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VACANCY TYPE DEFECTS AND RELATED PHENOMENA IN FACE-CENTERED CUBIC COPPER-ZINC ALLOYS

by

E. LANG and S. CANETOLI

1971

Joint Nuclear Research Centre
Petten Establishment - Netherlands

Reactor Materials Laboratory

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Measurements at different reference temperatures made evident that with the increase of the degree of short-range order the temperature coefficient of the electrical resistivity decreases.

The results obtained from the "as-quenched" state led to the establishment of "apparent" equilibrium curves which are compared with resistivity vs. temperature (equilibrium) measurements. From the above some conclusions on the temperature range of existence of SRO and of the variation of the temperature coefficient of electrical resistivity in dependence of the degree of SRO can be derived.

Isochronal recovery studies after cold-work show the influence of dislocations on the annealing behaviour. The isochrones upon low temperature deformation of Ms-72 exhibit apart from the well-known annealing stages at 100 and 250 °C two further substages at — 30 and 60 °C which have not yet been reported in literature.

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ABSTRACT

A study of the enhancement of short-range ordering (SRO) upon quenching in Cu-Zn^{30,28,20}, 15 % weight percent Zn solid solutions (alpha-brass) is carried out by electrical resistivity measurements. Extensive isochronal annealing experiments revealed the existence of one or two annealing stages depending on alloy composition and quench temperature. A tentative interpretation is given on the basis of isothermal annealing experiments yielding an activation energy of 0.60 eV (Cu-28 % Zn) for stage I and 1.10 eV for stage II and leads to the conclusion that two different types of defects (divacancy, single vacancy) are involved in high temperature quenches on alpha-brass. Low temperature quenches which resulted in an activation energy of 1.62 eV were related to self-diffusion supported processes.

Measurements at different reference temperatures made evident that with the increase of the degree of short-range order the temperature coefficient of the electrical resistivity decreases.

The results obtained from the "as-quenched" state led to the establishment of "apparent" equilibrium curves which are compared with resistivity vs. temperature (equilibrium) measurements. From the above some conclusions on the temperature range of existence of SRO and of the variation of the temperature coefficient of electrical resistivity in dependence of the degree of SRO can be derived.

Isochronal recovery studies after cold-work show the influence of dislocations on the annealing behaviour. The isochrones upon low temperature deformation of Ms-72 exhibit apart from the well-known annealing stages at 100 and 250 °C two further substages at — 30 and 60 °C which have not yet been reported in literature.

A discussion of available experiments and results on similar alloys is included.

KEYWORDS

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FCC
HIGH TEMPERATURE
ACTIVATION ENERGY
LOW TEMPERATURE
SOLID SOLUTIONS
ELECTRIC CONDUCTIVITY
TEMPERATURE
COLD WORKING
DISLOCATIONS

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I. INTRODUCTION *)

Diffusion processes in solids are commonly governed by atomic point defects, whereby in the case of self-diffusion in metals vacancies and/or vacancy type aggregates are the promoting type of defect. Their concentration and mobility increase exponentially with temperature. Therefore by an abrupt quenching from high temperature, vacancies (and/or their agglomerates) can be frozen-in in non-equilibrium concentrations. It is further commonly accepted that by plastic deformation at low temperature both dislocations and point defects can be generated and retained. During a subsequent annealing treatment, the defects can migrate to sinks such as chemical (impurity atoms) or physical lattice imperfections (grain boundaries, dislocations etc.) where they get trapped or disappear by annihilation.

Since all lattice defects increase the electrical (residual) resistivity in proportion to their concentration, informations on the annihilation mechanism and corresponding activation energies can be derived from resistivity measurements. Extensive investigations on this subject have been performed during the last 10 years on metals, whereas the kinetics of point defects in alloys, specially with respect to their contribution to ordering (or disordering) processes has up to the present found much less interest.

When an alloy showing the short-range order phenomenon is slowly cooled from high temperatures, the equilibrium degree of (short-range) order will not be achieved at low temperatures, though the existence curve of short-range order (SRO) increases with decreasing temperature, but the low thermodynamic equilibrium concentration of vacancies (and their low mobility) make self-diffusion rather inefficient at these temperatures.

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*) Manuscript received on October 6, 1970

When the alloy becomes quenched from high temperature, a state of order which depends on the quench temperature and the quench rate will be retained, i.e. for high temperatures an almost statistical distribution should be frozen-in. In addition, excess vacancies are retained which during a subsequent annealing treatment may enhance diffusion and hence increase the ordering rate. Due to this enhanced ordering rate, the equilibrium degree of SRO can be achieved in reasonable time even at a rather low temperature, provided the defects are at all mobile at these temperatures.

Also, by cold working such an alloy, a nearly completely disordered state will be produced due to moving dislocations, and therefore both the processes of re-arrangement of atoms via the introduced point defects (ordering) and of recrystallisation will occur during subsequent annealing.

In the present work, the enhancement of the short-range ordering process in alpha-brass by quenched-in vacancies and upon cold deformation has been detected by measurements of the electrical resistance, and its dependence on quench temperature, annealing temperature and alloy composition have been investigated. Apparent formation and migration activation energies of the vacancy type defects have been determined and the methods of their determination are discussed.

II. SOME REMARKS ON THE THEORY OF SHORT-RANGE ORDER FORMATION.

In a regular binary solid solution, both atom species A and B are distributed statistically on the lattice sites. This random distribution is defined by the fact that the probability for occupation of any lattice site by an A or B atom is equal to their atomic concentration c_A and c_B, respectively.

As commonly known, solid solution alloys may exhibit deviations from the statistical distribution since either equal or unequal configurations of the two species of atoms may be energetically favored. If this phenomenon occurs in relatively small regions of the alloy crystal, we speak of "short-range-order" (SRO).

Below a certain critical temperature in alloys of stoichiometric composition, the state of order may be extended even to long range regions, i.e. then each sublattice is occupied by one atom species only and we have "long-range-order" (LRO). According to COWLEY[1] the atom distribution in a binary alloy can be quantitatively described by the short-range order coefficients:

$$\alpha_i = 1 - \rho_i^{AB}/c_B \tag{1}$$

Herein p_i^{AB} is the probability of finding a B-atom on a lattice site of the i^{th} neighbour shell of an A-atom. The probability of also finding there an A-Atom is:

$$p_i^{AA} = 1 - p_i^{AB} = c_A + c_B\,\alpha_i \tag{2}$$

For random distribution, all α_i-values are zero, α_1 is positive for short-range segregation, and negative for short-range order. For complete order α reaches a maximum value which depends on lattice type and alloy composition.

Changes in the atomic arrangement strongly influence the physical properties of the alloy. With long-range order the resistivity will always decrease as compared to statistical distribution. Short-range order may cause either a resistivity increase as found for example in Au-Ag[2] and Cu_2NiZn[3] or a decrease as in case of Cu-Al[4]. It should be mentioned here that according to DEHLINGER[5] short-range segregation may also be accompanied by a resistivity decrease.

For Cu-Zn-alloys of the α-type the existence of SRO has been theoretically calculated[6,7] a long time ago and experimentally demonstrated by (indirect) measurements of specific heat[8,9], electrical resistivity[10,11,12,13,14,15], internal friction[16,17] etc. Direct evidence by means of diffuse X-ray- and/or neutron-scattering experiments could not be obtained up to now because of the small difference in scattering power of Cu- and Zn-atoms[18].

Anyway, it is now commonly accepted that the resistivity decrease found on α-brass in specific experiments by various authors is associated with short-range order and not with short-range segregation. The existence of long-range order in α-brass above - 30°C has been excluded by several investigators (see for example ref. 18) because of the rather low ordering energy of this system.

Quenching of a Cu-Zn alloy from a temperature T_q to a (lower) temperature T_o results in a resistivity increase compared to values for a slowly cooled sample*), i.e. of an alloy in thermodynamic equilibrium. Taking into account formally both the SRO contribution and the vacancy increment, we can split up the total resistivity increase in:

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*) All ρ-values herein are related to the same reference temperature, in our case mostly to LN_2-temperature.

$$\Delta\rho_{total} = \Delta\rho_{vac} + \Delta\rho_{SRO} \qquad (4)$$

An estimation of the relative magnitude of these two contributions cannot be given a priori: in the following we will consider them as equally important.

The vacancy increment is proportional to the frozen-in vacancy concentration:

$$\Delta\rho_{vac} = a \,.\, c\ (T_q) = A \,.\, c'\ (-Q_F/kT_q) \qquad (5)$$

During annealing the vacancies migrate*) with a certain jump number per second ν to insaturable sinks where they annihilate after having performed a total number n of jumps. The consequent decrease in vacancy concentration

$$\frac{dc}{dt} = \nu/n\ F\ (c) \qquad (6)$$

is accompanied by a corresponding resistivity decrease:

$$d\Delta\rho_{vac}/dt = -\nu/n\ F'\ (c) \qquad (7)$$

where $F'(c)$ is a steady function of c.

Due to this migration of vacancies, a rearrangement of the two atom species of the alloy (i.e. short-range ordering) is possible, which gives rise to a resistivity decrease:

$$\Delta\rho_{SRO} = B.s \qquad (8)$$

here B is a dimensional number and s represents the numerical value of the additional resisivity. Initially after quenching we have a value $B\ s_o\ (T_q)$ which - during isothermal anneals - is decreasing the equilibrium value $B\ s_e(T_a)$.

---

*) For sake of simplicity we shall not deal here with vacancy annihilation via divacancy formation though this process due to the high vacancy concentrations met wihtin our experiments might be not negligible.

It should be emphasized here, that for annihilation of a vacancy in a well-annealed material, a large total number of jumps ($\simeq 10^7$) is necessary, whereas the degree of order (at least at the beginning of the anneal) will already increase by a very few atomic jumps.

The initial value B $s_o(T_q)$ corresponds to the initial quenched-in degree of short-range order which is composed of two parts:

i) the equilibrium value of SRO at quench tmeperature
ii) and the increase of order during the quench process by migration vacancies*).

Due to the term ii) it is almost impossible to freeze-in the equilibrium state of (dis-) order from high temperature since the vacancy concentration and mobility increase exponentially with temperature, and therefore the total jump number of vacancies during quench will also increase.

For the increase of SRO during annealing, an expression similar to eq. (6) can be given:

$$ds/dt = \frac{\Pi}{p} f\ (s - s_e) \qquad (9)$$

Here Π is the atom jump frequency ($\sec^{-1}$) and p is the mean number of jumps which have to be executed by each atom to establish the equilibrium value of SRO. Obviously p is a function of the degree of order itself. The atom jump number of course, is equal to the product of the total vacancy concentration $c + c_a$ **) and vacancy jump frequency ν.

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*) Increase of order corresponds to decrease of the resistivity increment.

**) c_a = thermal equilibrium concentration of vacancy at annealing temperature T_a.

$$\Pi = (c + c_a) \cdot \nu \qquad (10)$$

for $T_a << T_q$ follows $c_a(T_a) << c_o\ (T_q)$

The resistivity increment during annealing can be represented by

$$\rho_t = A \cdot c + B \cdot s \qquad (11)$$

having at $t = 0$ the initial value

$$\rho_0 = A \cdot c_o + B \cdot s_o \qquad (12)$$

and for $t = \infty$ the final value

$$\rho_\infty = B \cdot s_e \qquad (13)$$

If the quenched-in vacancy concentration is too small to bring about short-range order equilibrium, then $s_\infty > s_e$ will be attained by an isothermal anneal.

By combining eq. (11) to (13) we obtained:

$$\Delta\rho_{total} = \rho_o - \rho_\infty = A \cdot c_o + B(s_o - s_e) \qquad (14)$$

$$\Delta\rho_t = \rho_o - \rho_t = A(c_o - c) + B(s_o - s) \qquad (15)$$

For data evaluation, we have to make certain assumptions for the functions $F(c)$ and $f(s-s_e)$. The random migration of single vacancies*) to fixed, insaturable sinks can be described by a chemical reaction of first order, i.e.

$$F(c) = c \qquad (16)$$

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*) Including divacancies in our consideration, we have to put $F(c) = c^\gamma$, whereby the reaction order γ can attain a value of 2.

Similarly the ordering process may also be described by a chemical reaction equation, setting

$$f(s-s_e) = (s-s_e)^{\beta} \tag{17}$$

β = order of reaction.

Combining equations (6), (9), (10), (15) and (17), we obtain:

$$dc/dt = - \nu\, c/n \tag{18}$$

$$ds/dt = - \frac{(c + c_a)}{p} \cdot \nu \cdot (s-s_e)^{\beta} \tag{19}$$

For all isothermal annealing temperatures used in our experiments c_a is several orders of magnitude smaller than c and may therefore be neglected:

$$ds/dt = - \frac{c}{p} \cdot \nu \cdot (s-s_e)^{\beta} \tag{19a}$$

Inserting eq. (18) and (19a) in the differentiated eq. (11), we obtain:

$$d\rho t/dt = \dot{\rho}_t = - c\, \nu \left[A/n + \frac{\beta (s-s_e)^{\beta}}{p}\right] \tag{20}$$

Integration of eq. (18) between c_o and c, respectively o and t yields:

$$c = c_o \exp\left(- \frac{\nu}{n}\, t\right) \tag{21}$$

Inserting this result in eq. (19a), we get by integration between s_o and s, respectively o and t:

$$\frac{s-s_e}{s_o-s_e} = \left\{1 + (\beta-1)\,(s_o-s_e)^{\beta-1}\, \frac{c_o n}{p} \left[1-\exp\left(-\frac{\nu}{n} t\right)\right]\right\}^{\frac{1}{1-\beta}} \tag{22}$$

III. EXPERIMENTAL DETAILS

1. Specimen

Experiments have been carried out with Cu-Zn alloys*) of following composition:

Ms-64: Cu = 63,77 weight %
Zn = 36,20 %
Ms-70: Cu = 70,51 %
Zn = 29,46 %
Ms-72: Cu = 72,66 %
Zn = 27,29 %
Ms-80: Cu = 80,10 %
Zn = 19,87 %
Ms-85: Cu = 85,02 %
Zn = 14,97
impurities <0,03%, mainly traces of
Si, Pb, Fe, Mg.

According to the Cu-Zn-phase diagram[19,20], , all these alloys can be expected to be of the α-type, although a recent analysis [21] of the Cu-Zn-phase diagram would allow for precipitation of a β-phase in brass samples with a Zn content >35% at temperatures below 100°C. Yet from the accordance of the isochronal annealing curves of the various alloys (Ms-64, Ms-70, Ms-72, Ms-80, Ms-85), we can state that precipitation most probably has not occurred in our experiments.

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*) We thank Prof.Dr. V. Gerold from the Max-Planck-Institut in Stuttgart for supplying us with these alloys.

Such a process would have influenced the electrical resistivity in a much stronger way. Further it has to be taken into account that for ordering only a few vacancy jumps are necessary, whereas for precipitation of a second phase a much higher number would be required. We refer further to our x-ray and micrograph investigations on Ms-64 described elsewhere [22] which gave no evidence for the occurence of a second phase in this alloy during annealing.

The sample material was available in 0.1 mm thick foils from which specimens of appropriate shape were cut [23].

2. Quenching

The samples were quenched by means of one of the previously described quench techniques (drop, tilt or pull method, see ref. 23) from a He-atmosphere into water ($\pm$ 18°C) or - in some cases - into an aqueous $CaCl_2$-solution cooled by a refrigerator unit to convenient temperatures (down to -60°C). The apparatus for the drop method which was mainly used is presented schematically in Fig. 1.

This assembly has been modified and improved in the course of these experiments, and Fig. 2 shows a view of the facility in its present form. The sample to be quenched is suspended by means of a spotwelded thermocouple inside the stainless steel tube (1) which is located inside the quench furnace (2) working up to 1000°C. By this arrangement the quench temperature can now be determined with higher precision. To start quenching - a somewhat critical procedure in the apparatus of Fig. 1 - the thermocouple wires are cut by means of a specially developed shearing device (3), and the sample drops through the simultaneously opened ball valve (5) into the quench bath (5). By means of a vacuum pumping plant (6) and an inert gas (He, Ar) refill system (7) heating before quench can be performed under vacuum or inert atmosphere.

Fig. 2 also shows the reference cell for the measuring thermocouple (8), a L&N potentiometer for temperature determination (9) and the regulated power supply for the quench furnace (10).

Before starting quenching, the samples were recrystallized by an one hours' anneal in a purified He-atmosphere at 560 ± 10°C. The furnace was brougth to the desired quench temperature at which the sample was kept for an appropriate period to establish thermodynamic equilibrium.

Detailed investigations of the quench rates achievable with the methods used are reported in ref. 23. Common values are of the order of 30.000°C/sec. In most cases samples of four compositions (Ms-64, 72, 80, 85), were quenched together in order to provide identical conditions (quench temperature, quench rate, etc.). The maximum quench temperature was limited to 750°C by the onset of Zn-evaporation.

After quenching, the specimens were briefly etched in dilute HNO_3, washed in distilled water and alcohol and then mounted on a ceramic specimenholder (STENAN). After quenches into $CaCl_2$-solution (-50°C) or when the annealing was started at -50°C, the samples were mounted - without etching - with in an alcohol cryostat (COLORA) at -70°C, thus preventing any warming-up of the specimen.

3. Techniques of measurement

The sample resisitivity was determined with a four probe method mostly at LN_2-temperature and in some cases also at -70°C and at 0°C. Care was taken to obtain uniform temperature distribution in the reference baths by thoroughfully stirring them during the measuring period.

The sample DC-current of 1 A was controlled to 1 ppm deviation by a TINSLEY Constant Current Controller, the potential drop along the specimen was measured by a TEMF-free Diesselhorst potentiometer (WOLFF) with a precision of 1×10^{-7}V. Zero detection was obtained by a TINSLEY galvanometer with a high sensitive photocell-preamplifier.

Potentiometer, reference cells and resistors as well as the main parts of the current controller were maintained at constant temperature ($20 \pm 0.1^{\circ}$C) by suitable thermostats.

In order to avoid a precise determination of the sample geometry, the measured resistance values were plotted in a relative form comparing them with certain definite values obtained from annealing or as-quenched curves. In only a few cases has the electrical resistivity of the samples been determined directly.

4. Low temperature deformation experiments.

Some few tentative deformation experiments on samples of Ms-70 and Ms-72 at low temperature have been performed by passing a specimen, which had previously cooled to LN_2-temperature, through a hand-operated rolling mill, into liquid nitrogen. From preceding experiments on the same sample material, the rolls of the machine had been set-up in an appropriate manner to obtain the desired degree of deformation in one pass.

5. Annealing treatments

Annealing treatments of quenched samples were performed in ultra-thermostats filled with alcohol (for -60 to 10°C), distilled water (10 to 90°C) and silicon-oil (90 to 300°C), respectively.

The temperatures of the annealing baths were stabilized to ± 0.2°C. On the way from the annealing to the measure (reference) bath, the samples were briefly washed in an acetone bath of 10°C. The temperature of the annealing bath and of the sample was monitored for several runs by a Cu-Const thermocouple and recorded by a 2-line recorder. By this means, annealing times taken by a stop watch could be corrected correspondingly. The standard annealing time interval for an isochronal annealing step was 15'.
Several results on Ms-64 reported here have been taken from a previous work[22].

6. Equilibrium measurements

To investigate the temperature range of existence of SRO and the related variation of the temperature coefficient of electrical resistivity, measurements of the electrical resistance have been done under both equilibrium and quasi-equilibrium conditions.
For this purpose, the sample to which current and potential leads and a thermocouple were connected by spot-welding, has been heated - after the usual recrystallization process - in the quench furnace to desired temperatures in the range from 200° to 650°C and its resistance measured in function of time ("at-temperature measurement"). When no further variation could be detected - i.e. the alloy had attained its equilibrium state of order - the procedure was repeated at another appropriate temperature.

Long time measurements at temperatures below 200°C were done in an oil-filled thermostat unit. Before and after the whole procedure, some reference measurements at LN_2-temperature, at 0° and 25°C, have been made in order to detect the total variation the sample had suffered from the heat treatment.

The sample current (1 A DC) was supplied by a P.A.R. constant current controller and the voltage drop of the sample and of a standard resistor connected in series, together with the thermocouple output, were automaticallly recorded by a DYMEC DATA SYSTEM.

IV. RESULTS

1. Equilibrium curves obtained by quenching experiments.

In order to investigate the maximum variation of the degree of SRO achievable by quenching and annealing, the equilibrium curves of four alloys have been established. For that purpose a specimen of each alloy has been equilibrated (after the initial recovery anneal) at certain temperatures in the range form 600 to 150°C (in some cases to 100°C) for an appropriate period, quenched into water (18°C) and transferred immediately (in 20 sec.) into an alcohol bath at -50°C. Measurements of the electrical resistivity were performed at LN_2-temperature and at 0°C (ice-water-bath). The annealing and subsequent quench at a certain temperature were repeated until no further variation of the electrical resistivity could be notified, i.e. the thermodynamic or the "quasi" equilibrium had been established.

The results are presented in Fig. 3 a-d. In this figure the relative resistivity change $(\rho - \rho_{200})/\rho_{200}$ vs equilibration (and quench) temperature is plotted; the total heating time at temperatures above 250°C amounted to 30 min., the low temperature annealing times are indicated in the figure. Fig. 3 further includes the initial resistivity increments $(\Delta\rho/\rho_{ref})$ upon quenching from various temperatures as taken from the isochrones plotted in Fig. 5-15 (see section 3).

As a common feature of all curves, we observe an increase of the electrical resistivity increment with decreasing quench temperature which is followed by a rather abrupt decrease below about 400-500°C depending on alloy composition. Finally, below about 200°C the resistivity does not change appreciately.

By showing maxima, the equilibrium curves also imply that samples quenched from two different temperatures (for example Ms-80:T_1 = 360°C, T_2 = 580°C) will contain the same initial degree of SRO.

The relatively great scatter of the points beyond the maximum may be attributed to inaccuracies in the determination of the exact quench temperature and to the different quenching and handling procedures applied in the various quenches (see paragraph IV.3). In this connection it should be mentioned that upon quenching from above ca. 400°C a resistivity decrease (i.e. onset of ordering or annealing) is already noticed during the 0°C measurement. This is in agreement with the characteristics of the corresponding isochronal annealings reported hereafter. Measurements at 0°C are therefore subjected to greater errors which also enter into the determination of the temperature coefficients.

The curves of Ms-64 and Ms-72 show a very similar shape both at -196° and 0°C. The total variation of the electrical resistivity achievable by thermal treatment amounts for these two alloys to about 4.5% (at LN_2-temperature).

For Ms-80 and Ms-85 we only find a total change of about 3.5%, and here the shape of both curves is very similar. The influence of the alloy composition on the total variation is quite reasonable, since the achievable degree of SRO should increase with the total number of Zn-Zn-bonds which can be transformed into Cu-Zn-pairs. The relative dependence on the equilibration temperature*) seems to be specific for each alloy - at least for measurements at LN_2-temperature. The curve maximum shifts from 380°C for Ms 64/72 to about 500°C for Ms-80/85 and is independent of the measurement temperature. It has been further found that in all cases the the achievable resistivity variation measured at 0°C is smaller than the change detected at LN_2-temperature**).

For the equilibrium measurements as well as during isochronal annealings, the LN_2-resistivity values have been always lower than the 0°C-values; indicating that α -brass alloys have a positive temperature coefficient of electrical resistivity***), contrary to some fcc-CuNiZn-alloys for which SCHUELE and COLLELLA[25] detected a negative temperature coefficient. This phenomenon had already been stated for resistivity variations induced by neutron irradiation, measured in-pile at the irradiation temperature[22,24].

In their investigations on order phenomena in Cu-Ni-Zn-alloys SCHUELE et al[3] used to calculate an apparent temperature coefficient of the electrical resistivity defined by:

$$\alpha = \frac{R_{0^o} - R_{LN_2}}{R_{0^o} \cdot 196} \qquad (23)$$

---

*) i.e. slope of the curves in Fig. 3.

**) This is not yet straightly evident from the plotting in Fig. 3 since there the relative resistivity variations are are related to different reference values giving rise to an apparently much greater divergency.

***) in a previous work[22] we determined for a Ms-64 sample equilibrated at 200°C a temperature coefficient of $\alpha = 1.73 \times 10^{-3}$ degree^{-1} in the temperature range from 0°C to 130°C.

Applying this formula to our results, we obtain the curves represented in Fig. 4. It is obvious from this that the variation of the temperature coefficient with the quench temperature - i.e. of the state of order - is masked by the change of the reference (R_0o-) values (see equ. 23) which also vary with the quench temperature. We consider it therefore preferable to plot a temperature coefficient defined by:

$$\beta = \frac{R_0{}^{o} - R_{LN_2}}{196} \qquad (24)$$

The relative variation of this term with quench temperature is shown for four different alloys in Fig. 5. The temperature coefficient turns out to increase with the degree of SRO while the relative variation seems to depend on alloy composition.

2. Equilibrium curve obtained by at-temperature measurements.

The results of the resistance vs. temperature measurements on a Ms-70 sample are plotted in Fig. 6. Starting from a cold-rolled ("as-obtained") specimen, measurements had been made upward (to 700°C) with a constant heating rate of 5°C/min and then downward equilibrating the specimen at each indicated temperature. In the next figure the derivative of this curve i.e. the temperature dependence of the temperature coefficient β is represented.

We realize from these two figures the following features:

a) The initial resistance of the sample at -196°C is higher by about 16% as compared to that of the annealed state , yet the temperature coefficient is about the same. From this we may conclude that by the complete heat treatment only a recovery of the initial cold-work of the sample has been attained but the initial and final state of order - as far as detectable by these measurements - remained unchanged.

b) During heating we remark at about 250°C the onset of ordering and recovery (recrystallisation) which is completed at about 400°C. This is in agreement with our findings on annealing of samples deformed at low temperature (see Fig. 38, 39).

c) We also observe an <u>increase</u> of the temperature coefficient β with temperature, of about 26% in the range between 0 and 700°C. This seems to be in contradiction to the results revealed from the quasi-equilibrium and annealing experiments and will be discussed in detail later.

d) At low temperature $<100^\circ$C we find again higher values of β, a fact which can also be detected in the R vs. T-curve.

e) The variation of β on heating in the temperature range from 200°C to 400°C is only an apparent one since the alloy is neither in an equilibrium state of order nor recovered.

