neighbors of columns passing through the void itself and being thus different in nature from the others.

B. Method of Computation

Despite the restrictions just mentioned, it is still interesting to calculate the amount of strain experienced by successive $\langle 111 \rangle$ atomic planes in the neighborhood of the surfaces of an octahedron.

Since the continuum approach to plastic deformation is unable to account for lattice relaxations in the vicinity of surfaces, an atomistic approach must be taken. The Morse potential was chosen for this study because of its simplicity. A finer description of the atomic interactions

in FCC metals has been proposed by Harrison⁷ but the presence of several relative minima in the potential functions complicates considerably the calculations. If r_{ij} is the distance between atoms i and j , the Morse potential can be written as:

$$\Phi(r_{ij}) = D \{ \exp [-2\alpha(r_{ij}-r_0)] - 2\exp [-\alpha(r_{ij}-r_0)] \}$$

where r_0 , the equilibrium distance of approach of the two atoms, D the disassociation energy and the constant α are given by Girifalco and Weizer.⁸

No attempt was made to calculate the actual strain distribution around such a complicated volume as an octahedron. The relaxation of $\langle 111 \rangle$ planes were estimated for two simplified cases: (1) a half infinite crystal bounded by a $\langle 111 \rangle$ plane. The results of these calculations provide a good approximation for very large voids; (2) two half infinite crystals, bounded by $\langle 111 \rangle$ planes and separated only by a few missing planes. This configuration was taken as an approximation for small voids.

The method of calculation has already been published.⁹ The numerical work was carried out on a CDC 6600 computer. Interaction energies were obtained by summation over 4000 atoms (i.e., up to the 11th nearest neighbor) or over 500 atoms (i.e., up to the 6th nearest neighbors).

The distortions $\delta_1, \delta_2, \delta_3$ are defined on Fig. 6 and represent the displacement in percent of the interatomic spacing of the bulk of the lattice.

C. Results

The following results were obtained in the first case; i.e., half infinite crystal bounded by a $\langle 111 \rangle$ plane:

Table I

	Large lattice (4000 atoms)	Small lattice (500 atoms)
δ_1	3.671%	3.667%
δ_2	0.726%	0.709%
δ_3	0.169%	0.147%
δ_4	0.050%	0.147%

The calculations made with a "small lattice" are not significantly different from those obtained with many more atoms. A "small lattice" was therefore used for the second problem in order to simplify the programming work and shorten the machine time.

For the case of two half infinite crystals separated by n missing planes (Fig. 7) the following lattice distortion values were found:

Table II

Distortion	Number of missing planes		
	1	2	3
δ_1	10.1%	4.4%	3.6%
δ_2	10.08%	1.41%	0.78%
δ_3	8.22%	0.78%	0.16%

The meaning of these results can be summarized in the following conclusions:

1. The strain fields present around voids drop very sharply with the distance, and the displacements are much less than those encountered around dislocations. This is verified qualitatively on the pictures of voids presented in this paper. The intensity distribution perpendicularly to the $\langle 111 \rangle$ surfaces varies very rapidly and the image width of the strain field does not exceed 0.04 to 0.05 ξ_g (where ξ_g is the extinction distance corresponding to the operating beam $\underline{g}$). Images of dislocations commonly exceed 0.2 ξ_g .

2. Due to the direction and sharpness of the strain field, this additional contrast effect on voids can only be observed in single crystals oriented along directions such as $\langle 110 \rangle$ or $\langle 111 \rangle$ which give maximum contrast with $\langle 111 \rangle$ beams operating since $\beta' = \frac{\partial}{\partial z} (\underline{g} \cdot \underline{u})$ is largest in this case.

3. Two half infinite crystals separated by one missing plane is a limiting case which is an approximation of the two dimensional loop. The distortions do not decrease rapidly and more terms would be needed in order to obtain a correct picture. We can see however that a complete "collapse" takes place since $\delta_1 + 2 \sum_i \delta_i \rightarrow 1$ which indicates that the initial gap tends to be filled completely.

4. For the case where two planes are missing, we see that the strain field on each side of the voids are expected to be of the same order of magnitude as the void itself; thus the image of a 10 Å void may extend over 30 Å. With three planes missing the same holds true and tends to

indicate that images of voids smaller than $40 \text{ \AA}$ may exaggerate the size of the voids. Such small voids, although visible in properly oriented crystals under appropriate diffraction conditions may be invisible under other circumstances.