3. Isochronal annealing curves upon quenching.

Isochronal annealing curves have been produced on quenching from temperatures of (nominal) 300°, 400°, 500°, 600° and 700°C into water at 18°C. A typical isochronal annealing curve is represented by Fig. 8. For comparison all annealing curves of each alloy composition have been normalized to a certain resistivity value (R_{ref}) lying on the linearly increasing part of the curve. The corresponding results obtained for Ms-85 using the drop method (into water) are plotted in Fig. 9. The next figure shows three annealing curves obtained on the same alloy by the pull method of quenching[23]. Fig. 11 and 12 represent the results on Ms-80 as obtained for tilt*) and drop method quenches, respectively.

In Fig. 13 and 14 are plotted the isochrones of Ms-72 quenched from the indicated temperatures by the drop method. The curves in Fig. 14 have all been obtained from one specimen, whereas in Fig. 13 a new specimen had been taken for each quench. Since the results agree fairly well, it can be concluded that a preceeding quench and anneal does not influence the following one, and that experiments performed on different samples of the same alloy are comparable with each other.

In Fig. 15 results on Ms-64 taken from ref. 22 and obtained with the tilt method[23] are shown. Another set of isochrones done on Ms-64 upon quenching by the drop method[23] is represented in Fig. 16.

Since some of the isochrones showed a rather high decrease rate at ambient temperature, a quench from 550°C into an eutectic $Ca-Cl_2$-solution at -50°C has been performed on four samples of differing alloy composition, and the subsequent annealing started at -50°C. The results obtained are represented in Fig. 17.

The last three figures show a peculiarity for the isochrones of Ms-64 after quenching form about 500°C (see Fig. 15, 16, 17) and from 298°C (Fig. 16). These curves exhibit a rather linearily decreasing stage at above 100°C which cannot be detected in the other isochrones. An explanation for this behaviour is not at hand at the moment.

The common feature of the isochronal annealing curves of all investigated alloys is a continuous resistivity decrease

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*) The samples used in these experiments had not been given the usual 1 hours' anneal at 560°C prior to quenching and they have been mounted after quenching at room temperature.

with increasing annealing temperature, down to a more or less broad minimum followed by an almost linear increase. This rather linear increase of electrical resistivity has been argued to correspond to the equilibrium state of SRO. Depending on alloy composition and on quench temperature, some curves exhibit more or less dominant two stages in the decrease section, whereas other curves show only one stage. The various curves show further a certain dependence of the initial resistivity increment $(\rho_q - \rho_{ref})/\rho_{ref}$ on the quench temperature which can be related to the quasi-equilibrium curve of Fig. 3a-d.

We must emphasize that in contrast to the work of CLAREBROUGH et al.[26] in our experiments the initial resistivity values (for Ms-72) after quenching from about 600°C are <u>higher</u> than those after a 300°C quench. This is due to our improved quench technique, and we refer in this connection also to the corresponding equilibrium curves. From the extensive investigations on Ms-64 (Fig. 16) it is however obvious, that the initial state of the samples upon repeated quenching from higher temperatures ($T_q \geq 500$°C) can vary rather considerably even for the same applied quench technique. Using the drop method the possible variation in the quench rate should be rather small[23]; the critical point that remains for the assignment of the isochrones is the exact determination of the real quench temperature. Since this temperature had only been detected by a thermocouple near the sample and not attached to it, a relatively great error may be involved in its determination. From the introductory remarks and from the equilibrium curves (Fig. 3), it is evident that the quench temperature strongly influences the frozen-in state of the alloy. In addition, the time of handling the samples at ambient temperature after quenching and before the anneal treatment will also influence the measured initial value ρ_q.

3.1. Influence of oxygen

Another parameter whhich is known to influence appreciately the quench and annealing behaviour of fcc metals is the oxygen content of the quench atmosphere. In order to detect this influence samples of different thickness (0.09 and 0.17 mm) were quenched, after heating in air or inert atmospheres, into water and their resistance measured at LN_2-temperature. Quenches were only made from higher temperatures where the effect was supposed to be more pronounced. The results obtained are plotted in Fig. 10. From this graph we reveal that by quenching from an oxygen atmosphere, the resistivity drop normally observed, is considerably reduced and the quenched-in resistivity values are almost independent of the quench temperature.

This phenomenon may be due to a trapping of the vacancies at oxygen atoms, thus preventing their migration and related ordering during the quench process. It should be stated that the oxygen effect is not reversible upon heating in hydrogen or under vacuum. It is further noted from Fig. 18 that because of its smaller thickness, the resistance of the thinner sample becomes more severely influenced by the presence of oxygen. We can also state that the thin sample, because of its smaller heat capacity cools faster during falling however the quench process in the quench bath is more efficient than for thick samples.

We have to emphasize that these investigations are only indicative and not yet complete.

3.2 Temperature coefficient

For an investigation of a possible temperature dependence of the annealed resistivity increment, isochrones have been taken on Ms-72 upon quenching from 560°C into a $CaCl_2$-solution (at -50°C) at three different measurement (reference) temperatures (LN_2, -70°C, 0°C). The results are plotted in the form $R_q - R_a$ in Fig. 19*) . If the temperature independent residual resistivity alone was influenced by the migration of the vacancies and the increase of SRO related with it, the measured variations ΔR should be independent from the measurement temperature. But as one realizes, from the presentation in Fig. 19, the total resistivity change and the curve shape do depend on the measurement temperature, indicating that apart from variations of the residual resistivity ρ_o (corresponding approximately to the values measured at LN_2-temperature) variations of the temperature dependent part of the resistivity are also involved in the annealing element.

We want to emphasize that the percentage decrease as well as the $\Delta\rho$-values induced by the annealing are greatest in magnitude for the lower temperature of measurement. Obviously the difference of the measured resistance values increases with the onset of ordering during annealing and decreases when destruction of SRO becomes dominant. Further, the discovered temperature dependence**) seems to be nonlinear, since there is only little difference between the curves measured at -70°C and 0°C, respectively.

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*) R_q (T_q, T_m) = sample resistance upon quenching from T_q as measured at T_m.
R_a (T_a, T_m) = sample resistance upon annealing at T_a as measured at T_m.

**) The curves of Fig. 19 indicated further a slight shift of the minima in dependence of the measure temperature

In Fig. 20 we have plotted three apparent temperature coefficients*) which were evalueated from the measured values of Fig. 19. The following figure represents the variation of the temperature coefficient β**) during annealing. From both these figures it is found that the temperature coefficient of the electrical resistivity is a function of the degree of SRO and seems to depend on the (measurement) temperature.

4. Isothermal annealing experiments

After having detected by several sets of isochronal annealing experiments the ranges of temperature in which the quenched defects migrate, various isothermal annealings have been performed.

Fig. 22 shows some first results[22] of the isothermal annealings of Ms-64 at 155 and 175°C, respectively, upon quenching from 350°C. From the plot $(\rho_o - \rho)/\rho_o$ we realize the final value ρ_∞ (at $t = \infty$) to be a function of the annealing temperature -a behaviour quite different from that of pure metals which can be understood on the basis of the temperature dependence of SRO. For the evaluation of an imaginary activation energy we plotted these isotherms in a normalized form $(\rho_o - \rho)/(\rho_o - \rho_\infty)$ (Fig. 23). By the cross-section method we reveal therefrom an activation energy of 1.62 ± 0.05 eV, and we can further state from Fig. 24 the process to be a uniquely activated one.

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*)
$$\alpha = \frac{\rho_{T1}(T_a) - \rho_{T2}(T_a)}{\rho_{T2}(T_a)\ (T1 - T2)}$$

**)
$$\beta = \frac{\rho_{T1}(T_a) - \rho_{T2}(T_a)}{T1 - T2}$$

After quenching Ms-64 samples from 600°C we measured the isotherms presented in Fig. 25; obviously these isotherms seem to show the same general characteristics as those of Fig. 22 apart from the fact that there are two stages detectable. By plotting them, too, in a normalized form, we deduce an activation energy of 1.3 ± 0.04 eV (Fig. 26) which is rather near to the 1.2 eV determined by CLAREBROUGH et al[26] quenching Cu-30% Zn from 600°C.

Finally we quenched the same material (Ms-64) by the pull method from 750°C. By isothermal annealing we obtained the curves plotted in normalized form in Fig. 27. Using the cross-section-method we analysed in this case an activation energy of 1.0 ± 0.04 eV (Fig. 28). The most remarkable result obtained from these experiments is that the activation energy is decreasing with increasing quench temperature.

Whereas the above annealings have been performed upon quenching from a temperature at which, according to Fig. 16, only one clear stage in the isochrones is found, we tried in some further experiments on Ms-72 to investigate the processes involved in the two annealing stages.

From the isochronal annealing curves (Fig. 13/14) we learnt that two stages are present after quenching from 600°C. We therefore performed isothermal anneals at temperatures near to the center of each stage after quenching Ms-72 alloys from 600°C. In order to complete the stage I annealing, we added an isochronal treatment up to a point where we found the stage II process to become involved. It proved to be extremely difficult to obtain by quenching (even by quenching several specimens together) samples of the same initial state (i.e. degree of SRO, defect concentration) -a condition to be fulfilled for a reliable analysis of isotherms. This is due to the already mentioned difficulties in determination of the quench temperature, to variations of the quench atmosphere and post-quench handling procedures, etc. The curves we finally selected as representative of stage I annealing are plotted in Fig. 29 and 30 in the form $(\rho_o - \rho)/\rho_o$. The corresponding curves for stage II are shown in Fig. 31 $(\frac{\rho_o - \rho}{\rho_o})$ and Fig. 32 $(\frac{\rho_o - \rho}{\rho_o - \rho_\infty})$, respectively.

In Fig. 33 we have plotted the result from the cross-cut method of the determination of the activation energy of stage I. Two sets of curves yielded 0.56 and 0.63 eV, respectively. The different relaxation times found in these two sets of isothermal anneals are probably due to different sink concentrations of the samples, since NOWICK and SLADEK[27] have shown that deformation of quenched samples gives rise to an increased vacancy decay rate. The relatively great error in the determination of the activation energy is supposed to be caused by different contributions of the stage II process in the various isothermal annealings as well as to a certain scatter of the initial state of the different samples used for the evaluation. Fig. 34 represents the evaluation of the activation energy for stage II annealing . We calculate from two sets of curves (see above) a mean value of 1.08 eV. Performing the measurements during isothermal annealing (stage II) of a Ms-72 sample quenched from 600°C at two different reference temperatures (-60°C and LN_2 - temperature) we obtain the curves of Fig. 35. We state again that the resistivity decrease is smaller for the higher measurement temperature.

As a common feature of all isotherms, we find both for stage I and stage II annealing, the resistivity decrease rate to be the faster the higher the annealing temperature. With regard to stage I we noted that the achievable variation of the electrical resistivity is almost independent of the annealing temperature. This does not seem to hold for the 32°C-isotherm, probably because this annealing temperature is high enough to activate a stage II contribution for the longer annealing times. For stage II we find that - as already mentioned - the total resistivity variation decreases with increasing annealing temperature (Fig. 31). This is reasonable if we take into account that the final resistivity value ρ_∞ corresponds to the equilibrium value (see Fig. 3) being a function of temperature. This latter finding is also in agreement with observations of CLAREBROUGH et al.[26] and FEDER et al.[11] on the same system.

The isotherms show us further that the electrical resistivity is more sensitive to changes in the atomic arrangement (i.e. in the state of SRO) brought about by migrating vacancies than to variations of the vacancy concentration itself: after having attained a certain final valued $\rho_\infty(T_a)$ in the isotherm of Fig. 31, we can achieve a new and higher equilibrium value by increasing the annealing temperature*). This is clearly related to a variation of the degree of SRO since increased annihilation of vacancies should lead to a decrease of resisitivity.

From this we conclude that small changes in the degree of SRO can still be brought about by the (non-equilibrium) vacancies left over after completion of an isotherm.

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*) It is further evident that decreasing the annealing temperature causes a decrease of resistivity but with a lower rate because of the reduced defect mobility.

CLAREBROUGH et al.[26] have concluded from corresponding experiments and results that vacancies in α-brass do not annihilate completely before about 200°C.

In contradiction to the results presented here and to those of CLAREBROUGH et al.[26], FEDER et al.[11] found upon quenching Cu-30% Zn from various temperatures (350, 450, 550°C) in all cases the same annealing curve with regard to shape and relative change. This must be explained by the assumption that in this experiment because of quenching powders which were sealed in glass bulbs, the effectively quenched state of SRO always corresponded to about 350°C, since at higher temperatures more vacancies are present which give rise to a faster ordering rate already during the (slow) quench process - as we have - learnt from our and CLAREBROUGH et al.'s experiments.

For small variations from equilibrium the approach to SRO is governed according to IIDA[28] by a first order reaction. For great variation as encountered in quenching and annelaing experiments, this must not be true: the reaction order of the process involved can be greater and even vary with the approach to equilibrium. An analysis of the isotherms in Fig. 29 and 31 showed that the processes under consideration do not follow a simple first or second order reaction.

5. Annealing upon cold-work.

Since sometimes it happened that the samples had suffered slight deformations during quenching, mounting etc., we wanted to investigate any possible influence of this treatment on the annealing behaviour, by cold-working fresh, annealed and quenched samples, respectively.

In some first experiments we quenched two Ms-72 samples from 600°C and strongly deformed one by torsion at -60°C and the other by bending it several times in liquid nitrogen. Both specimens were then isochronally annealed together and yielded the curves presented in Fig. 36. We find that both samples show the same annealing behaviour and there is no noticeable difference when comparing these curves to those obtained after quenching only (Fig. 13/14).

For the next set of experiments we took two Ms-72 sampels which previously had been annealed isothermally after quenching form 600°C. One sample was deformed by torsion at LN_2-temperature, and the other strongly clamped between vise jaws in LN_2. In this case we detected (Fig. 37) an increase of some percent in the samples' resistance after the cold-work, but subsequent isochronal annnealing showed only a very slight resistivity decrease above 50°C which must be attributed to ordering by self-diffusion, (see also the behaviour of the dummy specimen in Fig. 39).

We believe therefore that by these deformations neither detectable concentrations of point defects which would enhance ordering had been created nor that the initial state of SRO had been altered appreciately. The observed resistance increase upon deformation should therefore be referred to changes in the geometry of the sample or to a resitivity increment from some few introduced dislocations which would anneal not out before about 220°C (see Fig. 38). This latter explanation is supported by the experimental finding that the resistivity (re)-increase (for $T_a \geq 100^\circ C$) in Fig. 37 which should be attributed to disordering under equilibrium conditions, is somewhat less steep than that derived from the corresponding equilibrium curve (Fig. 3b): i.e. a superposition of disordering and recovery might take place as reported in Fig. 42. From these experiments it was concluded that the much smaller deformations which the samples in quenching experiments happened to obtain cannot have influenced their annealing behaviour.

In order to demonstrate the influence of real cold-work, a fresh (not recrystallized) Ms-72 sample was rolled at a very low temperature to about 50% reduction in cross-section. The subsequent isochronal annealing yielded the curve of Fig. 38, in which three features are evident:

a) The annealing curve exhibits <u>three stages</u> which will be discussed later in detail.
b) We state further a re-increase of the resistivity when attaining annealing temperatures 350°C. This must be explained - as in case of annealing upon quenching - by the achievement of equilibrium conditions, i.e. preponderating destruction of SRO.
c) For $T_a \geq 400^\circ C$ we obtain a plateau, i.e. the resistance does not vary with the annealing temperature. As these high temperature anneals have been performed in air, we conclude that the migration of vacancies - and hence ordering- during the quenching process of each high temperature anneal is blocked by oxygen atoms - as we have found in previous experiments (see V. 3.1).

Because of these new and interesting features we repeated the experiment on two Ms-70 samples which had both been annealed for 1^h at 560°C and then furnace cooled. One sample was 50% cold-worked by rolling at a very low temperature (about -196°C).

Subsequently both specimens were isochronally annealed and their resistances measured at LN_2 - temperature and at $0^{o}C$.

The results obtained are plotted in Fig. 39. Again the three annealing stages were confirmed, and we found - as for annealings upon quenching only - a smaller resistivity variation when measuring at $0^{o}C$. The dummy specimen remained unchanged up to about $100^{o}C$, then ordering and later disordering by self-diffusion started (see Fig. 39).

The resistivity re-increase above $350^{o}C$ is common for both samples making evident that both have attained equilibrium conditions*). In Fig. 40 we have therefore plotted the relative difference in resistivity variations of the deformed and the dummy specimens.

By plotting the relative variation of the temperature coefficient of electrical resistivity β during annealing we obtain Fig. 41. When comparing this figure with the corresponding plot obtained from isochrones upon quenching (Fig. 21) we first notice that in the latter case, the observed variations of β are higher, although the resistivity changes during annealing of the cold-worked sample are much greater than after quenching. There is no explanation for this at present.

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*) In these experiments we found for anneals at $T_a \geq 400^{o}C$ the typical resitivity decrease observed in tl quench equilibrium experiments since annealing was done under an inert gas atmosphere. Thus our explanation for the plateau in Fig. 38 seems to be justified.

As a further matter of fact, we see that below 100°C the temperature coefficient varies similarily for both dummy and deformed specimens. Since in Fig. 39 an annealing stage (IVa) below 100% can be detected for the cold-worked sample but not for the dummy specimen, we have to conclude that the mechanism of this stage (of the cold-worked sample) is not related to atomic re-arrangements since these would have influenced the temperature coefficient, too.

We also observe that despite the fact that the electrical resistivity of the deformed sample also continues to decrease*) in the temperature range $T_a \geq 220°C$ (stage V), the temperature coefficient of the deformed as well as of the dummy specimen decreases**) in the same range. This supports our point of view that the stage at $T_a \geq 220°C$ has to be understood as a superposition of the degeneration of the degree of SRO***) attained by annealing to 200°C and of the recrystallization process****).

As in the case of the at-temperature equilibrium measurements, we notice also here that the recrystalization process causes indeed a decrease of the electrical resistivity but no detectable alteration of the temperature coefficient.

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*) The resistivity decrease during stage IVc has to be attributed to an increase of the degree of SRO.

**) A decrease of the t.c. has to be related - according to the experience gained from quenching experiments - to a degeneration of SRO.

***) Causing an increase of the electrical resistivity.

****) Giving rise to a decrease of the electrical resistivity.

In a last experiment we have quenched two Ms-70 samples (after the usual recovery anneal) from 600°C into water. After that, one sample was 10% cold-worked by rolling at very low temperature (≈ -196°C) and then both samples were annealed together. With respect to the sample that had only been quenched, we found (Fig. 41) the normal annealing behaviour showing two stages in the decreasing part of the curve, above 150°C the linear re-increase of the electrical resistivity related with the disordering phenomenon, and finally above 430°C a further decrease due to the insufficient quench rate.

The most remarkable feature of the annealing curve of the quenched and cold-worked sample is the existence of a new stage located at -30°C, neither present in the annealing curve of the quenched sample nor in that after 50% deformation (Fig. 39). The following stage (IVb) should correspond to the first stage of the 50% deformed samples (Fig. 38/39) but is shifted from 60° to 90°C

The third and largest annealing stage of the quenched and deformed specimen is situated at 180°C as in case of Fig. 38/39. After completion of this stage the alloy shows a tendency to disorder with increasing annealing temperature, which gives rise to a small resistivity increase. But with the onset of the recrystallisation this initial resistivity increase is overcompensated, and we obtain the last recovery stage. Beyond 400°C the quenched and deformed sample has attained its equilibrium state with respect to SRO and concentration of dislocations, and the annealing curve coincides with the one of the quenched sample showing the usual re-increase and subsequent experiment-inherent resistivity decrease (for $T_a \geq 400°C$).

This conclusion is confirmed by the fact that when repeating the anneals at successively lower temperatures, both samples follow the equilibrium curve (of the quenched sample). Below about 210°C the resistivity values remain constant because of the reduced self-diffusion ordering rate leaving the alloy in a metastable state - as already reported above (IV.1)

V. DISCUSSION OF THE RESULTS

1. Equilibrium state of order.

Of great interest when dealing with order processes is the correlation of the measured variation of electrical resitivity ρ and the short-range order parameter S. Since theoretical calculations on this subject are not available, and even a comparison of $\rho_{equ.}(T)$ and S(T) is not possible because of lacking experimental data of S(T), we can only make an emperical estimation of the situation.

From the equilibrium curves in Fig. 3 we can state first that for all alloys the resistivity increment for quench (equilibration) temperatures above 400-500°C, is decreasing with increasing quench temperature. It had been assumed[22] that this behaviour is due to the fact that at around 450°C, maximum disorder is achieved in Cu-Zn-alloys and by further increasing the quench temperature only the vacancy concentration (and mobility) is increased which results in a noticeable ordering rate already during the quench process itself. The assumption of maximum disorder being achieved at 400-500° is also supported by the results of FEDER et al[11] which indicate a temperaure of 450°C for the onset of SRO in Cu-30% Zn.

From the cold-work experiments we learnt however, that the existence range of SRO must be extended to higher temperatures *) since the resistivity variation observed in the "order" stage of the isochronal annealing curves upon cold-working are rather greater than those after quenching. From a comparison of the equilibrium curve obtained by quenching and the cold-work experiments, we have to conclude that the random distribution, i.e. maximum disorder, is existent only at temperatures higher than 600°C. Our previous statement[22] has therefore to be modified such that 450°C is a critical temperature not with respect to order-disorder transition, but above this temperature -owing to our finite quench rate - we are no longer able to freeze-in the thermodynamic equilibrium state of SRO.

The apparent relative resistance decrease which we found for quenches from above 400°C, has also been detected in similar experiments by CLAREBROUGH et al. on Cu-Zn[26] and by WECHSLER et al. on Cu-Al[29] **). Our above-mentioned explanation seems to be valid in these cases, too, and is even supported by the fact

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*) In fact, our definition of SRO implied that Cu-Zn-pairs can be present even up to the melting point

**) It should be mentioned that by these authors[26, 29] also specific heat measurements have been performed which show similar characteristics as the resistivity equilibrium curves. The relatively high increase in the range of 150 to 300°C has been attributed to a destruction of SRO with increasing temperature.

that in the experiments of CLAREBROUGH et al.[26] when using a rather unefficient quench technique (air quench), the onset of resistivity decrease upon quenching is already found at about 300°C.

We should be aware that the total resistivity change $\Delta\rho_{total}$ is formally composed of a part $\Delta\rho_{order}$ due to an increase of SRO and a term $\Delta\rho_{vac}$ due to the quenched-in vacancies, $\Delta\rho_{vac}$ increases exponentiallly with quench temperature whereas the term $\Delta\rho_{total}$ decreases at higher temperatures (>400°C), demonstrating the predominant influence of the resistivity variations due to changes of the degree of SRO in Cu-Zn-alloys.

It might yet be possible that upon a very fast quench from rather high temperatures ($T_q > 750^{o}C$) - which because of the evaporation of Zn is technically very difficult to perform - the exponentially increasing vacancy increment $\Delta\rho_{vac}$ may overcompensate the decrease due to order formation during the quench. We find in the curves of Fig. 3 some hints of this phenomenon, since the decrease of $\Delta\rho_{total}$ is getting smaller at higher quench temperatures.

We further learnt from our experiments, that the shape of the curves above the maximum is - apart from the applied quench rate - also strongly determined by the kind of handling and measuring the sample receives after quenching, since due to high quenched-in vacancy concentration at these temperatures, we have, even at rather low temperatures, a relatively high reaction (ordering or annihilation) rate.

From Fig. 3 we realize further, that by thermal treatment below about 200°C the resistivity does not decrease appreciately even for rater long annealing times. This is due to the fact that at these temperatures the thermodynamic equilibrium concentration of defects and their mobility (ergo the self-diffusion rate) are far too low to bring about the equilibrium state of SRO in a reasonable time. We therefore attain at temperatures below about 200°C only a metastable state of order.

The "equilbrium curves" reported in Fig. 3 may therefore be considered representative of the equilibrium state of SRO only in the temperature range from about 200 to 400°C (or 500°C).

It is a matter of fact that the LN_2-resistivity in this temperature range is almost linearly dependent on the equilibration temperature for all investigated alloy compositions. This is in agreement with results of DAMASK,[13] who also found on Cu-30% Zn samples equilibrated and quenched from temperatures between 160° and 320°C, a linear dependence of the LN_2-resistivity on the equilibration temperature.

By freezing-in non-equilibrium concentrations of vacancies it is still possible - as has been demonstrated by the isothermal annealing curves - to achieve the thermodynamic equilibrium at low temperatures at least in so far as the mobility (and concentration) of the quenched-in defects is high enough (otherwise $\rho_f(T_a) > \rho_e(T_a)$). As has been pointed out in a previous paper[30] we may attain the thermodynamic equilibrium state of SRO even at ambient temperatures by means of high energy particle irradiation, which also provides an enhanced diffusion rate. Thus DAMASK[24] could establish by electron irradiation of Cu-30% Zn, the equilibrium state of SRO as low as at 50°C as indicated by a final LN_2-resistivity value fitting the straight line between 160° and 320°C.

We can now further explain the results represented in Fig. 13 of ref. 4 by the fact that SRO in Cu-25% Al becomes established by isochronal annealing and subsequent quenching in the temperature range from 200-300°C. Below 200°C annealing steps of 30 min. are not sufficient to establish equilibrium as can be seen by comparison with the annealing curve after low temperature neutron irradiation. Above 320^{o}C the quenching rate after the anneal is not sufficient to freeze-in the equilibrium because of the high defect concentration and mobility present in these samples.

A comparative discussion of the at-temperature equilibrium measurements will be given later on the basis of the Matthiessen rule and the dependence of the temperature coefficient of the electrical resistivity.

2. Isochronal annealing experiments upon quenching.

Few isochronal studies on quenched α -brass are cited in literature among which the works of CLAREBROUGH et al.[26], DAMSK[12,24] and FEDER et al.[11] have to be mentioned. In this paper curves of a quite different shape are reported, depending on quench conditions, alloy composition and the measurement temperature.

The question is now, how one can deduce from the rather complicated curves in Fig. 9-19 the respective contribution by the annihilation of the vacancies (or vacancy clusters) and/or the increase of SRO related with the migration of the defects. As said before, for α-brass both effects are supposed to lead to a resistivity decrease during annealing.

To resolve this, we shall first consider in which manner the different experimental parameters may influence the annealing results.

a) The quench temperature T_q determines (at a constant quench rate)
   1) the initial degree of SRO to be frozen-in,
   2) the quenched-in vacancy concentration.

b) The annealing temperature T_a determines (for a constant T_q) the jump frequency ν of the diffusion controlling defect (vacancy).

During an isothermal anneal ν is constant, whereas for an isochronal anneal the jump frequency increases with each annealing step $[\nu(T_a)]$. Since the order parameter s_e depends (according to the equilibrium curve Fig. 3 on the (annealing) temperature, the achievable degree of SRO for an isothermal anneal is given by T_a $[s_e\ (T_a)]$; for an isochronal anneal the driving force $s-s_e$ decreases with each anneling step until the equilibrium state of SRO ($s = s_e$) has been attained.

c) The measurement temperature T_m determines the absolute resistivity variations and the curve shape, because of the existence of a term $\delta\rho_{th}$ (T_a, T_n) which has to be discussed later.

d) The alloy composition influences the maximum increase of SRO achievable by annealing upon quenching from a certain temperature. Thereby is also given - as we have seen - the different shape of the equilibrium curves. To be correct we also have to take into consideration a dependence of the formation and migration activation energies on the alloy composition, as these parameters determine the quenched-in vacancy concentration c_q and mobility ν .

With regard to quench temperatures, we may distinguish two limiting cases; quenching from a rather low temperature (300-500°C) and from high temperatures (600-700°C). With a low temperature quench, only rather few excess vacancy will be frozen-in, the resistivity increment of which may not even be directly detectable Only the increase of SRO during annealing brought about by the migrating defects will cause a decrease of the total resistivity. We must argue that the vacancy concentrations frozen-in by quenches from around 300°C are not sufficient to bring about the total jump number necessary for establishment of the thermodynamic equilibrium at any annealing temperature, i.e. the equilibrium curve will not be attained even after all quenched vacancies have become annihilated*). For that reason we must also take into account, for annealing upon quenching from rather low temperatures the reaction rate caused by vacancies in thermodynamic equilibrium at the annealing temperatures, i.e. the contribution from self-diffusion.

However it is not quite clear why the isochrones do not intersect the equilibrium curve under these conditions, but exhibit this rather long lasting resistivity re-increase before ending up on the equilibrium curve. We shall discuss later some possible explanations.

As explained above, samples may exhibit due to the finite quench rate, about the same initial degree of SRO upon quenching from different temperatures, with the important difference that quenches from higher temperatures introduce more excess vacancies. Therefore, upon high temperature quenching -i.e. high vacancy concentration frozen-in - the reaction rate $F = c.\nu$

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*) CLAREBROUGH et al.[26] showed in fact that by annealing after a 300°C quench the resistivity does not fall below the equilibrium value of a slowly cooled sample -in contrast to annealing upon quenching from 600°C.

at a certain annealing temperature T_a is greater, and thus the equilibrium state of SRO is achieved much faster, than after quenches from lower temperatures. The important role of the excess migrating vacancies is shown directly, by the experimental curves. From these we can state that the initial reaction rate $d\Delta R/dt$, at the same annealing temperature, is greater for higher quench temperatures, although the distance to the SRO equilbrium can be even smaller at these quench temperatures. From this we conclude that it is not the difference of the degree of SRO $f(s_q - s_e)$, but the quenched-in vacancy concentration which determines the total reaction rate of the ordering process. The rate determining influence of the quench temperature is also indicated by the shift of the minima of the isochrones to lower temperature with increasing quench temperature (see Fig. 9 -19). This is in agreement with results by CLAREBROUGH et al.[26] as is shown by a comparison of their isochrones upon quenching from 600°C and 300°C, respectively.

From Fig. 17 it can be further revealed that the isochrone minima are shifted to lower (annealing) temperatures with increasing Zn-content (for same quench temperature).

This means that the ordering rate in annealing experiments upon quenching is faster the higher the Zn-content of the brass-alloy. This is rather evident since in a concentrated alloy only a few vacancy jumps are required to cause a variation of the degree of SRO. In alloys of lower Zn-content a greater total atom jump number is necessary to produce an efficient enough reaction to give rise to a detectable change of SRO.

In explaining the minimum values of the electrical resistivity during isochronal annealing - which do not represent the equilibrium state of SRO according to the equilibrium curves of Fig. 3 - we may first assume that they correspond to the equilibrium value at this (annealing) temperature plus the resistivity increment given by the vacancies not yet annihilated. On continuing the annealing treatment for $T_a > T_{min}$, the vacancies annihilate and at the same time the achieved degree of SRO degenerates according to the annealing (equilibration) temperature. When the excess vacancy concentration has attained the thermodynamic equilibrium value (c_a), the isochrone becomes identical with the equilibrium curve. These assumptions are in agreement with results by CLAREBROUGH et al.[26] who claim that excess vacancies in Cu-30% are not annihilated completely before 200°C.

The conclusion would be that we have to consider - as already mentioned - the isochronal annealing curves as a superposition of the SRO-phenomenon (which is enhanced by the migration of vacancies) and of the annihilation of the vacancies themselves. With regard to the relative contribution of the two effects, we can try to make a crude estimation of the vacancy resistivity increment by assuming a vacancy formation activation energy of 0.7 eV (see next section), a pre-exponential factor of $c_o = 3$ and a specific resistivity increment for vacancies of 2μΩcm/% - a value which is of the order of magnitude commonly accepted for pure fcc metals. From the equation

$$c_{vac} = c_o \exp(-Q_f/kT)$$

we then derive (for a quench temperature of 600°C) a frozen-in vacancy concentration of 3×10^{-2}% which corresponds to a resistivity increment of $\Delta\rho_{vac} = 6\text{x}10^{-2}$ µΩcm. Referring this value to the LN_2-resistivity of α-brasss (Ms-64), we obtain a relative resistivity increment of

$$\frac{\Delta\rho_{vac}}{\rho_o} = \frac{6\text{x}10^{-2} \;.\; 10^{2}}{4.45} = 1{,}35\%$$

Referring to the appropriate isochrones we find a total resistivity variation of about 4%, indicating that if the above data are reliable, about one third of the total resistivity decrease during annealing upon quenching from 600°C should be due to the annihilation of the excess vacancies. This effect when superimposed on the ordering process causes the typical shape of our isochrones.

On the other hand CLAREBROUGH et al.[26] concluded from a comparison of density variations and of heat evolution upon annealing of quenched α-brass samples, that the vacancies should not directly make a substantial contribution to the resistivity decrease, and that the annealing process represents only short-range-order formation, the kinetics of which are still determined by the availability of quenched-in defects.

From this another explanation for the shape of the isochrones might be that the sample during isochronal annealing does not uniformily attain in all its regions the same degree of SRO. Therefore at an (annealing) temperature where an almost thermodynamic equilibrium state of order is established, some more highly ordered regions of the sample have already started to disorder since their appropriate degree of SRO at the respective temperature is lower, and we obtain in total a resistivity increase.

A conclusive choice between the two arguments is still lacking, since exact data which might allow a reliable calculation of the vacancy resistivity increment in fcc alloys are not available, and specific techniques to separate the SRO and vacancy contribution have not yet been established. However, recent evidence has come to light[43] which strongly favours the second explanation.

3. Isothermal annealing experiments upon quenching.

The most interesting feature of the isochrones obtained after quenching is the existence of one or two annealing stages which have to be discussed in the light of the isothermal annealing experiments.
For α-brass quenching experiments, two annealing stages have not been previously reported in literature.
LI and NOWICK[33], however, using internal friction techniques in isothermal annealing experiments on the quenching of Cu-Al and Ag-Zn-alloys, detected evidence for two stages.

SCHULZE[2] and WILLIAMS et al.[34] found during isothermal annealing after high temperature quenches on Au-Ag-alloys a first stage in the form of a resistivity increase which was attributed by these authors to short-range order formation enhanced by migrating single vacancies.

This resistivity increase was accomplished in a relativly short time and was followed by a resistivity decrease (stage II) which should - according to the authors - correspond to the annihilation of the free migrating single vacancies.

This explanation cannot be adapted to our results since first the low temperature stage which has to be attributed to short-range-order formation is present only upon high temperature quenches*). Second the low temperature stage being much smaller than stage II and taking into account the relativly small resistivity increment related with the annihilation of vacancies (see paragraph V.2), we can also for this reason not accept stage I to be due to the enhancement of SRO by migrating single vacancies and stage II caused by the annihilation of these vacancies. Finally, the strongest argument against this is given by the different activation energies found for the two stages which cannot be related to the migration of one type of defect involved in two different processes.

Another point of view also referred to by LI and NOWICK[33] is based on the presence of freely migrating vacancies and of vacancies bound to impurity atoms. In these terms, stage I would correspond to the free movement of single vacancies which enhance SRO formation by their migration and get trapped at certain impurities (Zn-atoms?). The release from these traps and the subsequent ordering then give rise to stage II annealing. Thus LI and NOWICK[33] attributed the value of 1.08 eV, which they evaluated for the low temperature annealing stage of quenched ($T_q = 450^oC$) Cu-Al-alloys, to the free migration of single vacancies to impurity traps.

The activation energy of stage II of 1.6 eV was related to

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*) The short-range-order process which takes place after any quench temperature must be situated - when occurring separately form the vacancy annihilation - below the latter stage, since it has to be performed before the enhancing vacancies anneal out.

the release of these trapped vacancies*). However, we have to reject this argument since in these alloys, we do not primarily detect the annihilation of the vacancies, but only the enhancement of SRO formation due to their migration. The atom arrangement, however, can only be altered by freely migrating defects, i.e. we should have to find the same activation energy in stages I and II**). We feel that the process of stage II (1.6 eV) in this case is rather associated with a self-diffusion controlled ordering, tending to establish the equilibrium degree of SRO which had not been achieved during stage I annealing.

The next straight forward explanation of the experimental results would be to attribute the two stages to the migration of two different types of defects, namely divacancies which are more mobile in stage I and single vacancies in stage II. This point of view is supported by the fact that stage I becomes more dominant and even overlaps stage II with increasing quench temperature, i.e. increasing defect concentration. Thus the stage I -activation energy of Q = 0.60 eV (for Ms-72, T_q = 600°C) could be attributed to the migration of divacancies whereas the stage II-activation energy of 1.1 eV (Ms-72, T_q = 600°C) can be related to the migration activation energy of single vacancies***). However an analysis

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*) The same explanation had also been applied to the two annealing stages found in quenching experiments on Ag-Zn alloys by ROSWELL and NOWICK[41].

**) For a detailed discussion of this subject we may refer to the paper of SALOMON and SCHÜLE[35].

***) From these values it is obvious that when using high annealing temperatures, stage I is completed in a very short time and may even not be detectable (as shown by our isothermal results on Ms-64). For anneals at temperatures low enough, only the stage I process should be involved, whereas for medium annealing temperatures both processes - at different rates - will become activated.

should still be made to investigate any possible change in the relative concentration of vacancies and di-vacancies during annealing which could influence the determination of the migration activation energy.

The latter value (1.1 eV) is in rather good agreement with the 1.2 eV obtained by CLAREBROUGH et al.[26] for the activation of annealing in Cu-30%Zn quenched from 600°C. These authors have however - with regard to results on pure fcc metals - considered this activation energy too high to be related with free migration of single vacancies and they attributed it to migration of impurity (Zn) bound vacancies. We do not agree with this point of view, since results and calculations by LI and NOWICK[33] showed the migration activation energy of single vacancies in fcc alloys to correspond about to 0.6 x Q_{SD}*) whereas for vacancies in pure fcc metals commonly $Q_M = 0.4 \times Q_{SD}$ is found. Taking into account the generally accepted value of 1.8 eV for Q_{SD} in α-brass[16,36,37], we obtain just 1.080eV for Q_M in fairly good agreement with the value derived from our experiments. Thus we, too, proved that the migration activation energy of vacancies in fcc alloys has commonly higher values than those known for pure fcc metals. The activation energy found in our annealing experiments is also supported by a result from KÖSTER et al.[38] who derived an activation energy of 1.1 eV from annealing studies on cold-worked Cu-30%Zn. LI and NOWICK[33] determined by internal friction measurements on Cu-15%AL alloys quenched from 570°C, a vacancy migration energy of 1.08 eV and HOLMES[39] evaluated $Q_M = 1.05$ eV from quench experiments on the same alloy.

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*) Q_{SD} = self-diffusion activation energy

According to LI and NOWICK[33] we may assume for the formation activation energy of vacancies in fcc alloys the relation $Q_F = 0.4\ Q_{SD}$ yielding (with $Q_{SD} = 1.8$ eV) for α-brass a value of $Q_F = 0.72$ eV.

It should be mentioned that these relationships ($Q_M = 0.6 \times 0_{SD}$, $Q_F = 0.4 \times Q_{SD}$) are also fullfilled in the case of the Cu - 60% Ni alloy investigated by SCHÜLE and KEHRER[40] who found $Q_M = 1.1$ eV and $Q_F = 0.64$ eV ($Q_{SD} = 1.8$ eV).

An experimental determination of Q_F however seems rather difficult in this case (Cu-Zn) because of the SRO phenomena involved in all quench experiments. We consider it however possible to evaluate the activation formation energy of (di-) vacancies from a determination of the initial reaction rate dΔR/dt at an appropriate annealing temperature in dependence of the quench temperature - a procedure not yet examined.

Another feature still to be discussed is the result on Ms-64 indicating that the activation energy of stage II depends on quench temperature. The general result and the value of Q = 1.62 eV we found upon quenching from 350°C is supported by similar observations by CLAREBROUGH et al.[26], who determined on Cu-30%Zn a value of 1.7 eV after quenching from 300°C; FEDER et al.[11] even reported after quenching from 450°C (see our remark § IVc) this activation energy (1.7 eV) on the same alloy*).

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*) The idea that the process activation energy might depend on the initial degree of SRO can be rejected since the activation energy during isothermal annealing where the degree of order is also varying continuously is constant within experimental error, and further the alloy should exhibit - according to Fig. 3a - about the same initial SRO after quenching from 300 and 600°C, respectively.

Since CHILDS and LECLAIRE[16] found in internal friction experiments that the stress induced changes in local order (SRO) are governed by an activation energy of 1.7 eV and DAMASK[13] showed that annealing upon quenching from 320°C and anelastic measurements yield the same activation energy of 1.7 eV. We have to conclude that by quenches from low or medium temperature almost no substantial vacancy concentration become frozen-in, and ordering during annealing does occur with the aid of the vacancies in thermal equilibrium (self-diffusion). Thus the high activation energy found upon quenching from about 300°C is conceiveable. Two results given by FEDER et al.[11] may give further support to this conclusion.

These authors found the relaxation times for annealing at 190°C of a sample quenched from nominally 450°C and of one previously equilbrated at 120°C to be equal, that means no enhancement by quenched defects is present. They stated further that during annealing upon quenching from various low-temperatures the same relaxation time is always found, i.e. these quenches did not introduce different non-equilibrium vacancy concentrations but annealing and ordering occurs by self-diffusion, only.

According to the ideas of LI and NOWICK[33] the high activation energy obtained upon low temperature quenches could also be explained by assuming that in this case all vacancies are trapped*), and only after a high temperature quench are free single vacancies detectable, since then more excess defects than needed to fill up the traps are present. However, it remains the fact that an impurity-vacancy binding energy does not enter into the (measured) activation energy of the ordering process,

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*) The activation energy for release is the sum of the vacancy migration activation energy and the binding energy to impurity trap.

and we therefore cannot agree with this explanation.

Finally, we have to conclude from our results and from comparison with other ones that the self-diffusion activation energy in the ordered state seems to be lower than the commonly quoted value of Q_{SD} which normally is determined in high temperature experiments, i.e. at highly disordered state of the alloy. Further the self-diffusion activation energy as well as the migration activation energy of vacancies in α-brass decreases slightly with increasing Zn-content.

4. Isochronal annealing upon cold-work.

When discussing our cold-work results, i.e. in particular the ones represented in Fig. 38-42, we have to confront them with plastic deformation experiments done by DAMASK[13], KÖSTER et al.[38] and ERDMANN-JESNITZER and KAESLINGK[41].

We can first state that all results agree with respect to the location of the high-temperature stage (stage V) and its dependence on the deformation degree, yielding for higher deformation a shift of the annealing stage to lower temperatures*). We could further show this recovery stage to be a superposition of the recrystallization (dislocations) and the disorder process (atomic arrangement). Agreement also exists with regard to the respective magnitude of this annealing stage, which is dependent on the deformation degree and the temperature of measurement, Some small discrepancies in the annealing curves can be related with the different quench techniques used**).

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*) This result has also been confirmed by measurements of energy release upon cold-work (see ref. 41 and 42)

**) ERDMANN-JESNITZER and KAESLINGK[41] for example used samples of 3 mm thickness, thus their effective quench rate was probably much lower than in our case.

With respect to the low temperature recovery region, the isochronal annealing curves reported by other authors[13,38,41] show only one stage located at 150-180°C (stage IVc), though KÖSTER et al.[38] claim for three different activation energies in this recovery range. In this work we found upon 50% deformation besides this stage, another one located at about +60°C (stage IVb). This stage is also detected after 10% deformation of a quenched sample (Fig. 42). However, in this latter case we found a further new stage at -30°C (stage IVa) not present in the annealing curves of the 50% (only) deformed samples.

The question to decide now is whether this stage has to be related to the preceding quench process or to the different deformation degree. Since upon quenching from 600°C no stage at -30°C is found, we argue that because of the greater deformation energy developed in a (one step) 50% deformation and the unappropriate experimental conditions, annealing of this stage already occurs <u>during</u> deformation. When cold-working by 10% only, we can just retain the defects mobile at -30°C.

The explanation of the stage IV recovery is still in dicussion since KÖSTER et al.[38] attribute it to recovery processes and SRO formation; the latter giving rise only to a smaller resistivity decrease. DAMASK[13] as well as ERDMANN-JESNITZER and KAESLINK[41] have related the stage IV recovery uniquely to SRO-formation. From our results we, too, have to support the explanation of enhanced SRO-formation in stage IV by migration of point defects.

We found the relative resistivity variation of this region (IV)-the magnitude of which is the same as reported by other authors[13,38,41] for the same deformation degree - to depend on the measurement temperature in the same way as in our quench experiments. It has further been shown that stage IV increases with deformation degree*) and Zinc-content of the alloy[41]. These facts can be explained perfectly by SRO-formation since by a heavier deformation more Cu-Zn pairs will be separated, and we can even obtain almost random distribution not being achievable by quenching experiments. The Zinc-content is directly proportional to the maximum achievable degree of SRO which becomes destroyed by deformation. Further we may recall that in the temperature range of stage IV an increase of the mechanical properties has also been found[41] which we consider a strong evidence for the formation of SRO too. Electron microscopy investigations revealed further no hints for dislocation recovery processes in the stage IV region.

KÖSTER et al.[38] are wrong when concluding from the fact that upon slow cooling of an annealed sample only a relative resistivity decrease of about 1.5% can be obtained whereas on annealing after 90% deformation a resistivity change of about 8% is found, that the stage IV-process cannot be attributed to SRO-formation. We have to distinguish between annealings under non-equilibrium conditions - as met after cold-work - and those under equilibrium conditions as present upon slow cooling of a recrystallized sample. We had pointed out that by deformation, SRO is destroyed more completely than after high-temperature quenching, and hence the resistivity decrease on annealing is greater in the first case. In equilibrium experiments as slow cooling of a sample - only small variations of SRO, corresponding to the temperature range from 400 to 200°C are involved. Below 200°C as we have learnt the alloy will remain in a metastable state of order because of its very low self-diffusion rate

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*) It is evident that also stage V has to increase with deformation degree, see also ref. 38 and 41.

(see also Fig. 42). Therefore we should recommend the distinction of these two different cases.

It is still left to us to attribute the various annealing sub-stages upon cold-work to specific recovery processes On the basis of the results presented in Fig. 42, we would like to make a tentative interpretation in the following way: Stage IVa being present only after cold-work should be related to interstital migration, Stage IVb is thought to correspond to the low-temperature annealing stage upon quenching from a high temperature, and has been attributed to divacancies. Accordingly stage IVc should correspond to the high temperature annealing stage upon quenching where single vacancies are involved. We argue further that at least stage IVc represents vacancy enhanced ordering rather than annihilation of defects. It is then however to explain why the annealing stages (IVb and IVc) upon deformation are shifted by about 40°C to higher annealing temperatures. Such a temperature shift could be due to a smaller defect concentration after cold-work than upon quenching. But more probable is the increased presence of dislocations in the cold-worked material which reduce the effective defect jump number*) and/or restricts the growth of the short-range ordered domains.

DAMASK[13] had already pointed out that by an incresed dislocation density the mean free path of the migrating defects can be decreased by orders of magnitude.

The proposition of the interference of dislocations seems also to be supported by the annealing studies

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*) Number of jumps which are performed by the defect before getting trapped at sinks and by which SRO is increased.

after quenching of samples not previously recrystallized: in this case, too, the annealing stage was found shifted to higher temperatures with respect to the recovery of a completely annealed sample. A further evidence for this point of view is given by the work of ref. 41 showing that even after 90 minutes annealing at 375°C, the dislocation structure of weakly deformed α-brass samples has not yet changed. Thus an interference of the dislocations on the migration of the point defects and ordering has to be expected.

A definite resolution of the situation should be obtained from the determination of the activation energies of the respective annealing stages upon cold-work. This is being carried out at present.

5. Temperature dependence of the electrical resistivity increment due to SRO.

A common feature of the equilbrium curves reported in Fig. 3a-d and of the isochrones (Fig. 19, 39) as well as of the insotherms (Fig. 35) is the dependence of the resistivity variation on the temperature of measurement (reference temperature). From the non-congruence of the reported curves, we have to conclude that the process under investigation causes both a change of the residual resistivity ρ_{res} and a variation of the thermal resistivity ρ_{th}.

Such a different behaviour of the residual and thermal part of the electrical resistivity has already previously been mentioned in literature. ROSENBLATT et al.[12] seem to have been the first to report an opposite variation of the residual resistivity ρ_{res} and the thermal part ρ_{th} during prolonged annealing of Cu-30%Zn-specimens: with increase of SRO the residual resistivity

ρ_{res} was found to decrease whereas ρ_{th} increased. Also for a (neutron) radiation induced increase of SRO of α-brass samples, the same phenomenon has been noted. Later DAMASK[13], too, reported on opposite changes of a ρ_{res} and ρ_{th} during annealing of cold-worked or quenched α-brass samples. The phenomenon was not explained in detail by the authors.

To consider this probel once more, we should recall the limitations of the Matthiessen-rule which can be formulated as follows[5]:
Each deviation from the periodical lattice provides for an additional resistance which is independent from the (measurement) temperature (whereas the part of ρ due to thermal lattice vibrations is approximately proportional to the absolute temperature T). From this it is evident that the concentration of quenched vacancies as well as variations of the atomic arrangement (SRO) are detectable by alterations of this residual resistivity. It has also been demonstrated[31] that the temperature independence of this additional resistivity is only given if the lattice vibrations are isotropically distributed and the lattice imperfections (causing the additional resistivity increment) are of spherical symmetry. At (measurement) temperatures below the Debye-temperature T_D the lattice vibrations are commonly anisotropic and depend on the lattice direction[32]. Therefore deviations from the Matthiessen-rule have to be taken into account when comparing annealing experiments referred to different low (measurement) temperatures. At room and higher temperatures the lattice vibrations are more isotropically distributed and therefore the Matthiessen-rule is then applicable to lattice imperfections. However, if apart from point defects also ordering phenomena (SRO) are involved in the annealing experiments, we have to be aware that with alterations of the atom arrangement the vibrational spectrum can also change and hence the

thermal part of the electrical resistivity will change. This has been already confirmed experimentally[3]. To overcome this difficulty the (relative) measurements have to be performed at a temperature sufficiently low to make the vibrational part negligible. This condition should exist when performing the measurements - as in our case - at LN^2-temperature.

In our quench and cold-work experiments we were in fact confronted with these limitations of the Matthiessen-rule, and we evaluated when performing resitivity measurements after HT-quench and during annealing (after quench and/or plastic deformation) at temperaturesbetween -196°C and 0°C the following three rules:

a) the absolute (and relative) resistivity variations upon quenching and during annealing become smaller as the reference temperature becomes higher (between -196° and 0°C),

b) the temperature coefficient of the electrical resistivity (t.c.) - related to the above-mentioned temperature range - increases with increasing degree of SRO (or decreases with destruction of order).

c) the temperature coefficient is always positive and decreases as the respective temperature of measurement is made higher between (0° and -196°C).

In contrary to these findings we have to conclude from the at-temperature measurements (Fig. 7) -where both the influence of the measurement temperature and the variation of the degree of SRO are involved - that the t.c. (above 100°C) increases with increasing temperature (or with destruction of order).

We realize also from Fig. 7 that below about 100°C the t.c. increases with decreasing temperature. This is in agreement with statement c) above since below 100°C we have a metastable state of SRO and the influence of the measurement temperature is dominating.

For the behaviour above 100°C (t.c. increases with increasing temperature and/or destruction of SRO) it is not possible to separate the influence of the (measurement) temperature, i.e. the distance from T_D, from effects due to variations of the degree of SRO. To take into consideration these features*), we have to split up the electrical resistivity in the following form:

$$\rho_{total}(T) = \rho_{res}(SRO) + \rho_{thermal}(T) + \delta\rho_{th}(T,SRO)$$

where $\delta\rho_{th}$ takes into account all deviations from Matthiessen-rule.

In agreement with other authors[12,13,26] we suppose ρ_{res} to <u>decrease</u> with <u>increasing SRO</u> whereas $\delta\rho_{th}$ <u>increases</u> with increasing order and measurement temperature. Consequently for measurements at a certain constant temperature where the thermal part of the electrical resistivty cannot be neglected, this contribution, too, will continuously vary and the application of the Matthiessen-rule is not possible anymore.

Further, since the $\delta\rho_{th}$-term becomes greater with higher (measurement) temperatures, it may even overcompensate the variation in ρ_{res} due to alterations of SRO - as we detected in fact in some isotherms (Fig. 35) as well as in the at-temperature equilibrium measurements (Fig. 6/7).