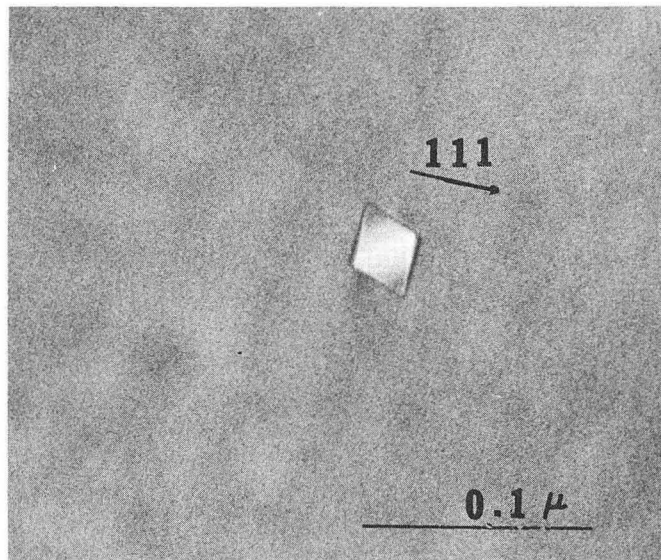
5. The results obtained for three missing planes do not differ appreciably from those obtained for a single half infinite crystal. Therefore, the assumption used in the first part of the calculations was justified: one facet of the octahedron can be considered as a section of a half infinite crystal since its atoms do not "feel" the presence of other atoms located on other facets. This assumption is valid for atoms which are distant from hinges and corners of the octahedron by more than a few atomic rows.

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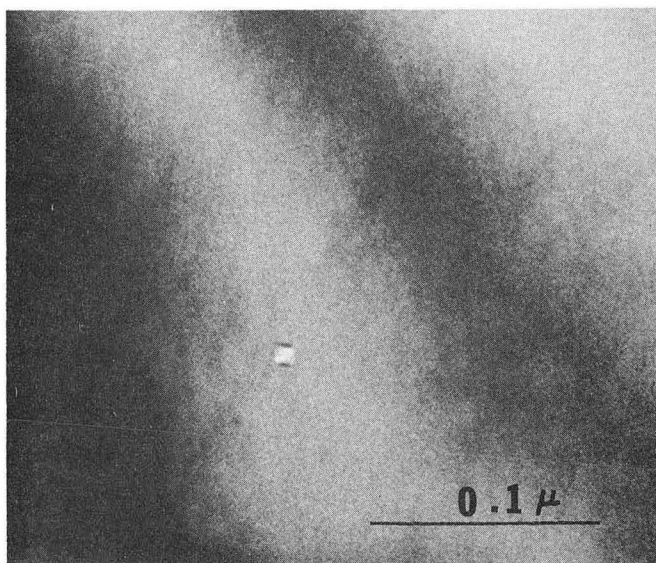
APPENDIX II - FIGURE CAPTIONS

- Fig. 1 Large void in (110) oriented foil and $\langle 111 \rangle$ beam operating.
- Fig. 2 a-Void in (110) oriented foil ($\sim 200 \text{ \AA}$)
 b-Photometric curve along the projection of the $\langle 111 \rangle$ direction
 of the operating beam.
- Fig. 3 Void with (111) truncation.
- Fig. 4 Large void with (100) truncation.
- Fig. 5 Variatious contrast effects on same void
- Fig. 6 Description of distortion parameters δ 's.
- Fig. 7 Two half infinite crystals separated by n missing planes.