The t.c. evaluated from equilbrium measurements upon

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*) The direct influence of impurities (vacancies) has been neglected.

quenching (Fig. 4/5) directly represents the dependence of $\delta\rho_{th}$ on the degree of SRO, since

$$\beta = \text{const.} + \frac{\delta\rho_{th}(TM2,Tq) - \delta\rho_{th}(T_{M1},Tq)}{T_{M2} - T_{M1}}$$

We see from this plot that a certain alteration in SRO, i.e. of Tq, causes different variations of $\delta\rho_{th}$ at T_{M1} and T_{M2}*) otherwise β would be constant, i.e. independent of SRO, respectively.

Adequately applied this reasoning is valid for both isochronal and isothermal annealing curves.

Finally we have should add that is is not possible to adopt the model used by SCHÜLE and KEHRER[3] to discuss order phenomena in Cu_2NiZn-alloys where also a decrease of ρ_{res} and an increase of ρ_{th} with increasing order have been found to our experimental findings concerning the temperature dependence of the reported apparent equilibrium and annealing curves, since our at-temperature equilibrium curve (Fig. 6) shows a shape quite different from theirs. We argue that the final explanation has to be sought in terms of certain deviations from the Matthiessen-rule and relations with the Debye-temperature. We are confirmed in this suggestion by the fact that from certain annealing experiments**) we revealed a variation of the resistance ratio R_{LN_2}/R_0o by about 3% - referred to the end of the annealing - which can be related to an alteration of the Debye-temperature due to SRO-formation.

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*) Reference temperatures T_{M1} and T_{M2}, respectively are constant.

**) See Fig. 19, 35 and 39.

VI. CONCLUSIONS

The principal experimental results can be summed-up as follows:

1. The variations of electrical resistivity found in quenching and annealing experiments on alpha-Cu-Zn-alloys can be explained on the basis of a predominant influence of the short-range order phenomenon.
2. It has been possible to establish apparent equilibrium curves of SRO for four alloys (Ms-64, Ms-72, Ms-80, Ms-85) by equilibrating and quenching samples from various temperatures in the range from 100 to 700°C.
3. From these curves as well as from isothermal and isochronal annealing curves it has become evident that both the electrical (residual) resistivity and the temperature coefficient of the electrical resistivity depend on the degree of SRO;
4. A R(T)-curve measured under equilibrium conditions (i.e. at-temperature) revealed that the dependence of the SRO induced resistivity increment on the (reference) temperature cannot be explained by the model proposed by SCHÜLE and KEHRER[3] but has rather to be attributed deviations from Matthiessen-rule and changes of the Debye-temperature caused by order-formation.
5. The experiments proved further that quenching gives rise to an enhancement of short-range-order formation during annealing even resulting in the thermodynamic state of SRO instead of the metastable state attained at low temperatures by equilibrium annealing experiments.

6. Isochronal anneals showed either one or two stages, depending on the quench temperature and the composition of the investigated alloy. A second annealing stage upon quenching had not been reported previously for α-brass.
7. The activation energy derived from isothermal annealing experiments after quenching Cu-36%Zn alloys from different temperatures, exhibited a dependence on the quench temperature. For a low temperature quench (350°C), we evalueated an activation energy of 1.62 eV which was attributed to the predominance of self-diffusion. Upon quenching from 750°C an activation energy of 1.0 eV was deduced which was related to the migration of free single vacancies.
8. An analysis of the two annealing stages found on Ms-72 upon quenching from 600°C by isothermal annealing experiments yielded a mean activation energy of 0.60 eV for the low-temperature stage A and 1.1 eV for the high-temperature stage B. A tentative interpretation of these results was made by attributing the stage of higher mobility (A) (which is present only upon high temperature quenches), to divacancies; the stage B was related to the migration of single vacancies giving rise to an enhancement of short-range ordering.
9. The anneals were not found to follow a simple reaction order (one or two).
10. Specific experiments gave evidence for a possible blocking of vacancy migration by oxygen atoms during quenching.
11. Plastic deformation experiments on Cu-Zn-alloys at LN_2-temperature have been performed for the first time. Upon 50% deformation, in addition to the well-known annealing stages at 180°C (IV) and 280°C (V), respectively, a new recovery stage at 60°C has been found. After 10% deformation upon quenching a further stage at -30°C has been detected.

12. A tentative explanation of the various annealing stages upon cold-work attributes sub-stage IVa to interstitial migration, sub-stage IVb to divacancies and substage IV c to vacancy enhanced ordering; the high-temperature annealing stage (V) is due to recrystallization processes.

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Our thanks are due to Dr. W. SCHÜLE who stimulated these investigations. We gratefully acknowledge the encouraging discussions and suggestions by Ing. M. Francini originating from a continuous interest shown in our work. The authors have further to thank Dr. P. Bianchessi for his valuable assistance in conducting the cold-work experiments. We are also indebted to Mr. S. Lloyd for carefully reading the manuscript and critical remarks.

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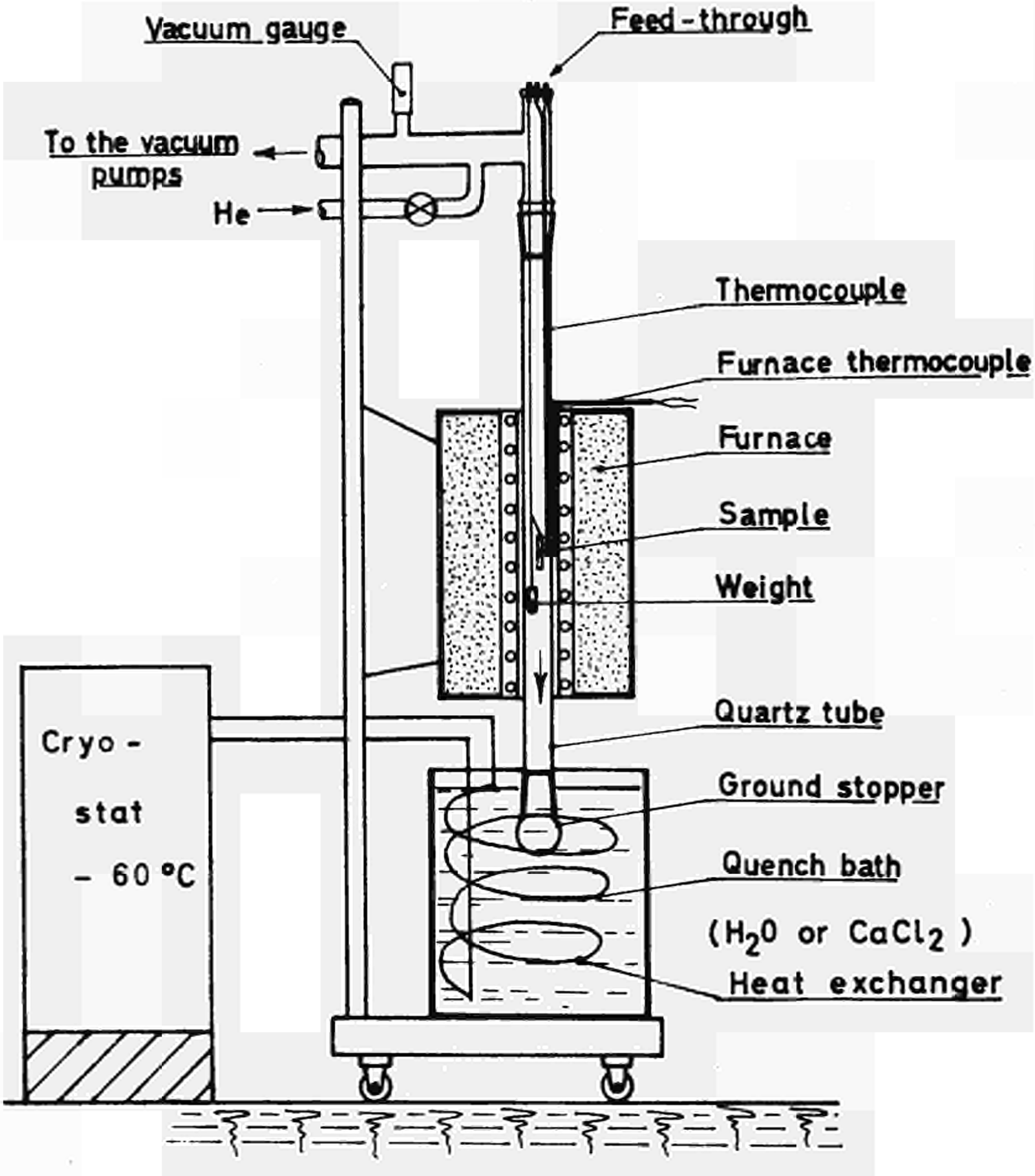


<u>Fig. 1</u>. Schematic draft of the quenching apparatus (drop method).

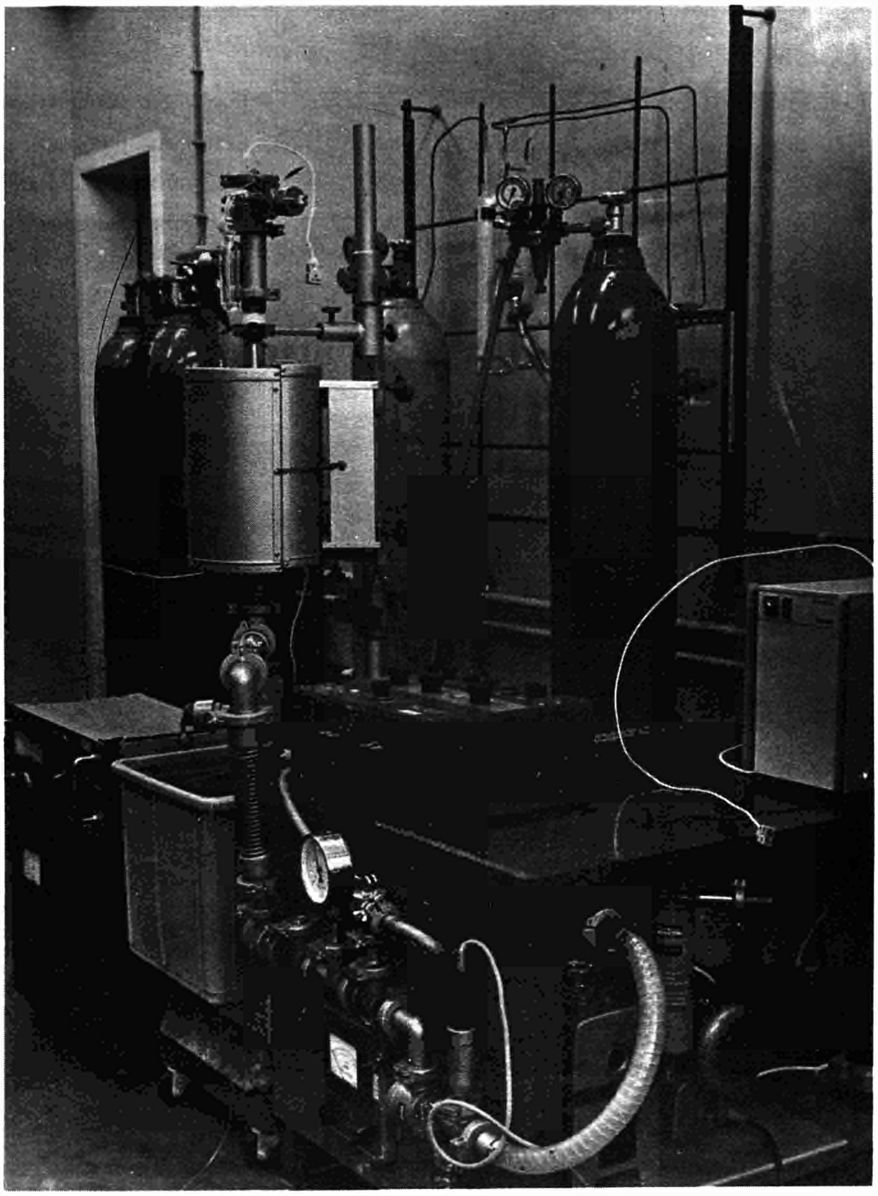


Fig. 2 View of the improved quench facility (for reference see context).

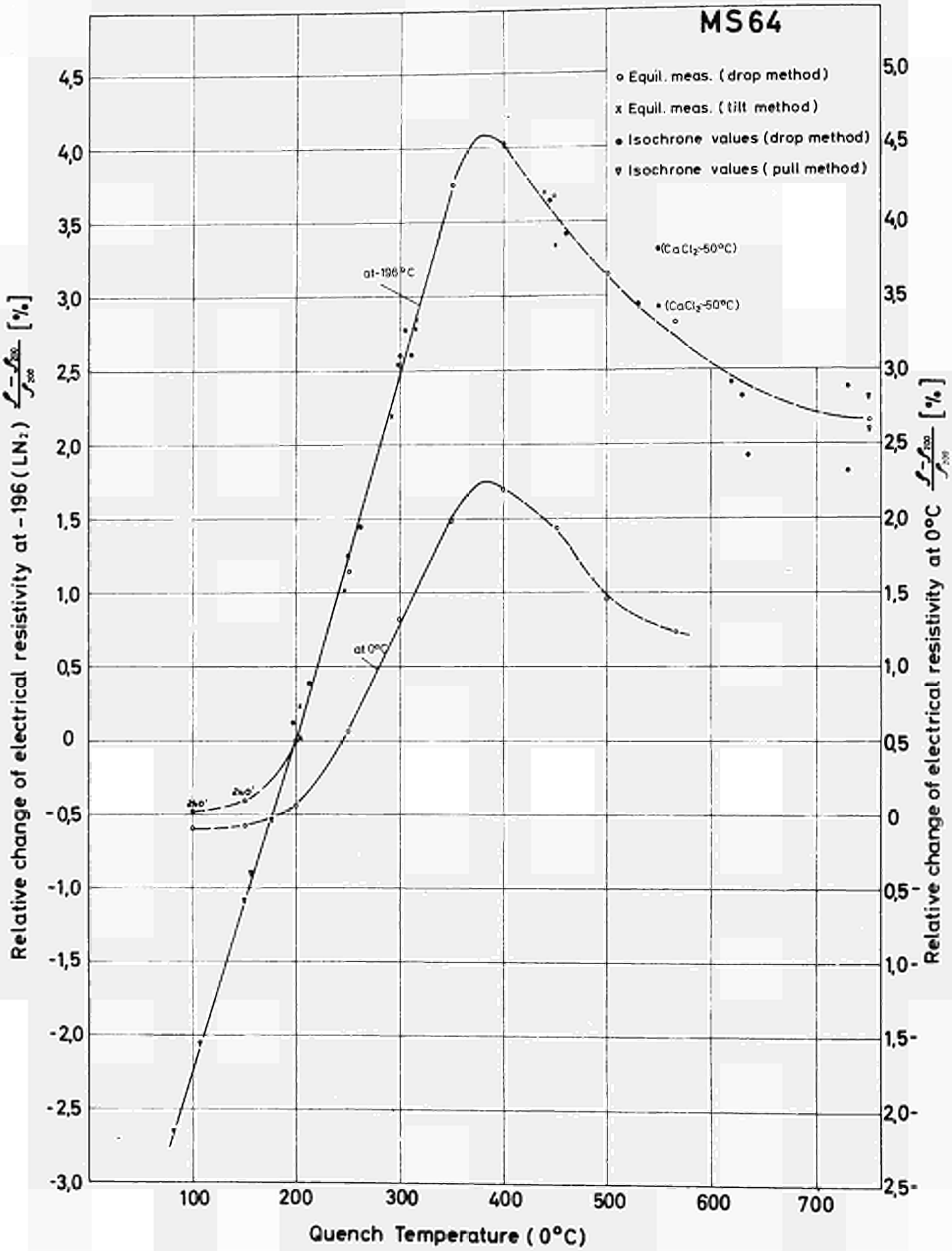
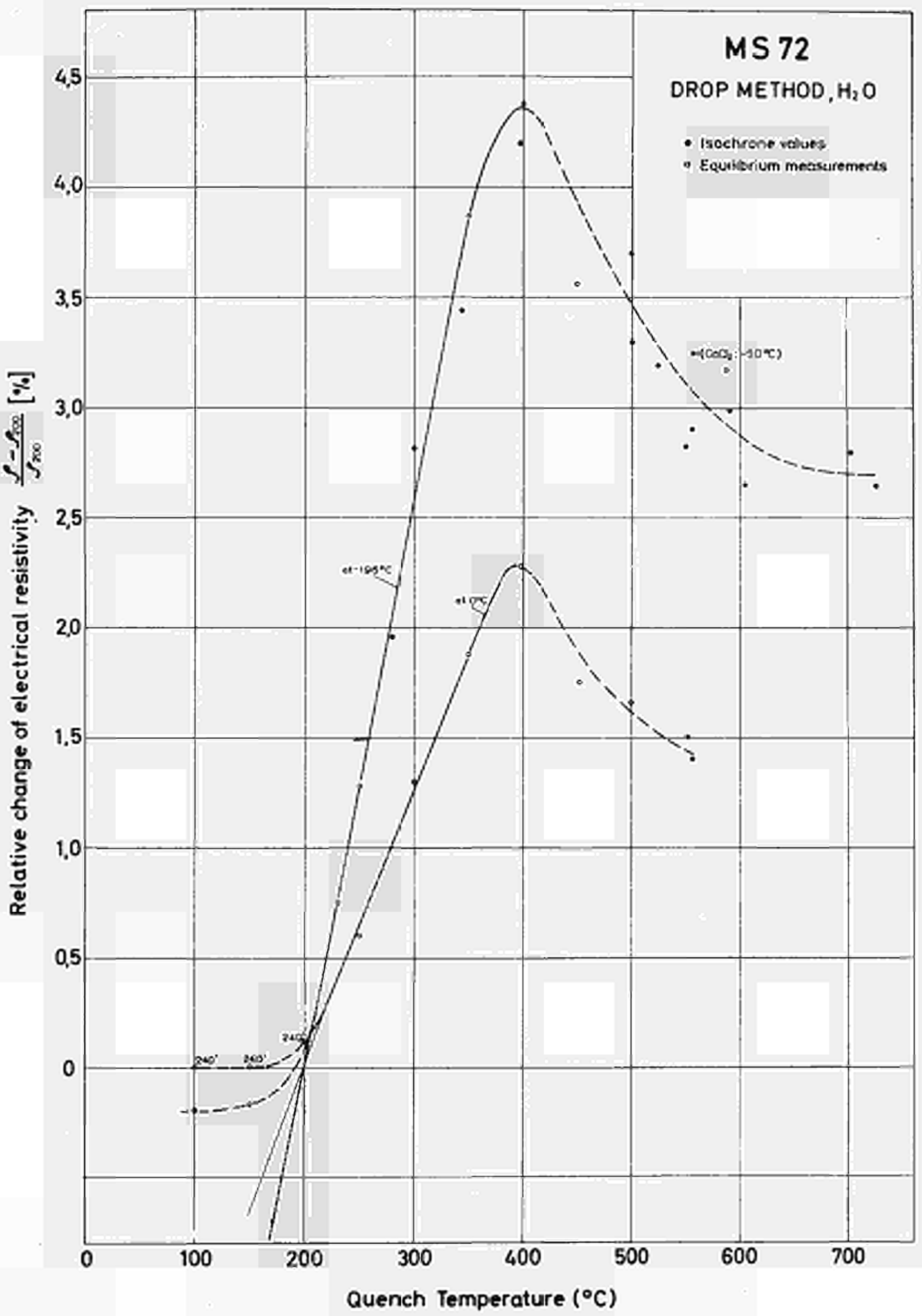
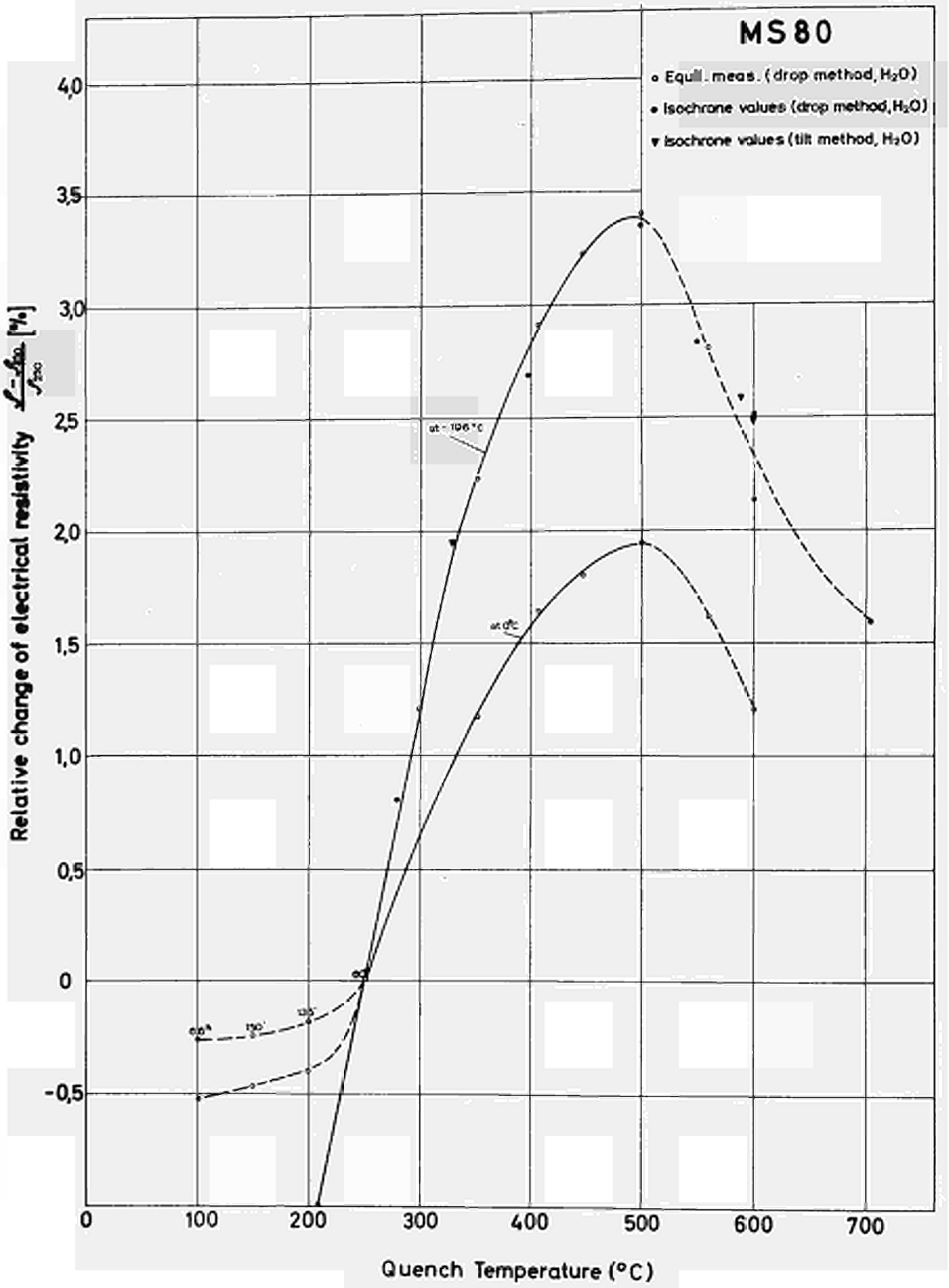
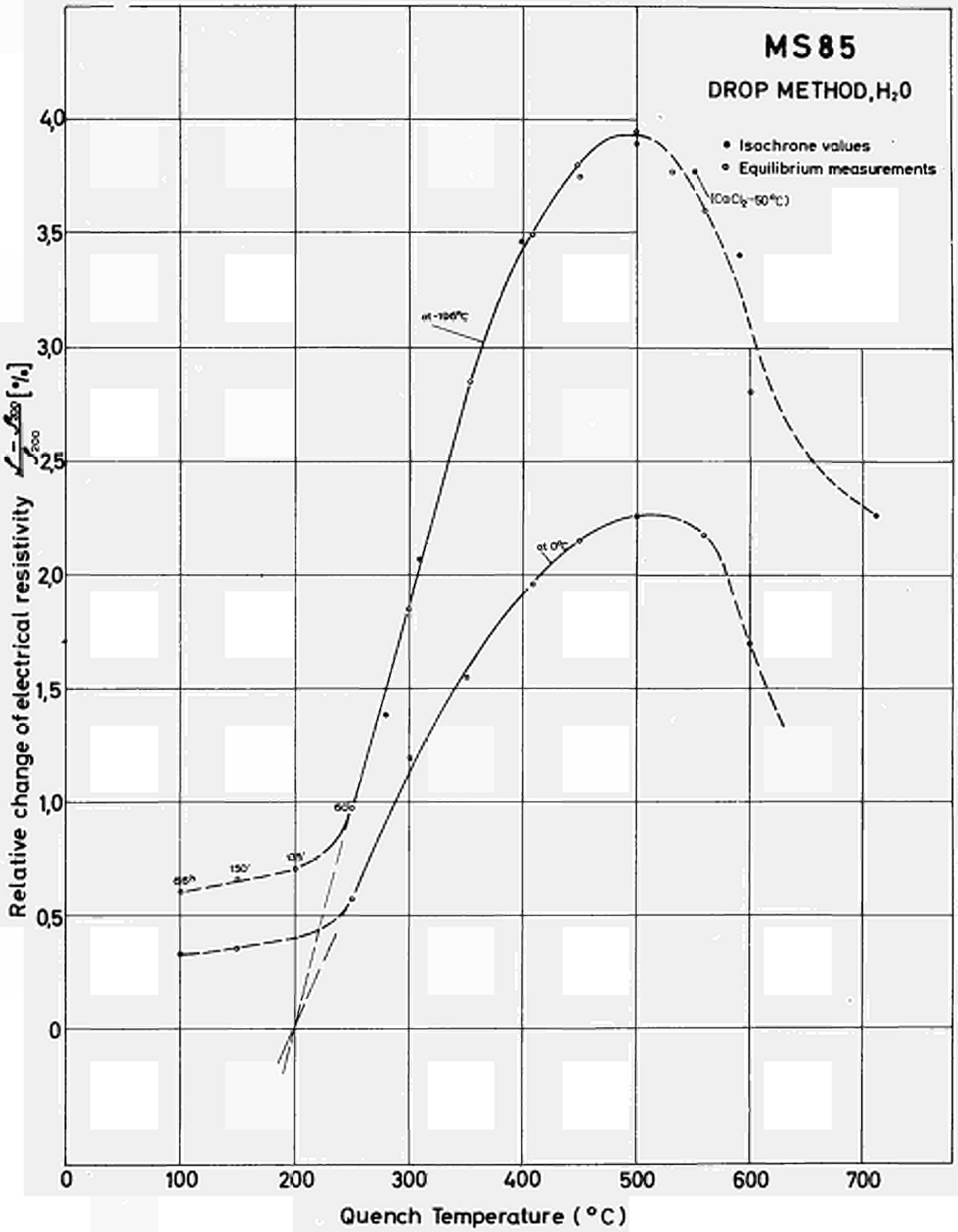


Fig. 3a-d Equilibrium curves of four investigated Cu-Zn-alloys (Ms-64, Ms-72, Ms-80, Ms-85). The relative variation of electrical resistivity $(\rho - \rho_{200})/\rho_{200}$ as measured at LN_2-temperature and at 0°C is plotted. Some points (Δ) are taken from the initial resistivity increment of the isochrones upon quenching from the temperature T_q.


MS 72
DROP METHOD, H_2O
● Isochrone values
○ Equilibrium measurements
(CaCl₂ : -50°C)
at -196°C
at 0°C
240'
360'
240'
Relative change of electrical resistivity $\frac{\rho - \rho_{200}}{\rho_{200}}$ [%]
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0
0
100
200
300
400
500
600
700
Quench Temperature (°C)


MS80
○ Equil. meas. (drop method, H_2O)
● Isochrone values (drop method, H_2O)
▼ Isochrone values (tilt method, H_2O)
at -196 °C
at 0°C
60h
150'
120'
Relative change of electrical resistivity $\frac{\rho-\rho_{250}}{\rho_{250}}$ [%]
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0
-0,5
0
100
200
300
400
500
600
700
Quench Temperature (°C)


MS85
DROP METHOD, H_2O
● Isochrone values
○ Equilibrium measurements
($CaCl_2$ -50°C)
at -196°C
at 0°C
68h
150'
135'
60'
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0
Relative change of electrical resistivity $\frac{\rho - \rho_{200}}{\rho_{200}}$ [%]
0
100
200
300
400
500
600
700
Quench Temperature (°C)

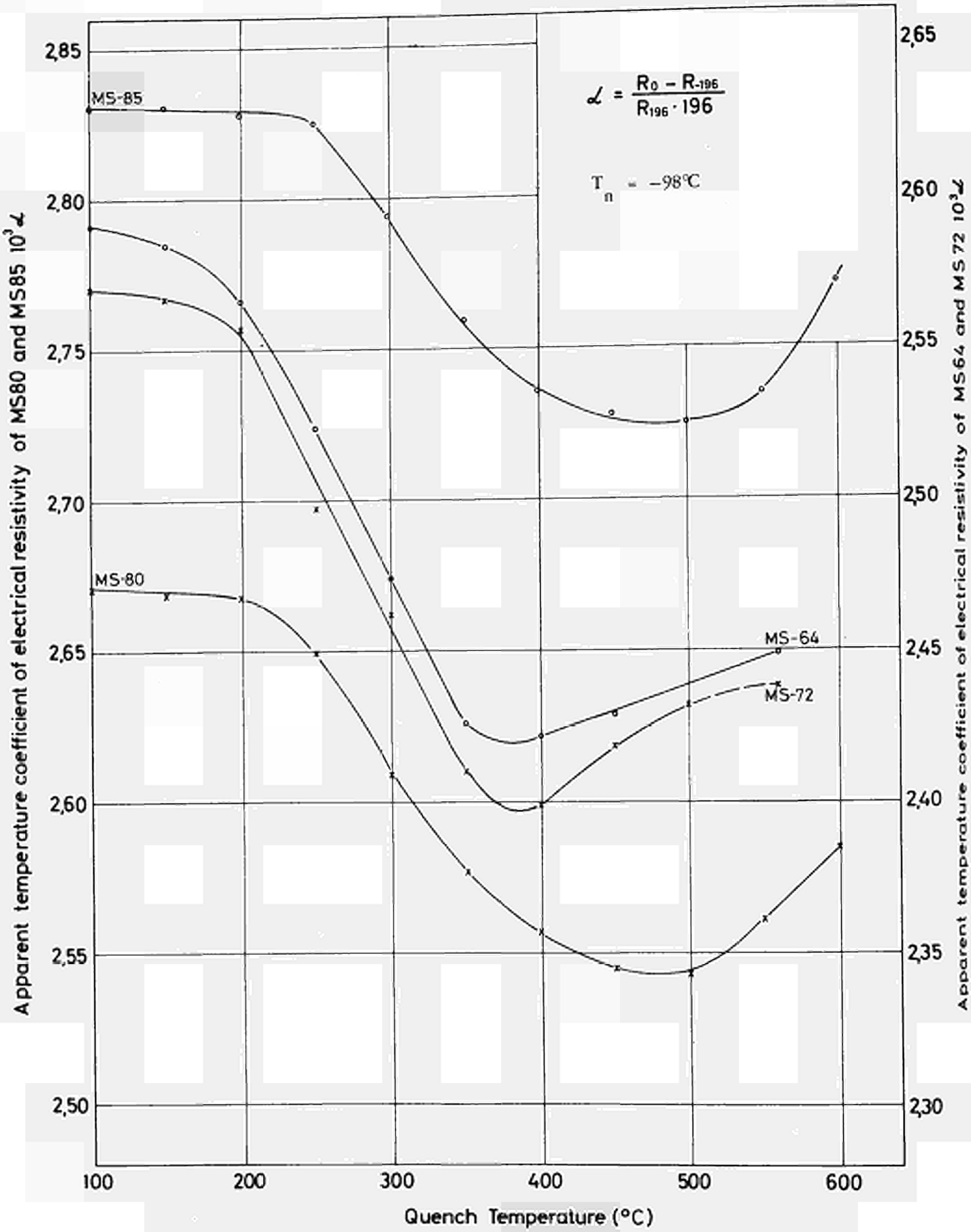


Fig. 4 : Variation of the apparent temperature coefficient of the electrical resistivity ($p_0 o$ - p_{LN_2})/ p_{LN_2} . 196 of four Cu-Zn-alloys as derived from the equilibrium measurements (see Fig. 3).

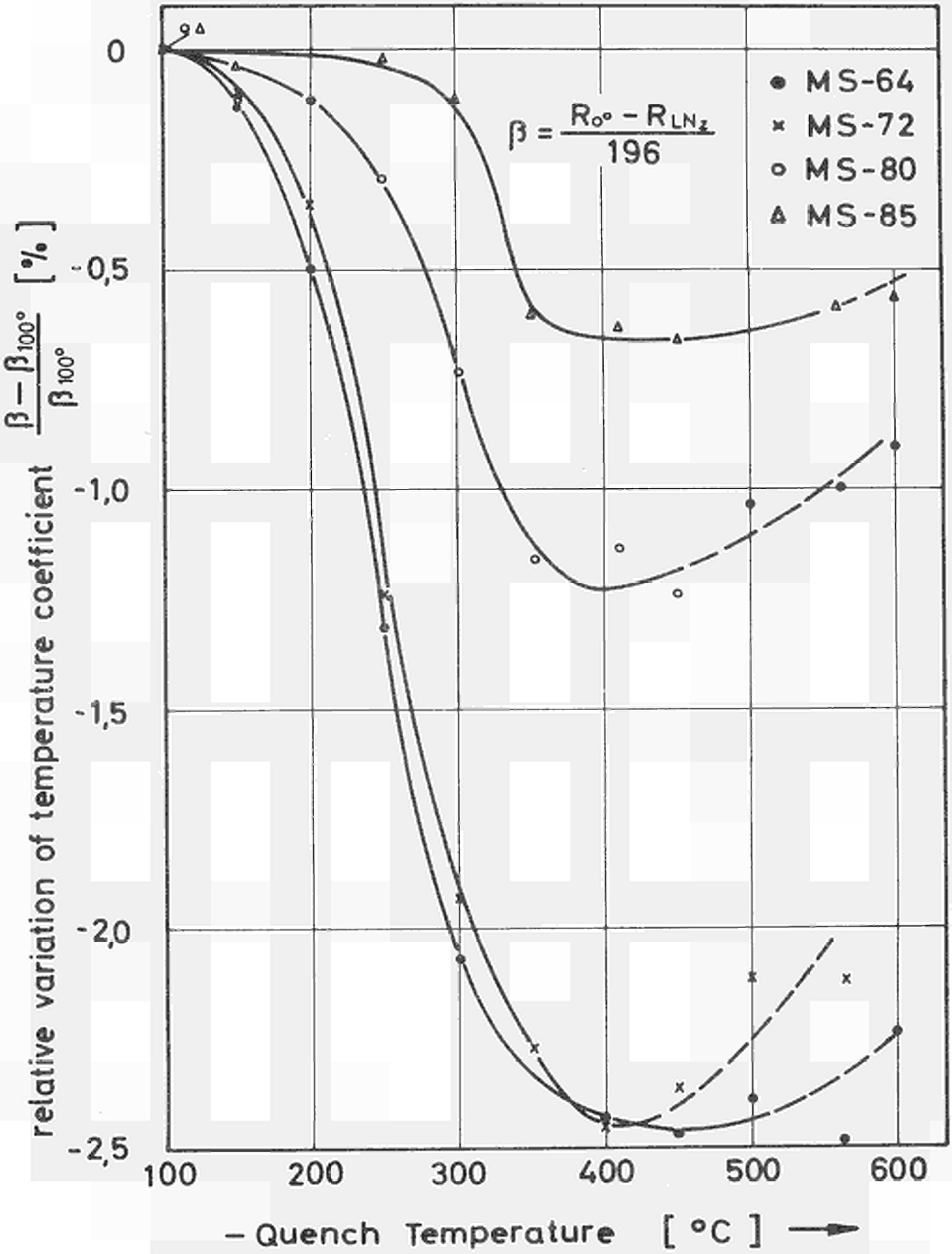


Fig. 5 : Relative variation of the temperature coefficient $\beta = (R_0o - R_{LN_2}) / 196$ in dependence of the quench temperature (calculated from the experiments of Fig. 3).

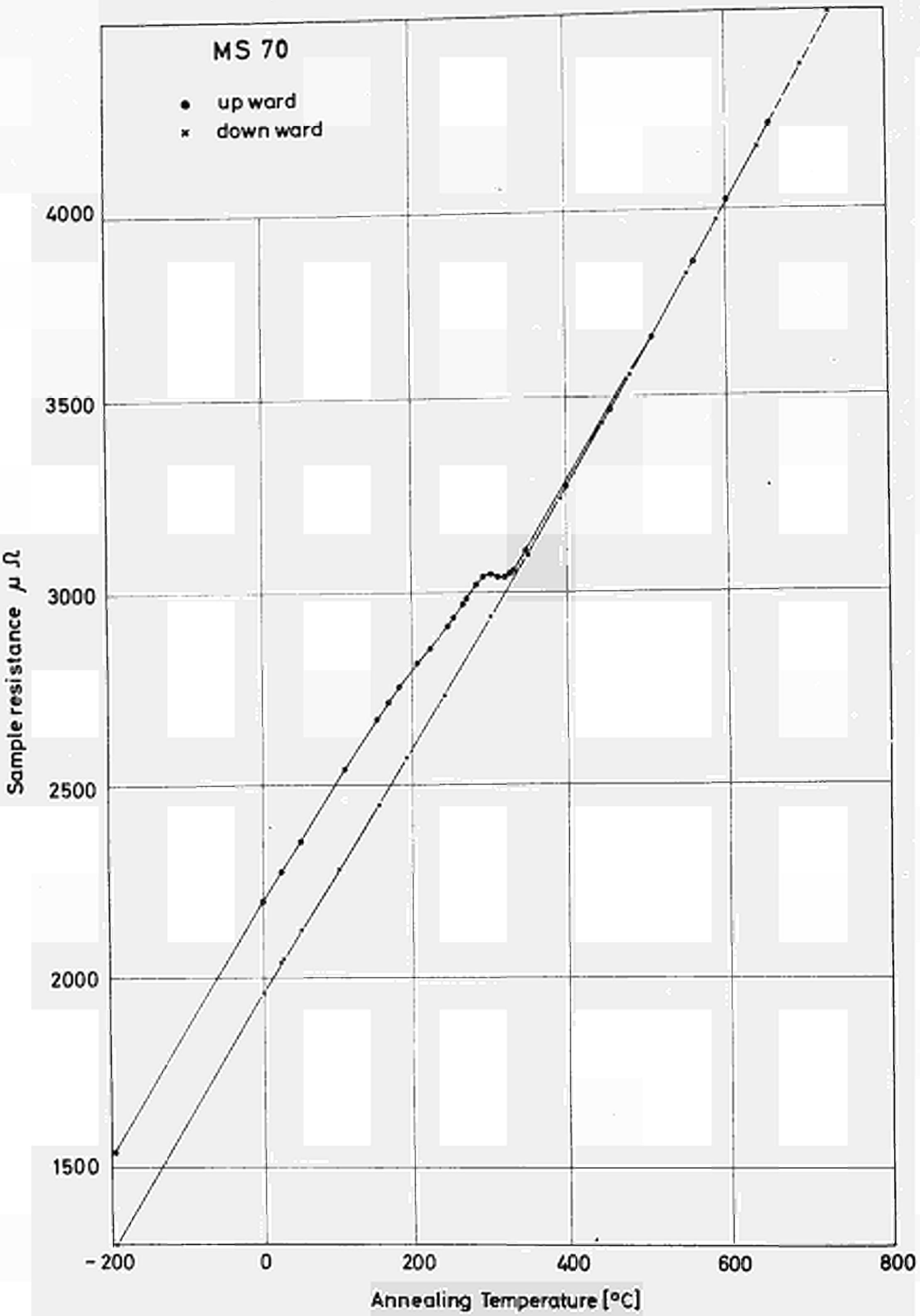


Fig. 6 : Resistance vs. temperature of a Ms-70 sample measured upward with a constant heating rate of 5° C/ min and downward under equilibrium conditions.

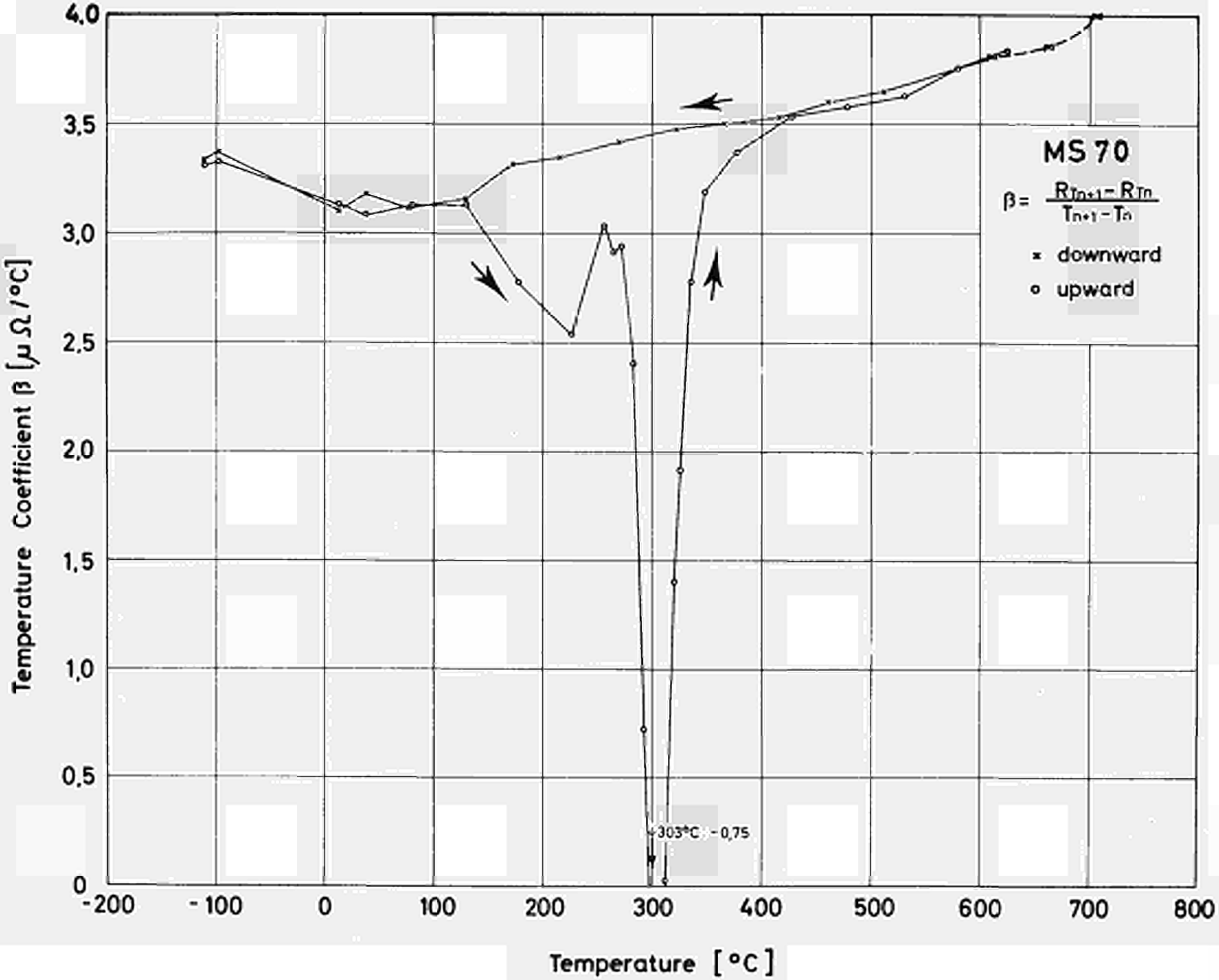


Fig. 7 : Temperature coefficient β of a Ms - 70 sample calculated as derivative of the curve in Fig. 6

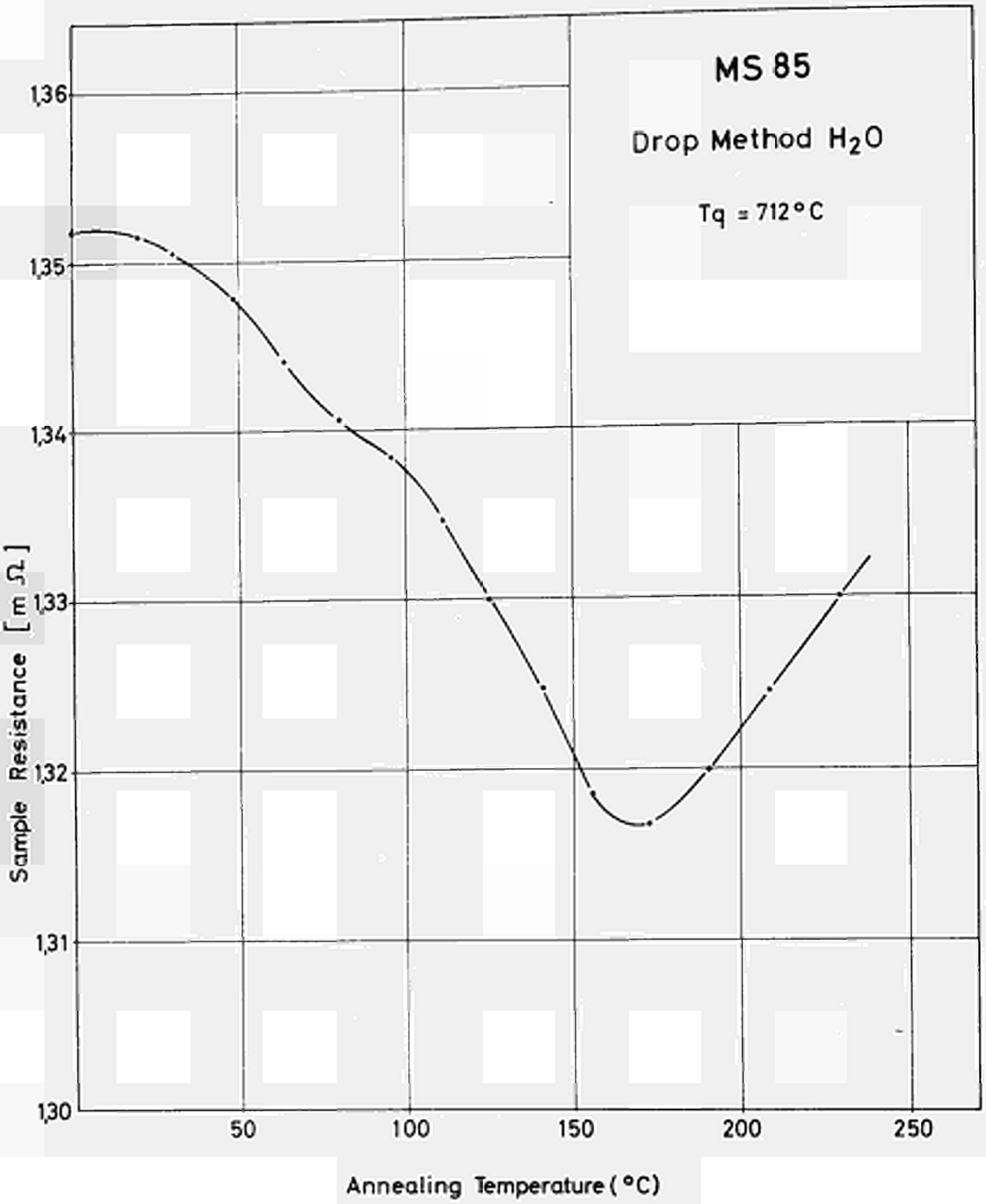


Fig. 8 : Change of the electrical resistance of a Ms - 85 sample quenched by the drop method from 712° C into water (18° C) during isochronal (15') annealing.

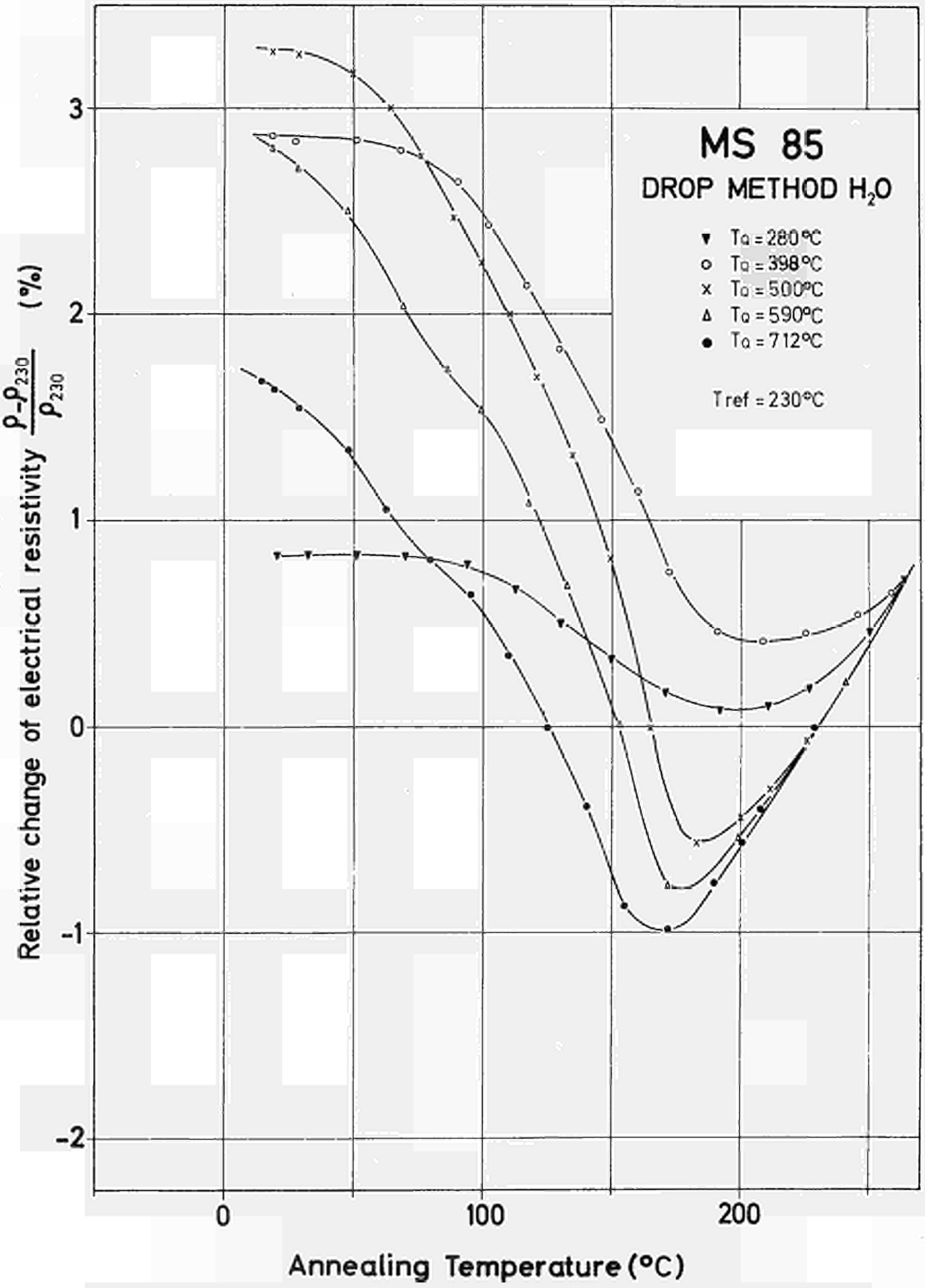


Fig. 9 : Relative change of electrical resistivity of Ms - 85 samples during isochronal annealing (15') upon quenching from various temperatures by the drop method into water (18° C) .