XBB 689-5660

Fig. AII-1



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Fig. AII-2a

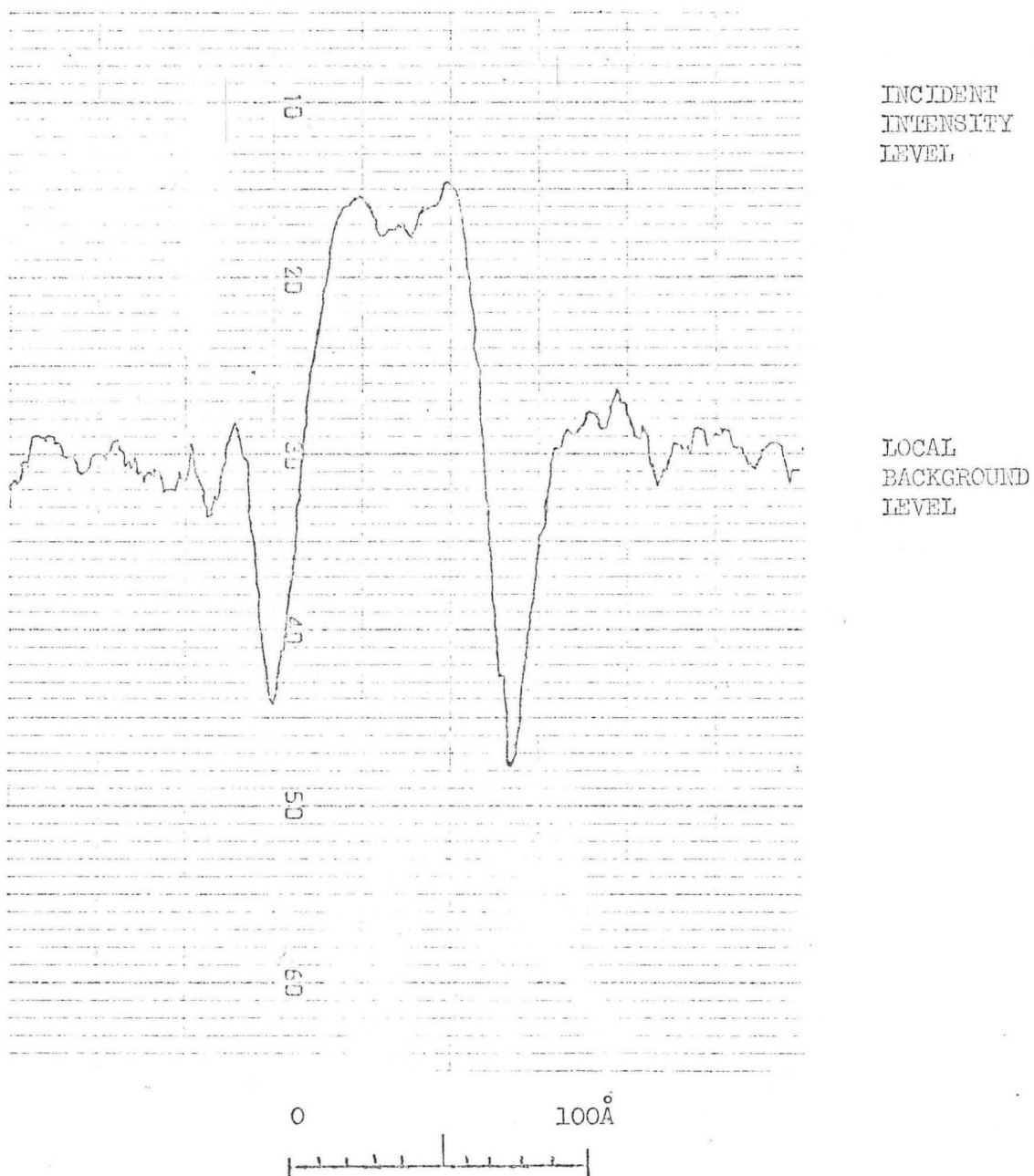
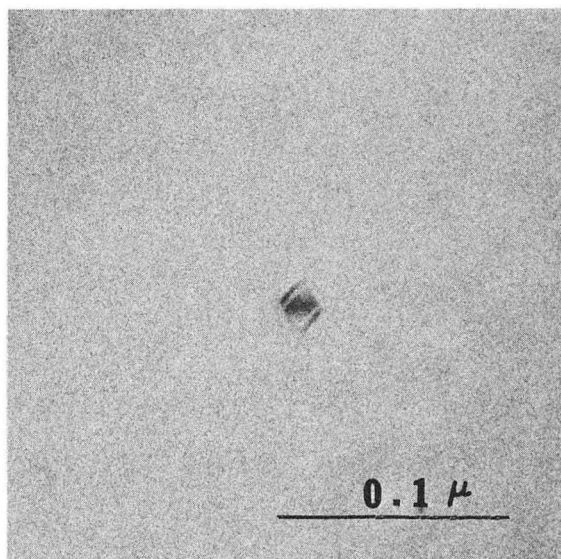
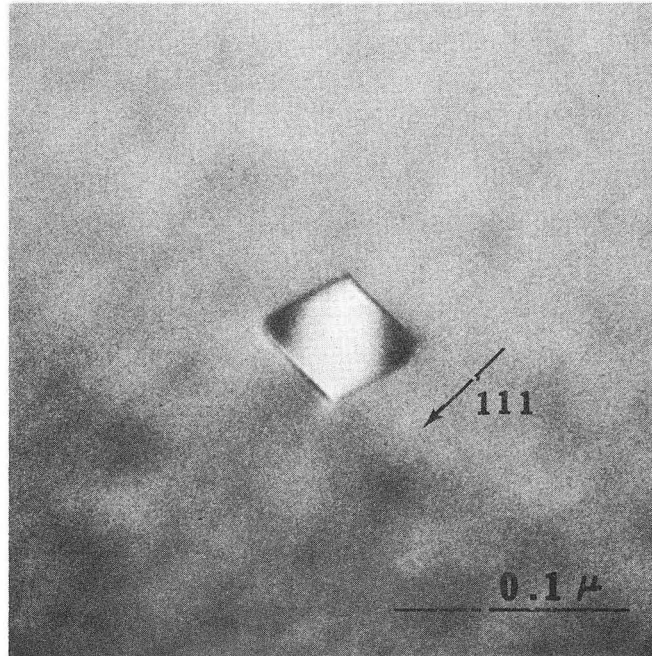