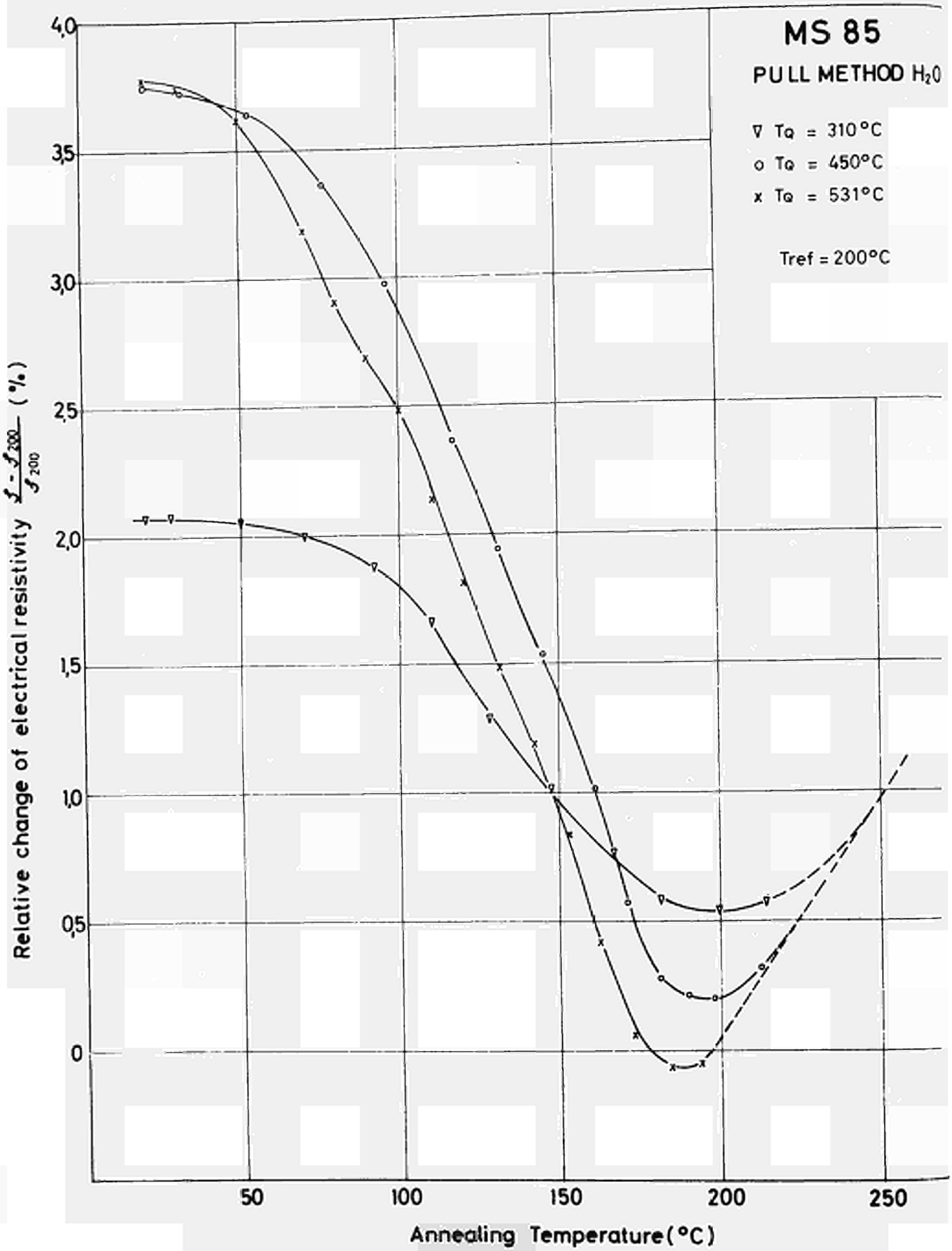


Fig. 10 : Relative change of electrical resistivity of Ms - 85 samples during isochronal annealing (15') upon quenching from various temperatures by the pull method into water (18° C) .

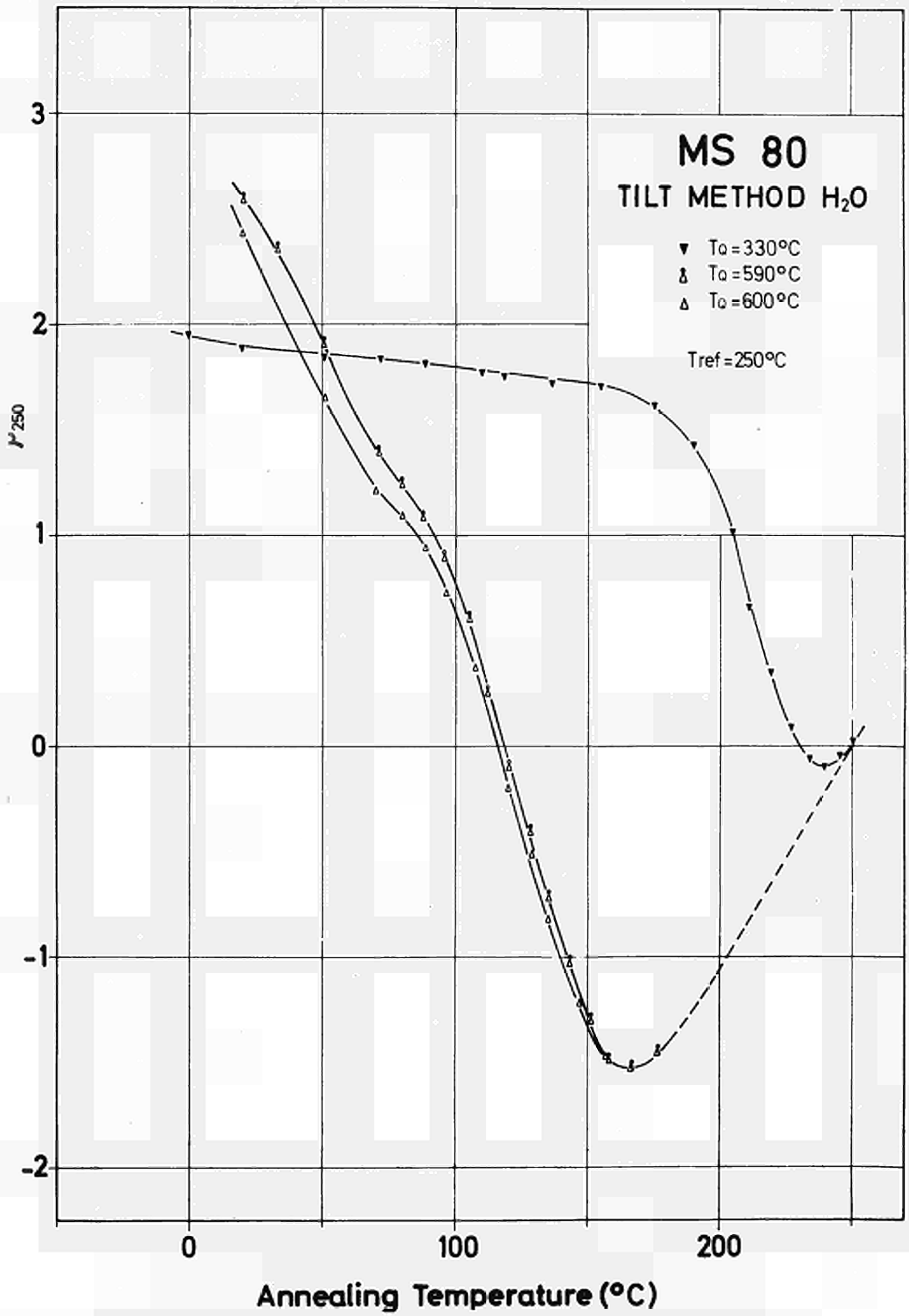


Fig. 11 : Relative change of electrical resistivity of Ms - 80 samples during isochronal annealing upon quenching from various temperatures by the tilt method into water (18° C). No recovery annealing at 560° C had been applied prior to quenching.

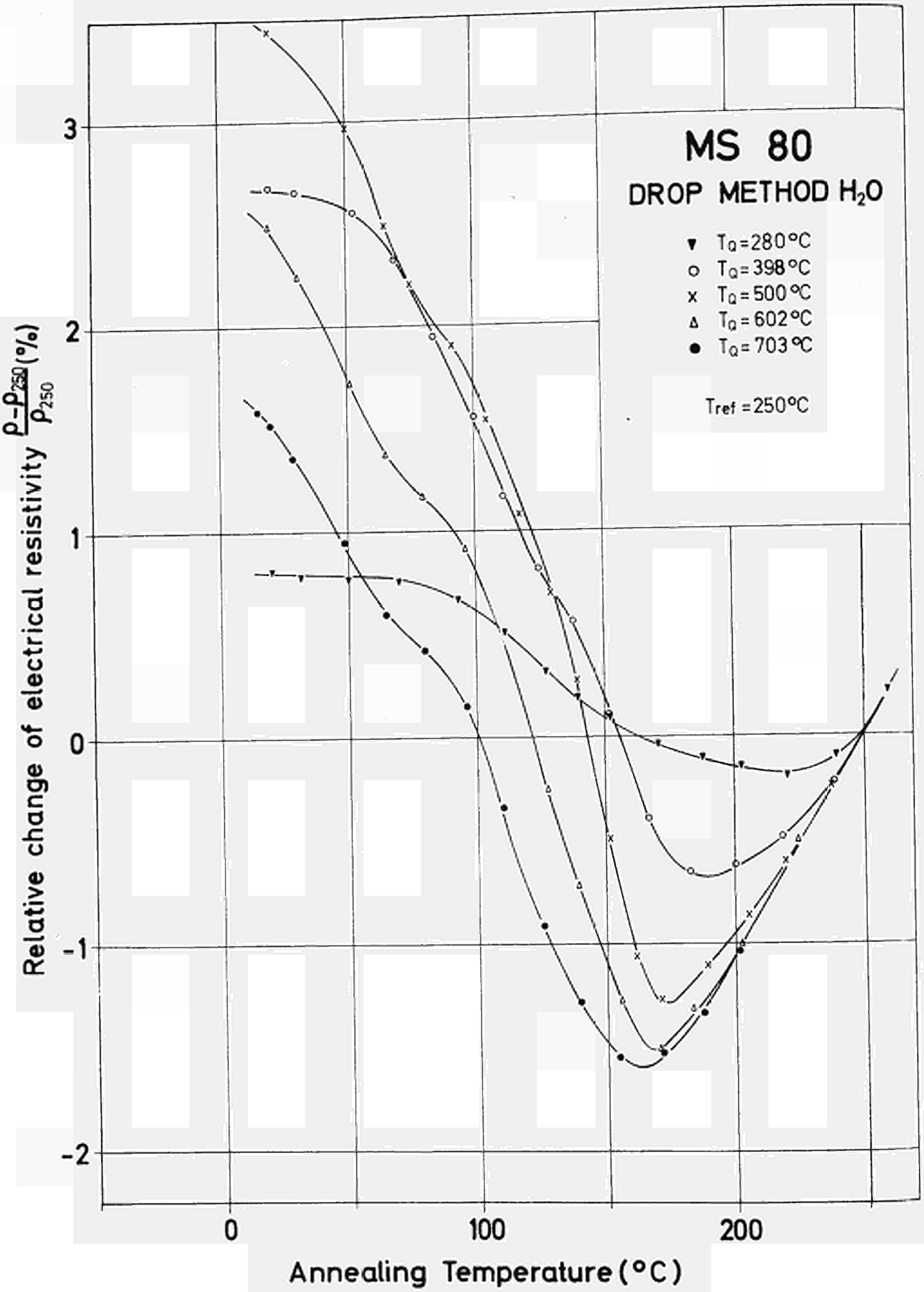


Fig. 12 : Relative change of electrical resistivity of Ms - 80 samples during isochronal annealing (15') upon quenching from various temperatures by the drop method into water (18° C).

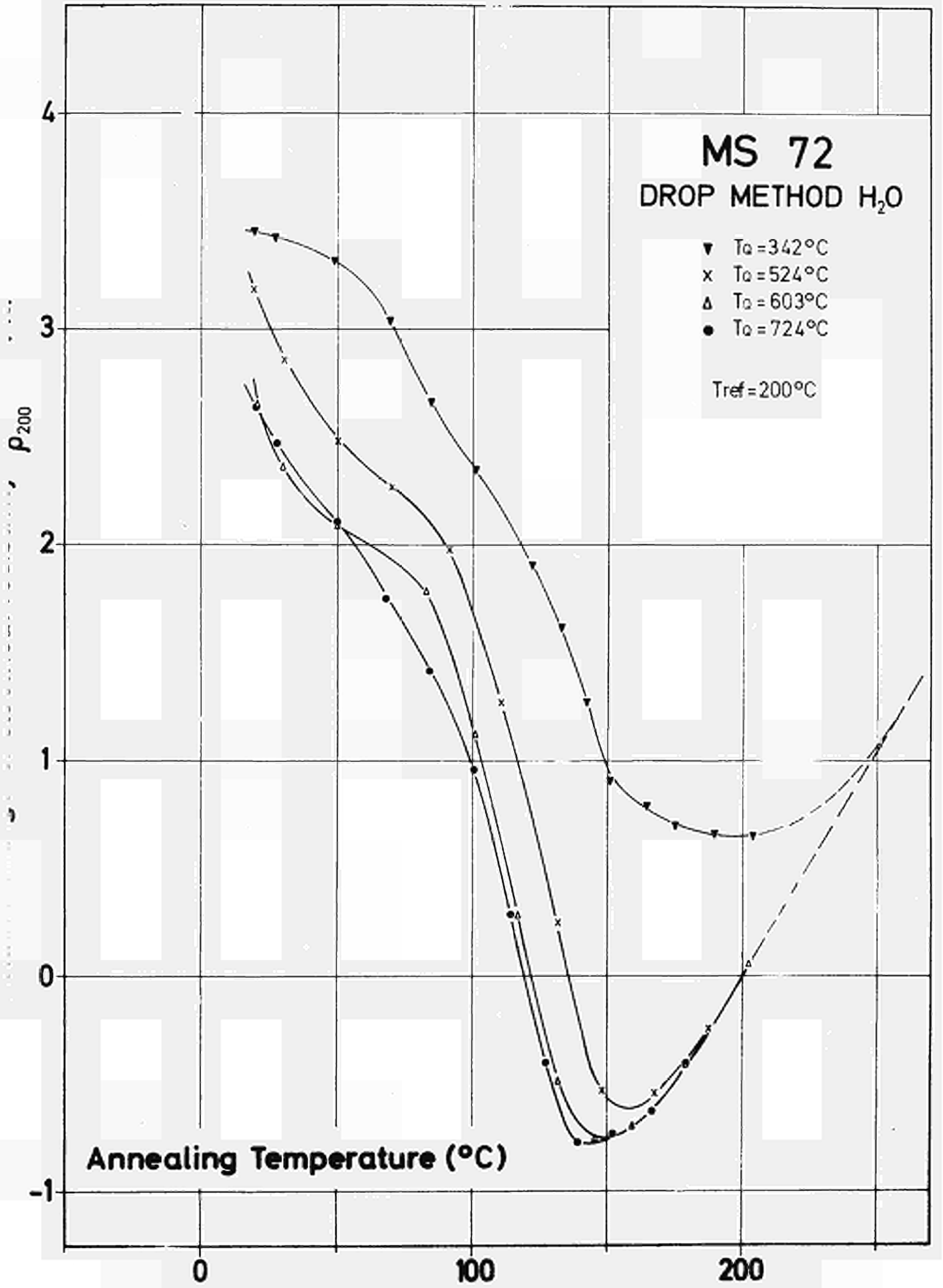


Fig. 13 : Relative change of electrical resistivity of Ms - 72 samples during isochronal annealing (15') upon quenching from various temperatures by the drop method into water (18° C). For each quench a new specimen was used.

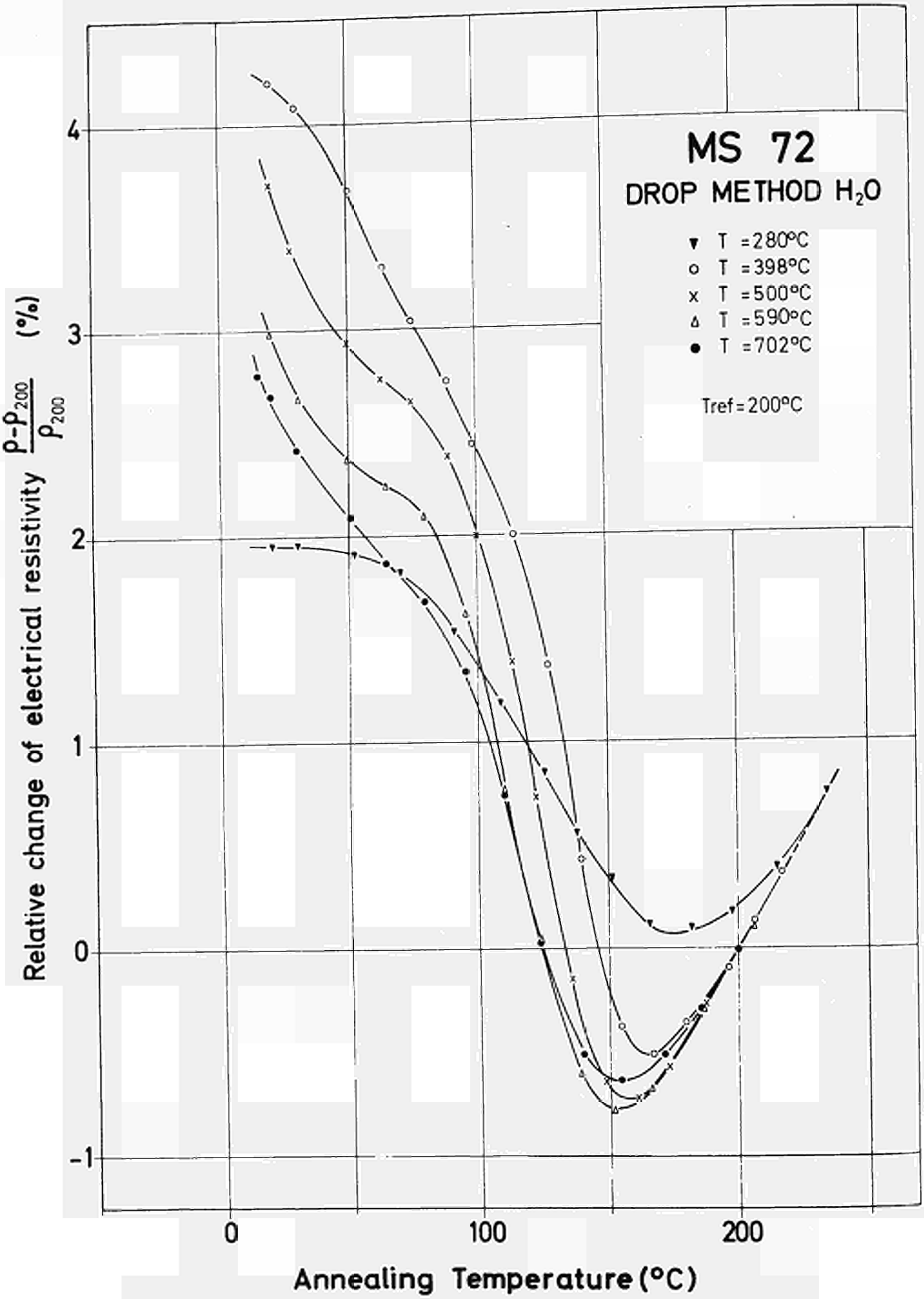


Fig. 14 : Relative change of electrical resistivity of Ms - 72 samples during isochronal annealing (15') upon quenching from various temperatures by the drop method into water (18° C). All quenches have been performed with the same specimen.

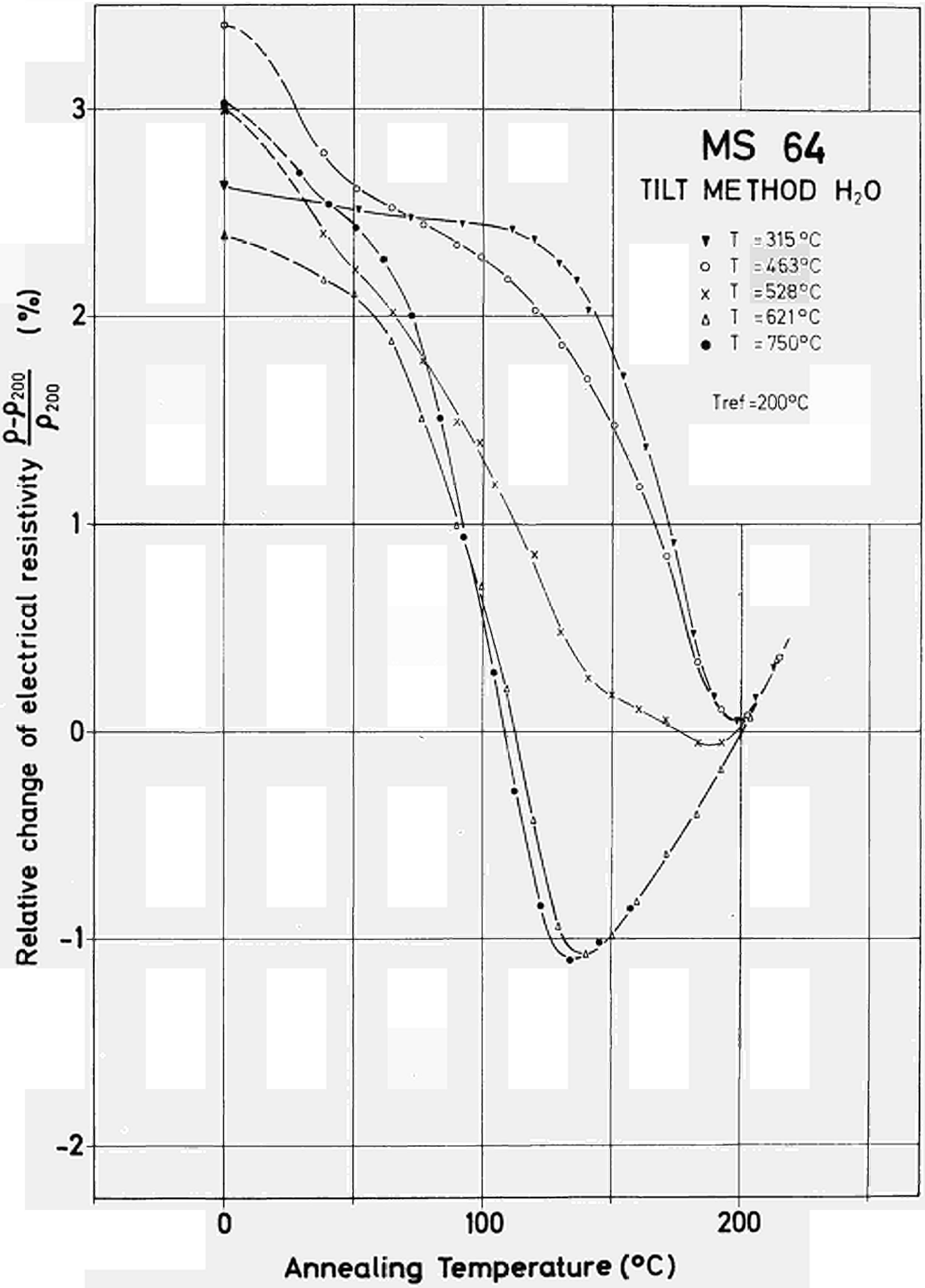


Fig. 15 : Relative change of electrical resistivity of Ms - 64 samples during isochronal annealing (15') upon quenching from various temperatures by the tilt method into water (18° C). These curves were taken from ref. 22 . No recovery anneal at 560° C had been applied prior to quenching.

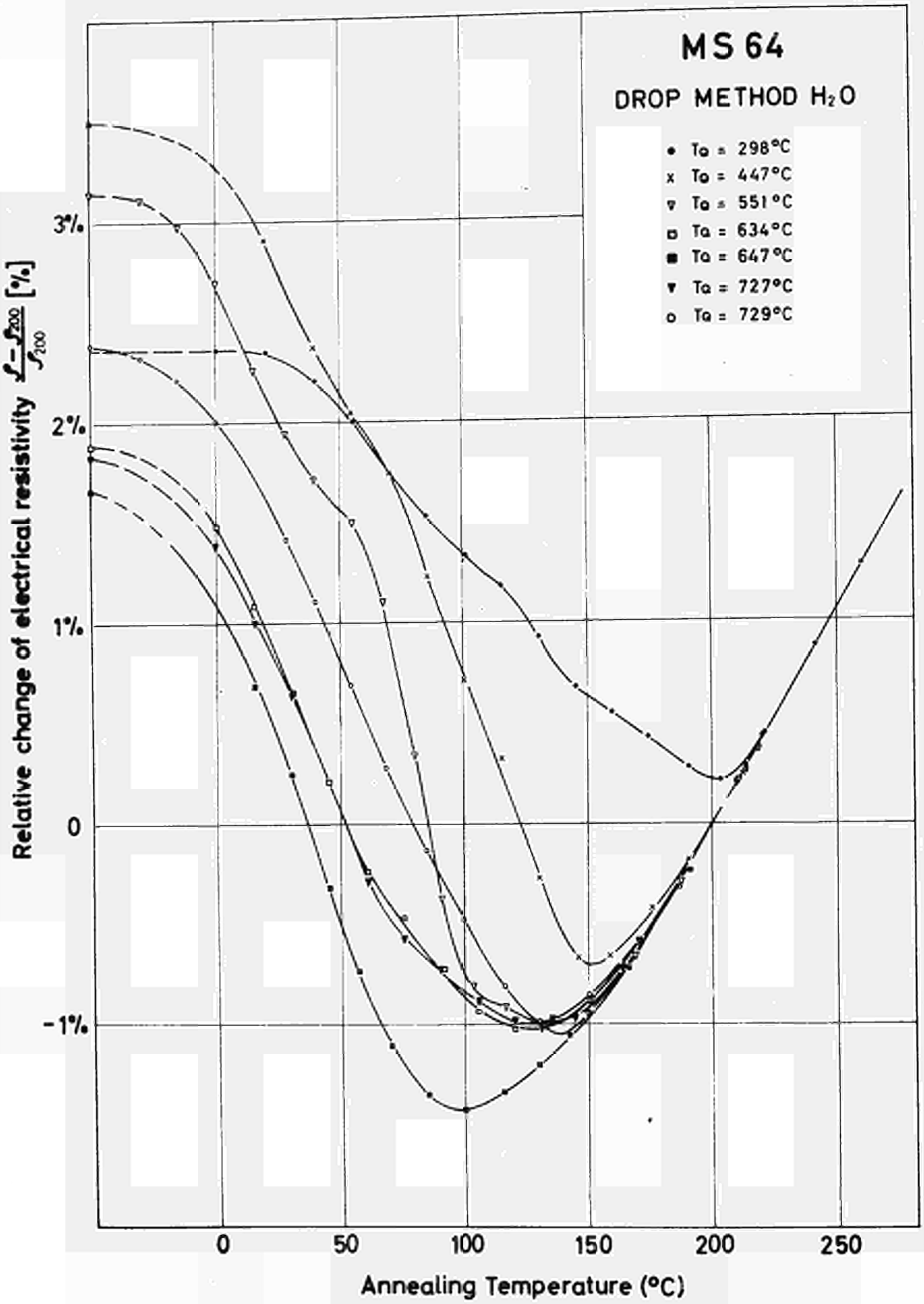


Fig. 16 : Relative change of electrical resistivity of Ms - 64 samples during isochronal annealing (15') upon quenching from various temperatures by the drop method into water (18° C). For mounting the samples were immediately transferred from the quench bath into an alcohol bath at - 60° C.

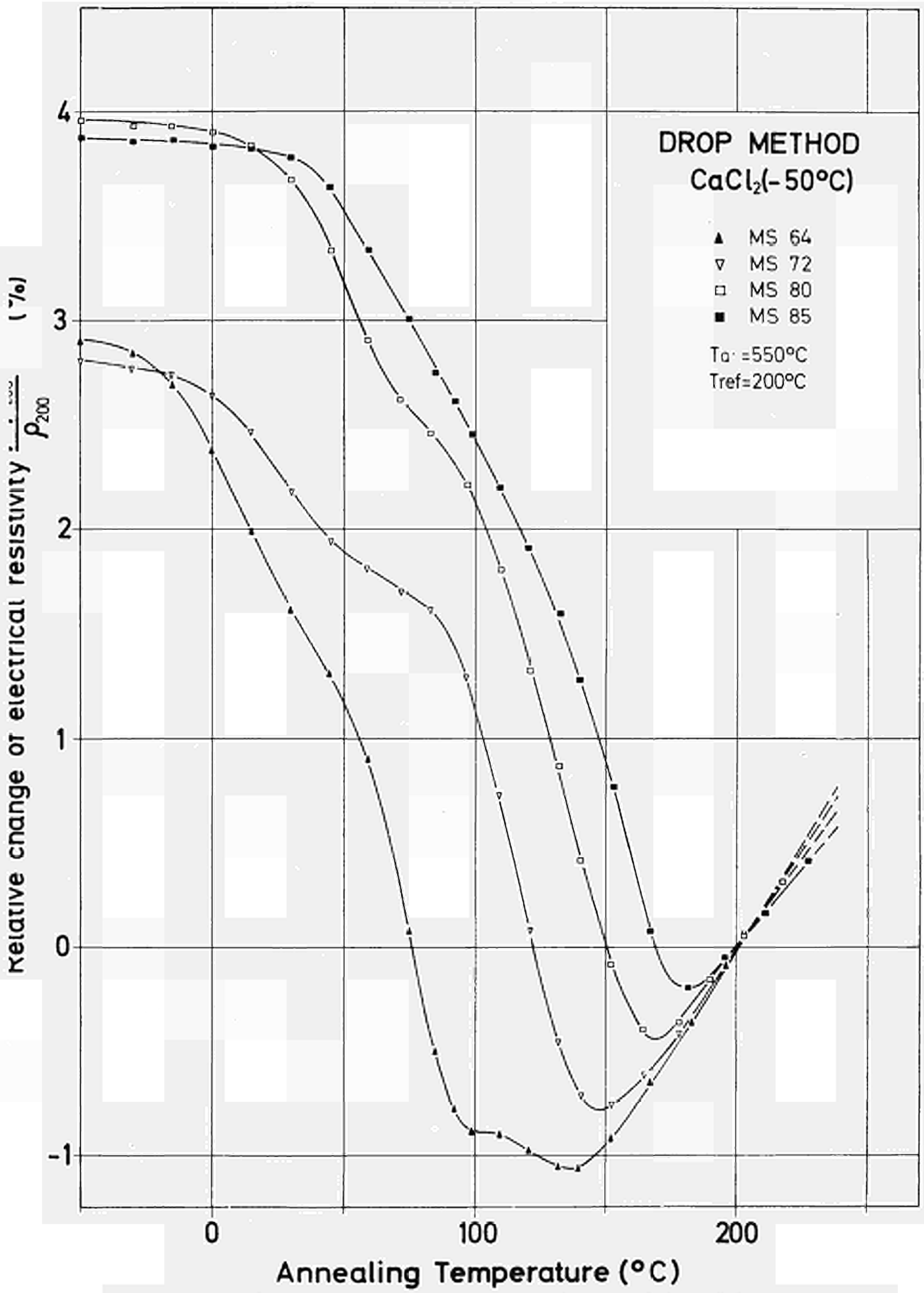


Fig. 17 : Relative change of electrical resistivity of four different brass samples (Ms-64, Ms-72, Ms-80, Ms-85) during isochronal annealing (15') upon quenching from 550° C by the drop method into a $CaCl_2$- solution at - 50°C. Sample mounting was done in an alcohol bath at -60° C.

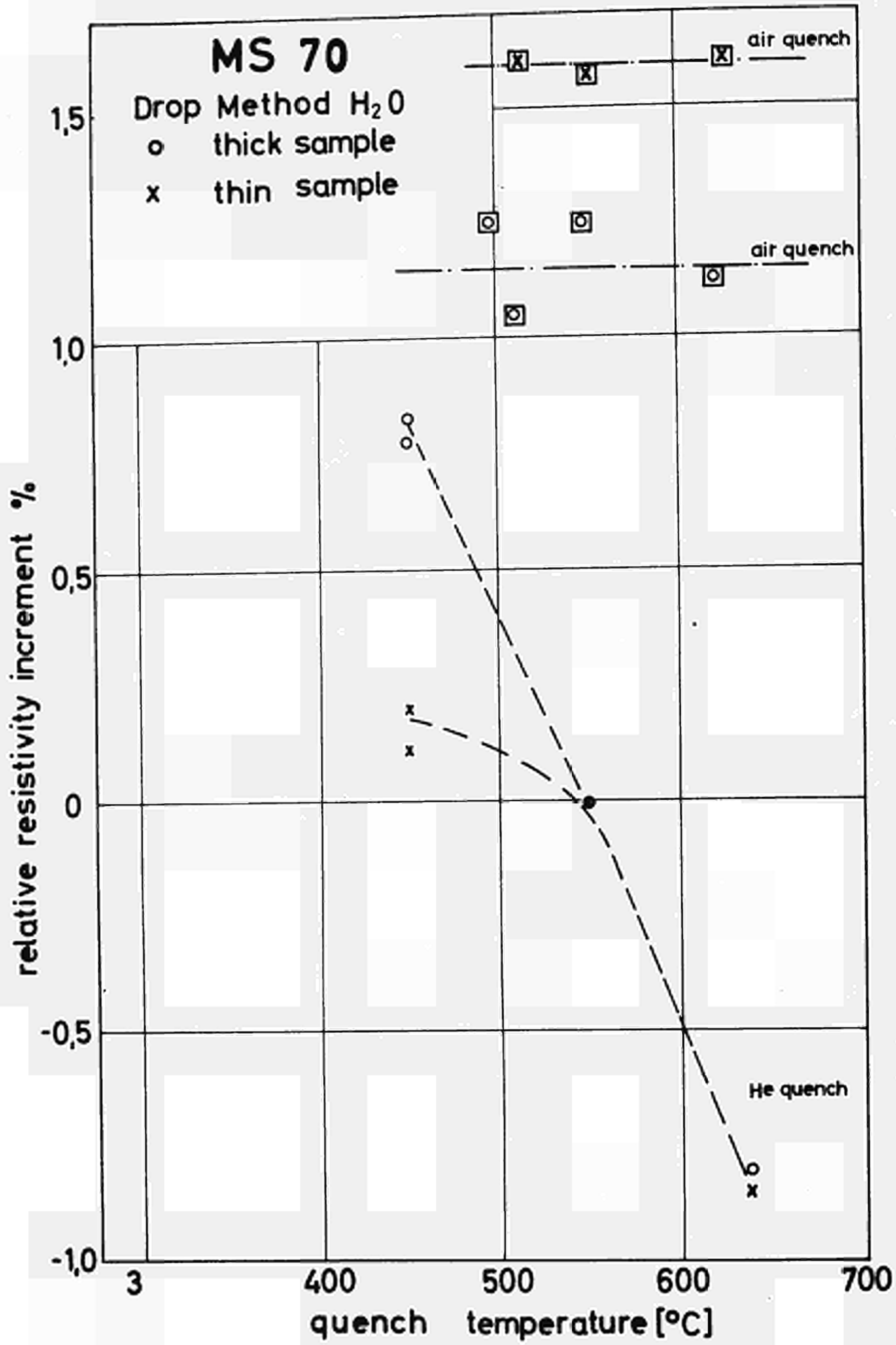


Fig. 18 : Plot of the relative resistance values of two Ms - 70 samples of different thickness (0.09 and 0.17 mm) quenched by the drop method from inert atmosphere and air, respectively, into water.

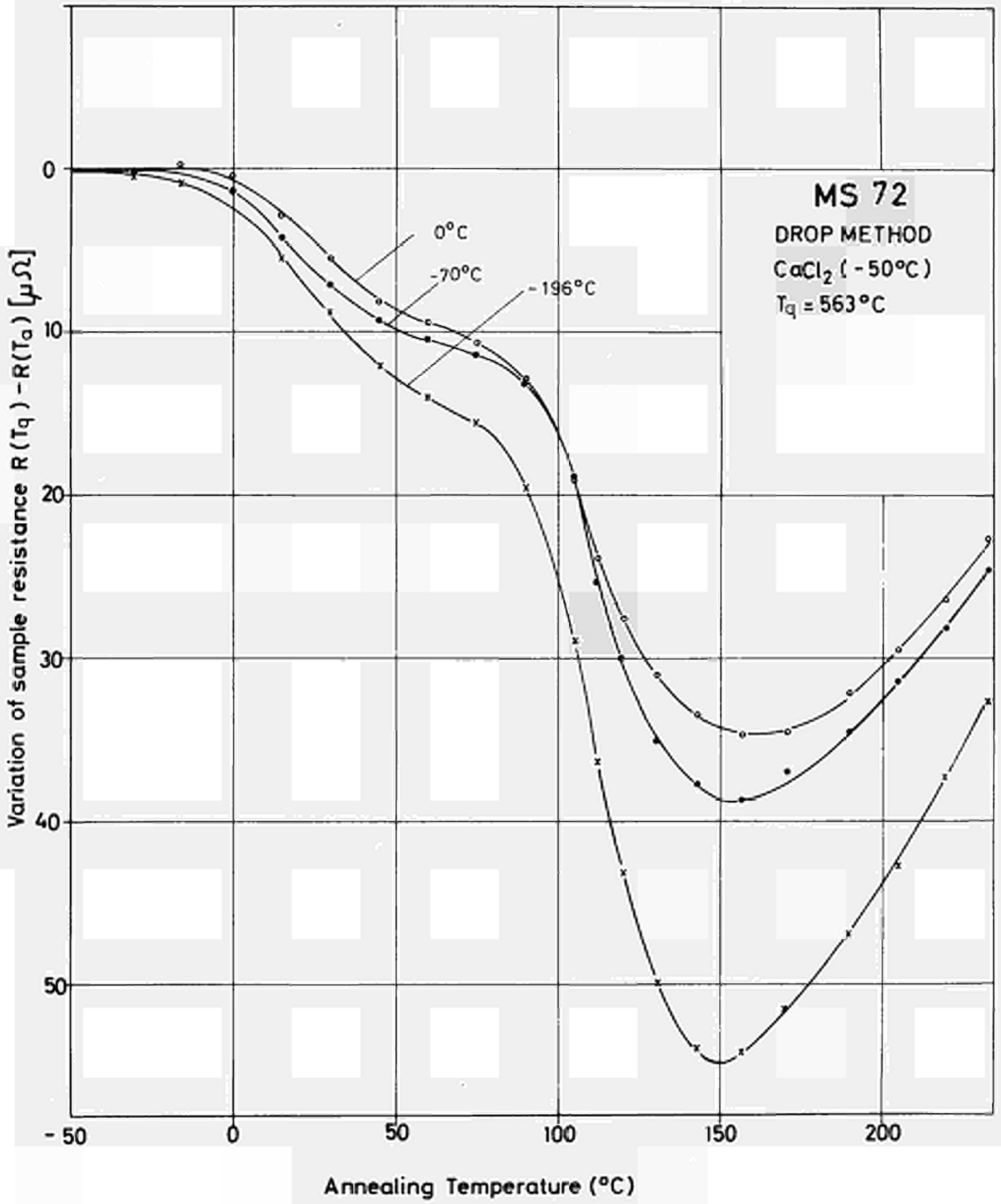


Fig.19 : Relative change of the electrical resistance of a Ms - 72 sample during isochronal annealing (15') upon quenching from 563° C by the drop method into a $CaCl_2$-solution at - 50° C. The resistance was measured at LN_2-temperature, at - 70° C and at 0° C.

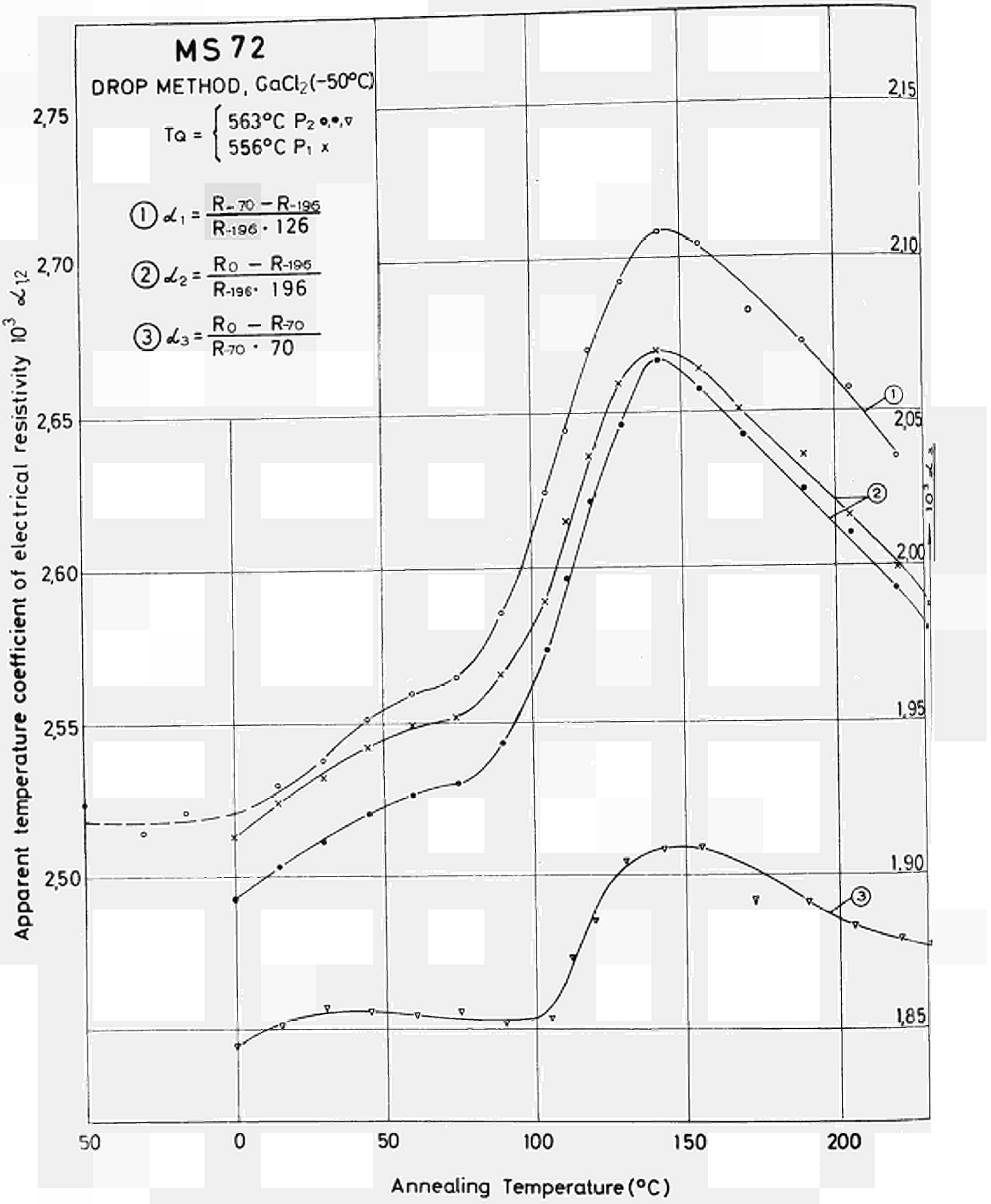


Fig. 20 : Variation of the apparent temperature coefficients of the electrical resistivity of a Ms - 72 sample during isochronal annealing upon quenching from 560° C and measurement at three different reference temperatures (see Fig. 19).

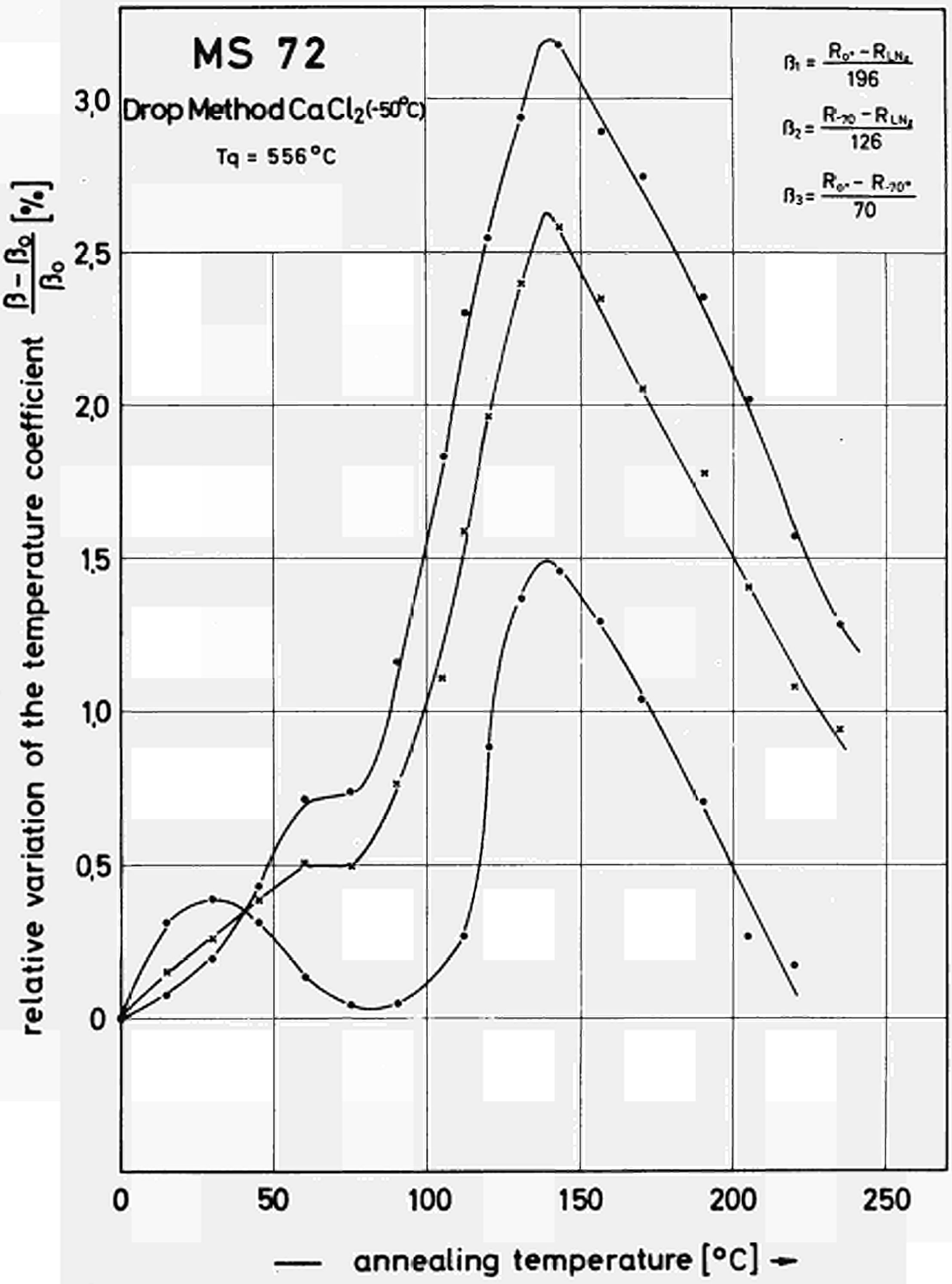


Fig. 21 : Relative variation of the temperature coefficient β (for definition refer to context) in dependence on the annealing temperature (calculated from the experiments of Fig. 19).

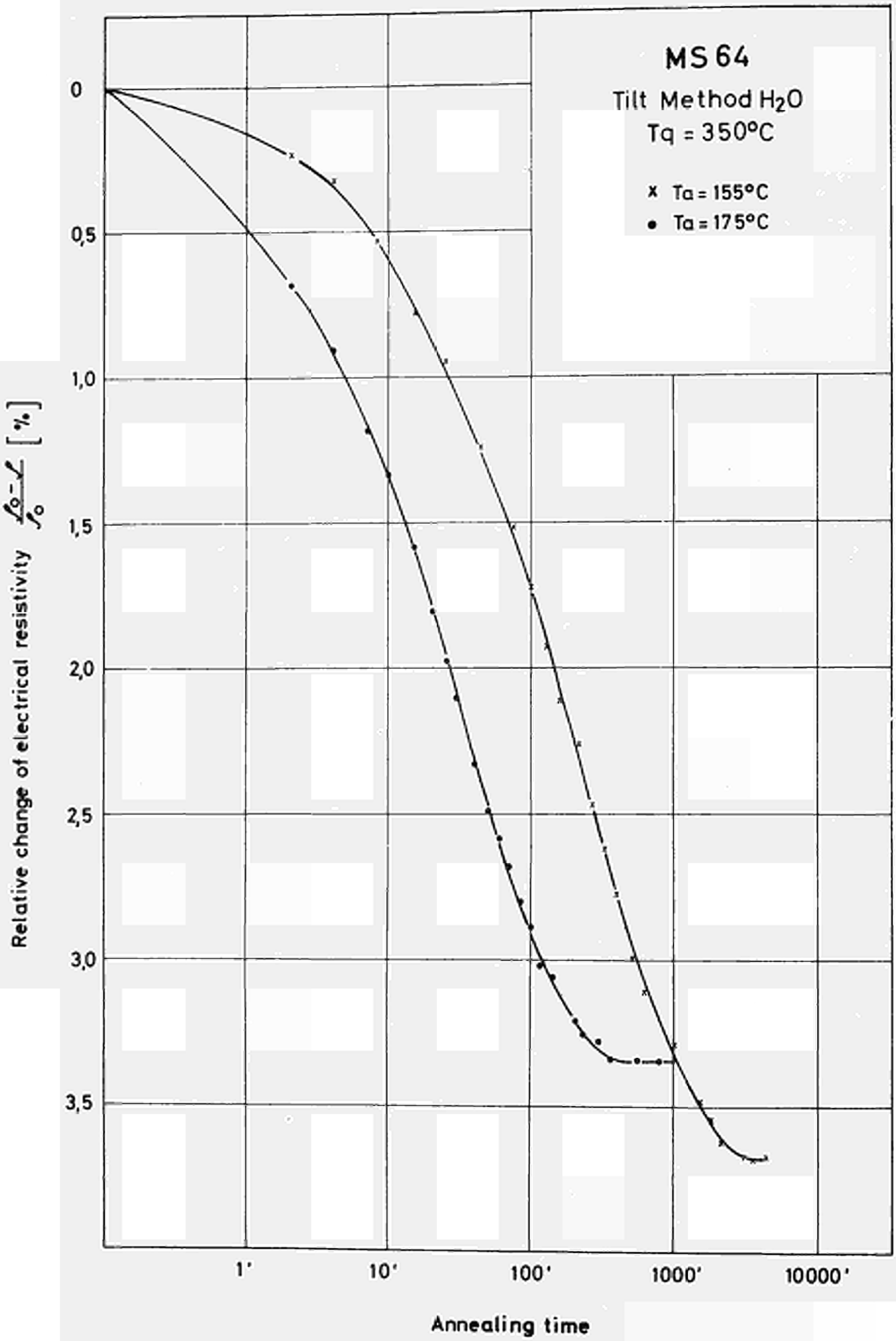


Fig. 22 : Isothermal annealing curves of Ms - 64 upon quenching from 350° C into water by the tilt method.
The relative resistivity change ($\rho_o - \rho$)/ ρ_o is plotted.