Fig. IIA-2b



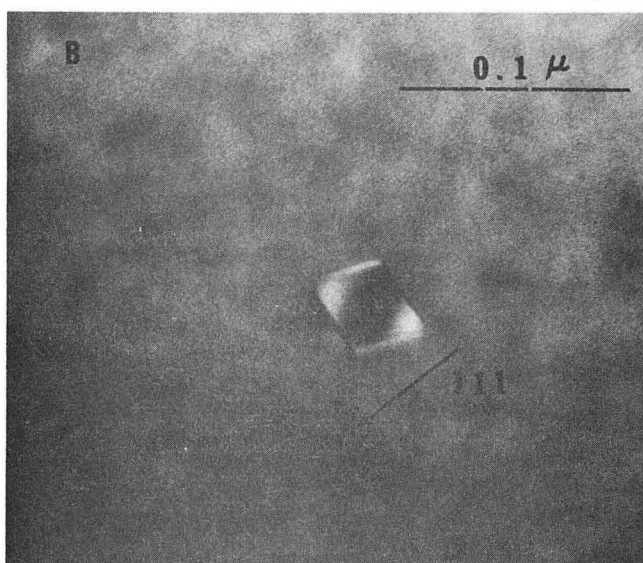
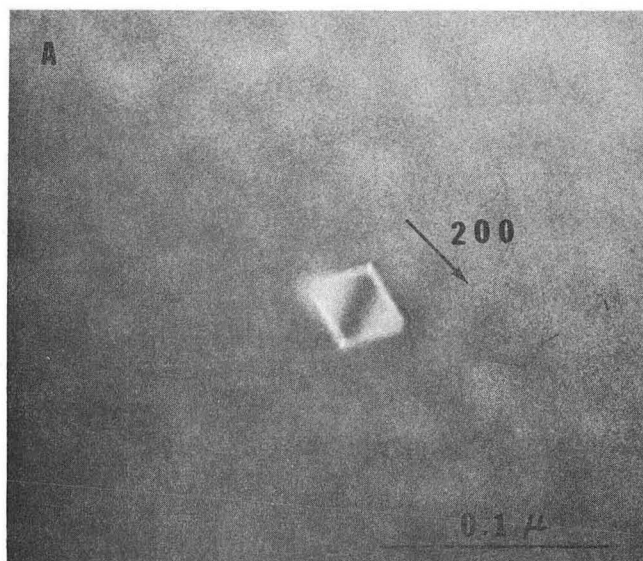
XBB 689-5662

Fig. AII-3



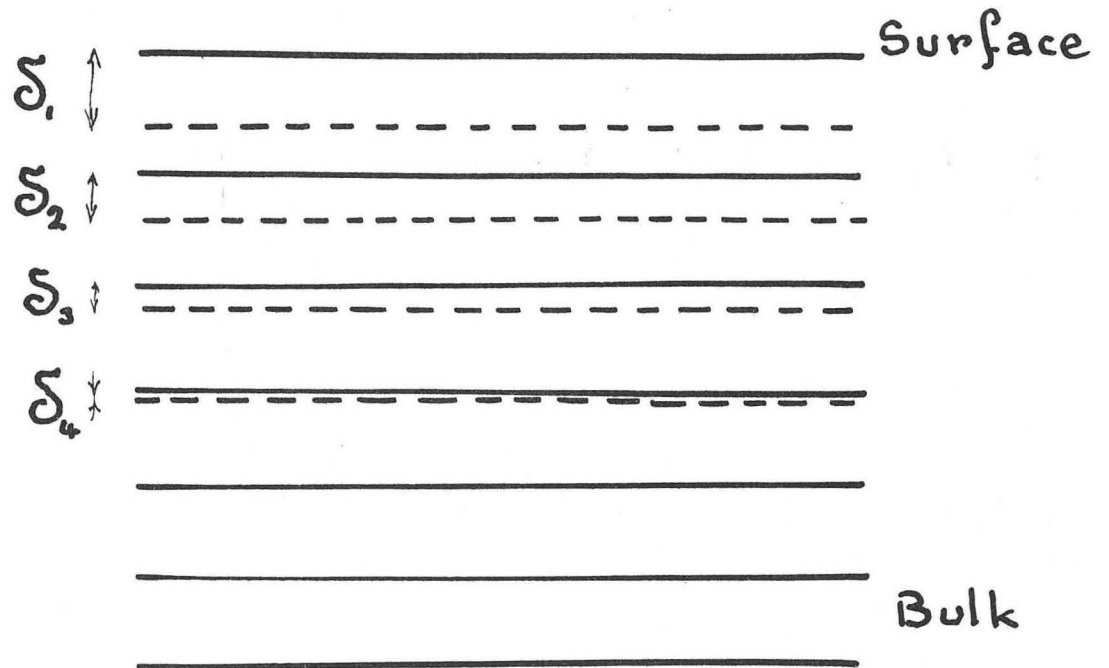
XBB 689-5663

Fig. AII-4



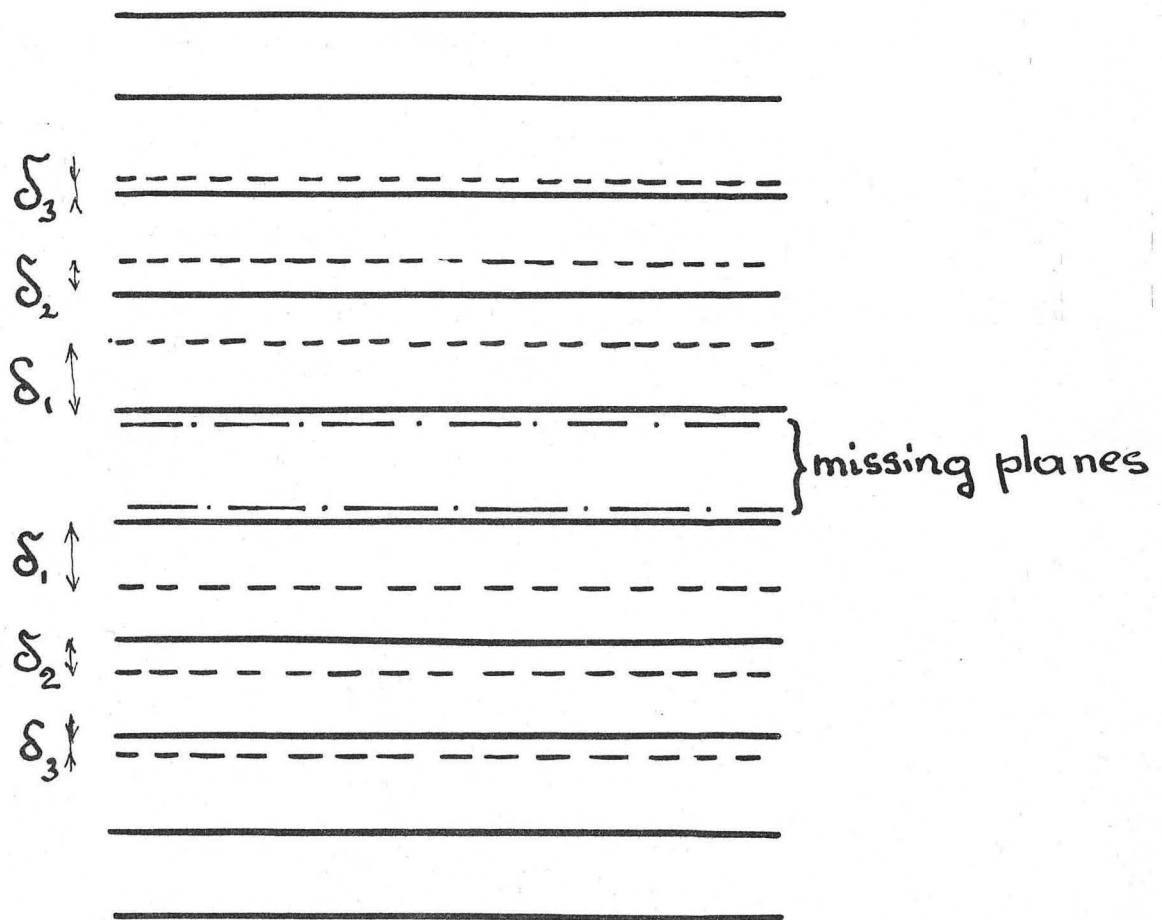
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Fig. AII-5 a-b



XBL 688-5638

Fig. IIA-6



XBL 688-5639

Fig. IIA-7

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