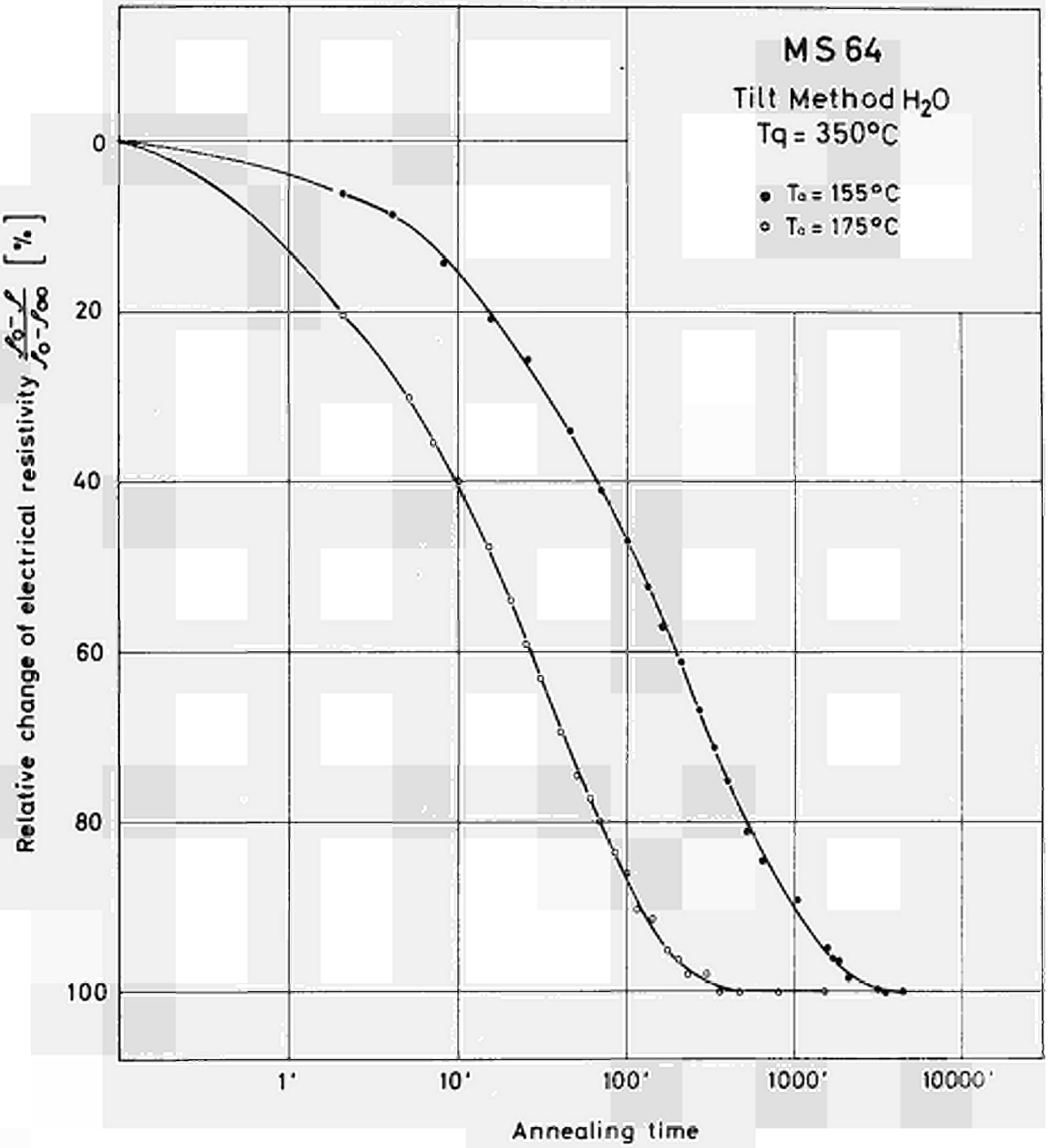


Fig. 23 : The isotherms of Fig. 22 are plotted in a normalized form.

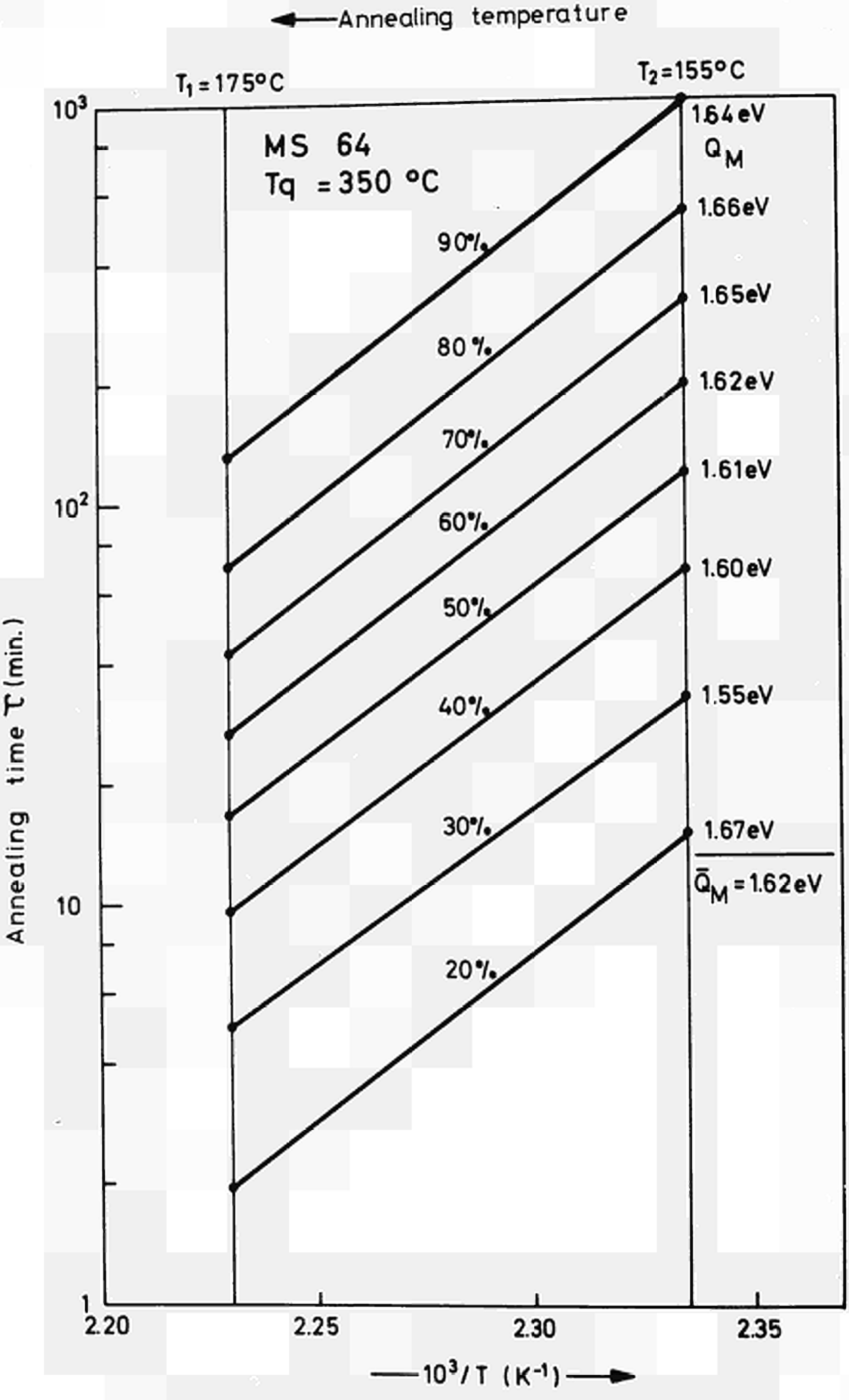


Fig. 24 : Determination of the activation energy of the isothermal annealings of Fig. 23.

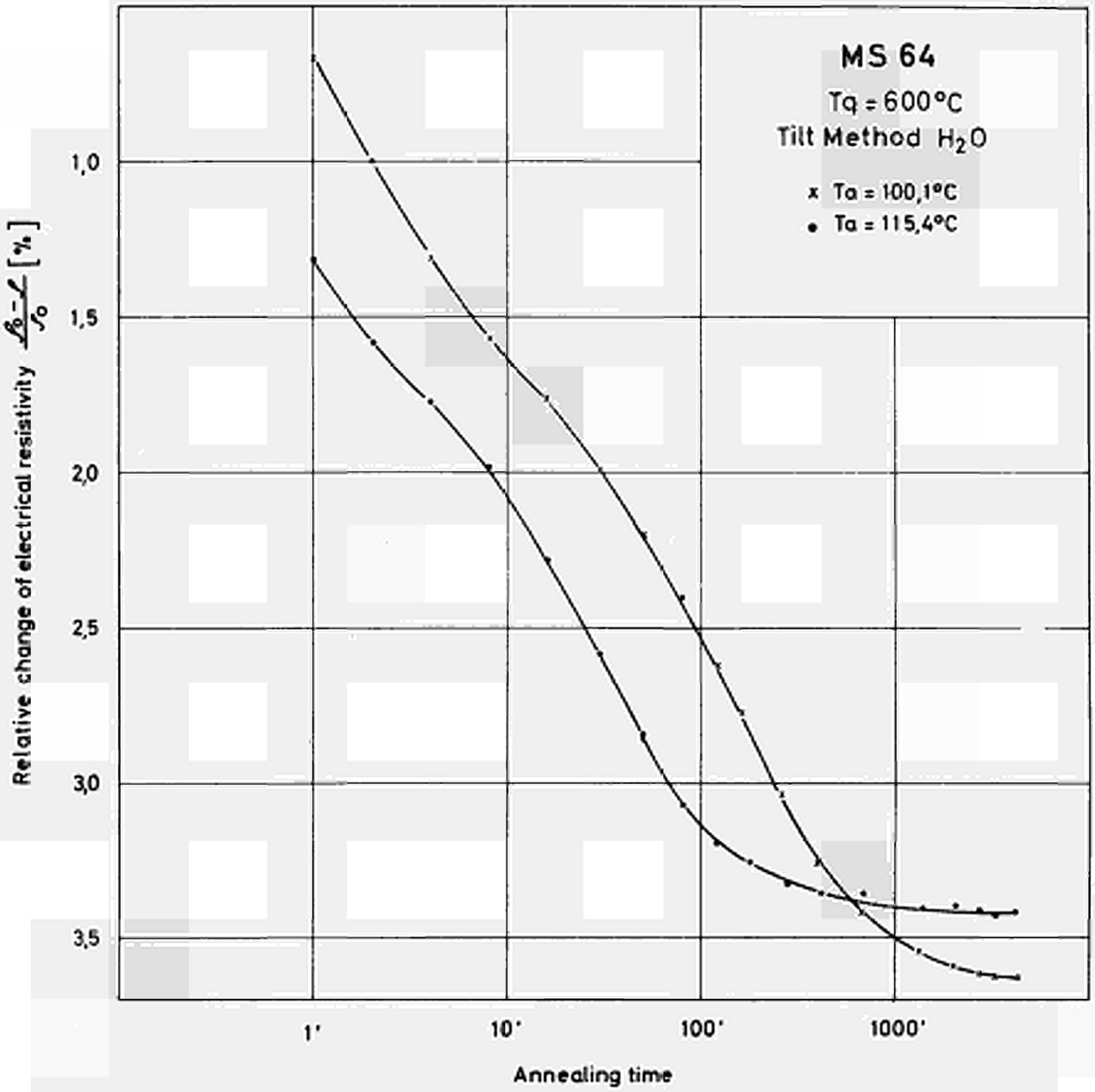


Fig. 25 : Isothermal annealing curves of Ms - 64 upon quenching from 600° C into water by the tilt method.
The relatively resistivity change $(\rho_o - \rho) / \rho_o$ is plotted.

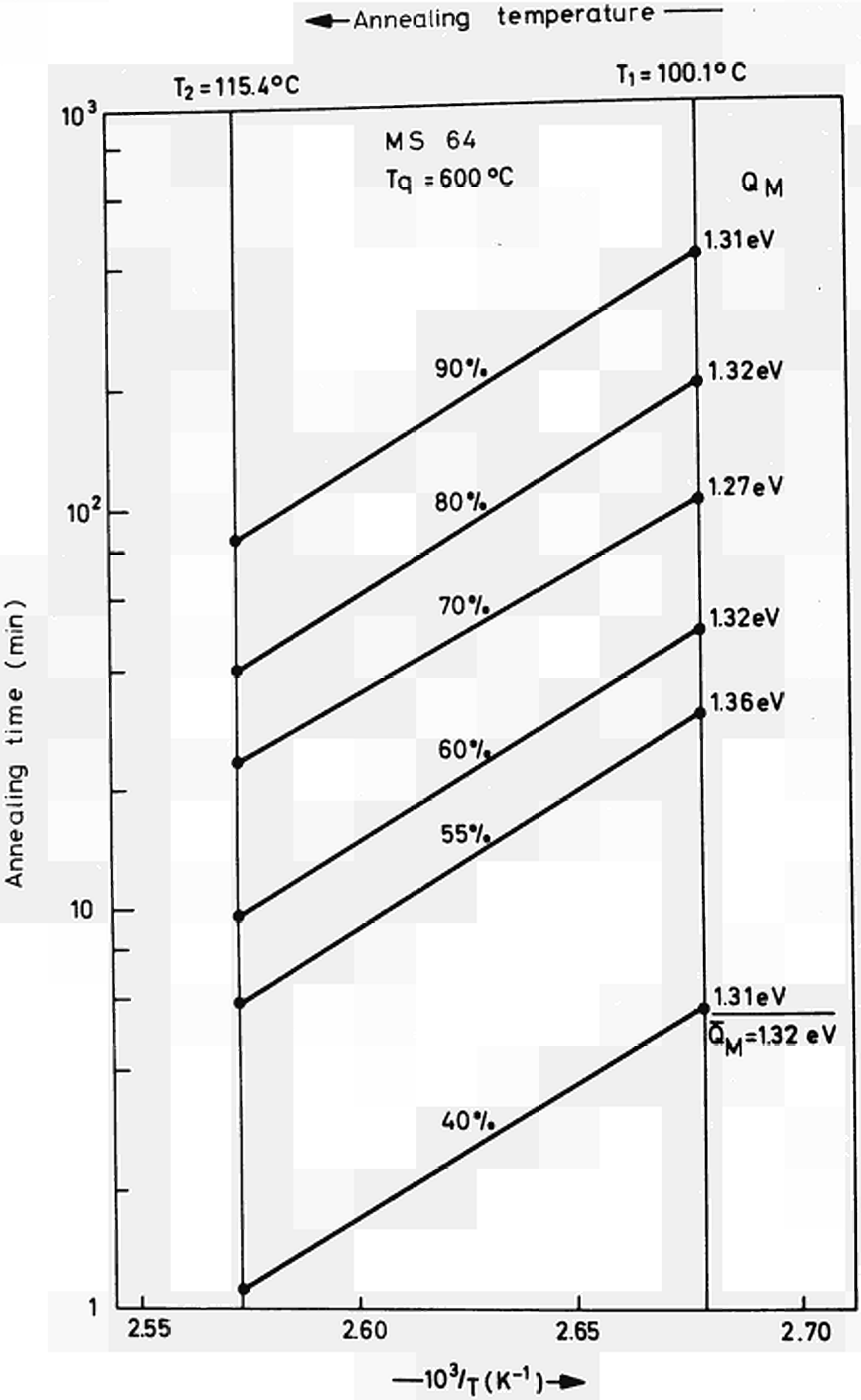


Fig. 26 : Determination of the activation energy of the isothermal annealings on Ms - 64 quenched from 600° C (Fig. 25)

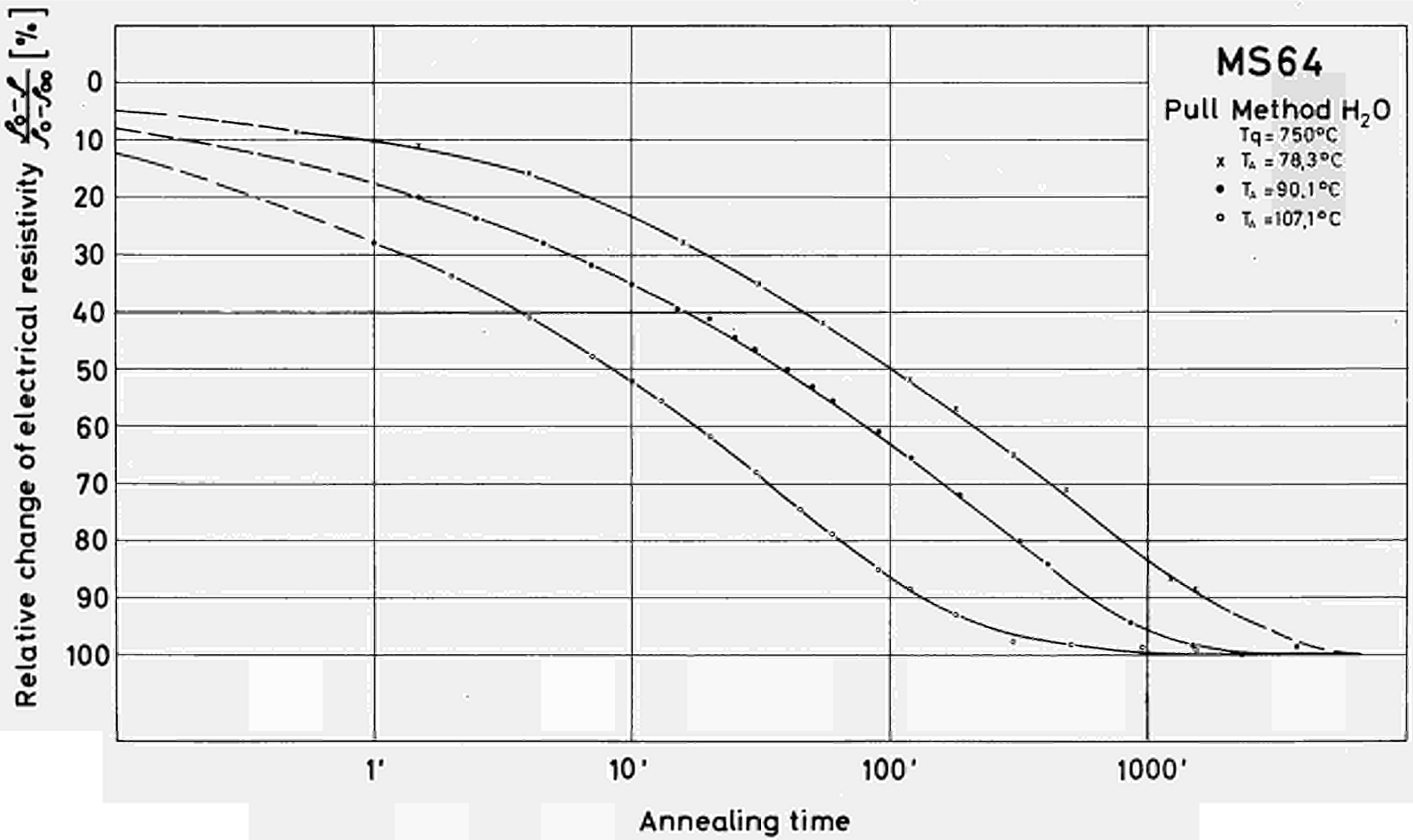


Fig. 27 : Isothermal annealing curves of Ms - 64 upon quenching from 750° C into water by the pull method. The curves are plotted in the normalized from (ρ_o - ρ)/ (ρ_o - ρ_∞).

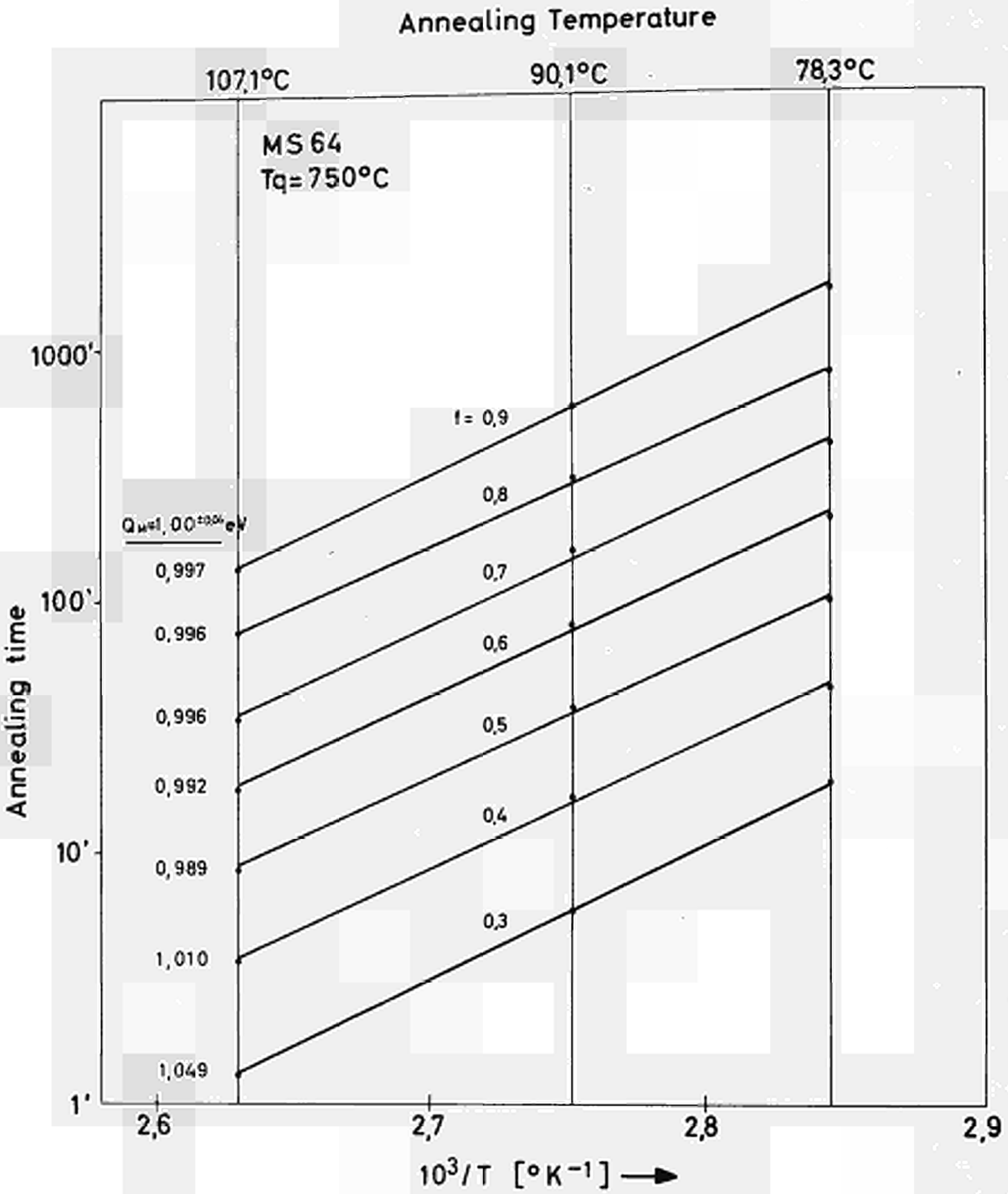


Fig. 28 : Determination of the activation energy of the isothermal annealings on Ms - 64 quenched from 750° C (Fig. 27).

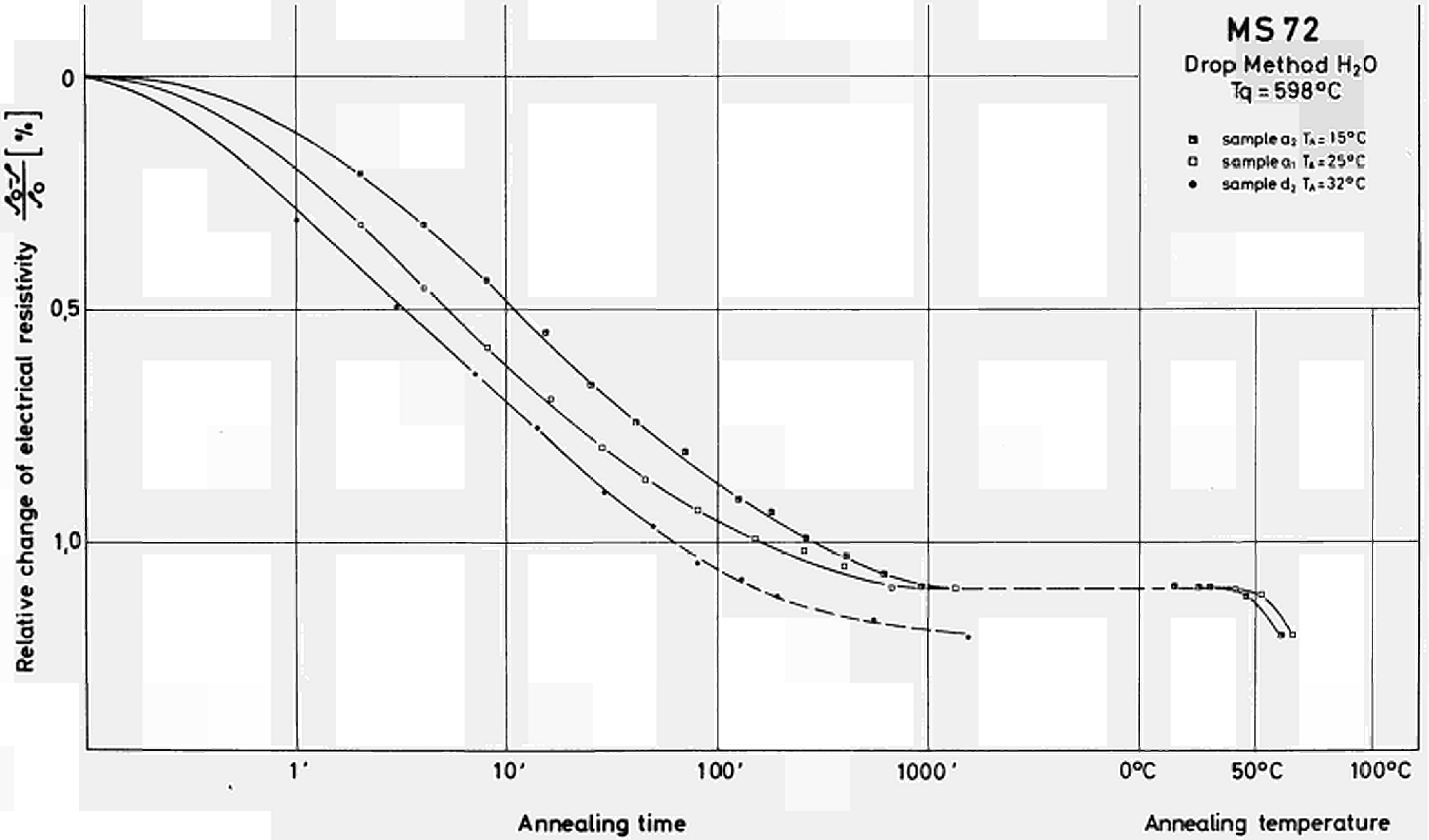


Fig. 29 : Isothermal annealing curves (stage A) of Ms - 72 upon quenching from 600° C into water by the drop method. The relatively resistivity change $(\rho_o - \rho) / \rho_o$ is plotted.

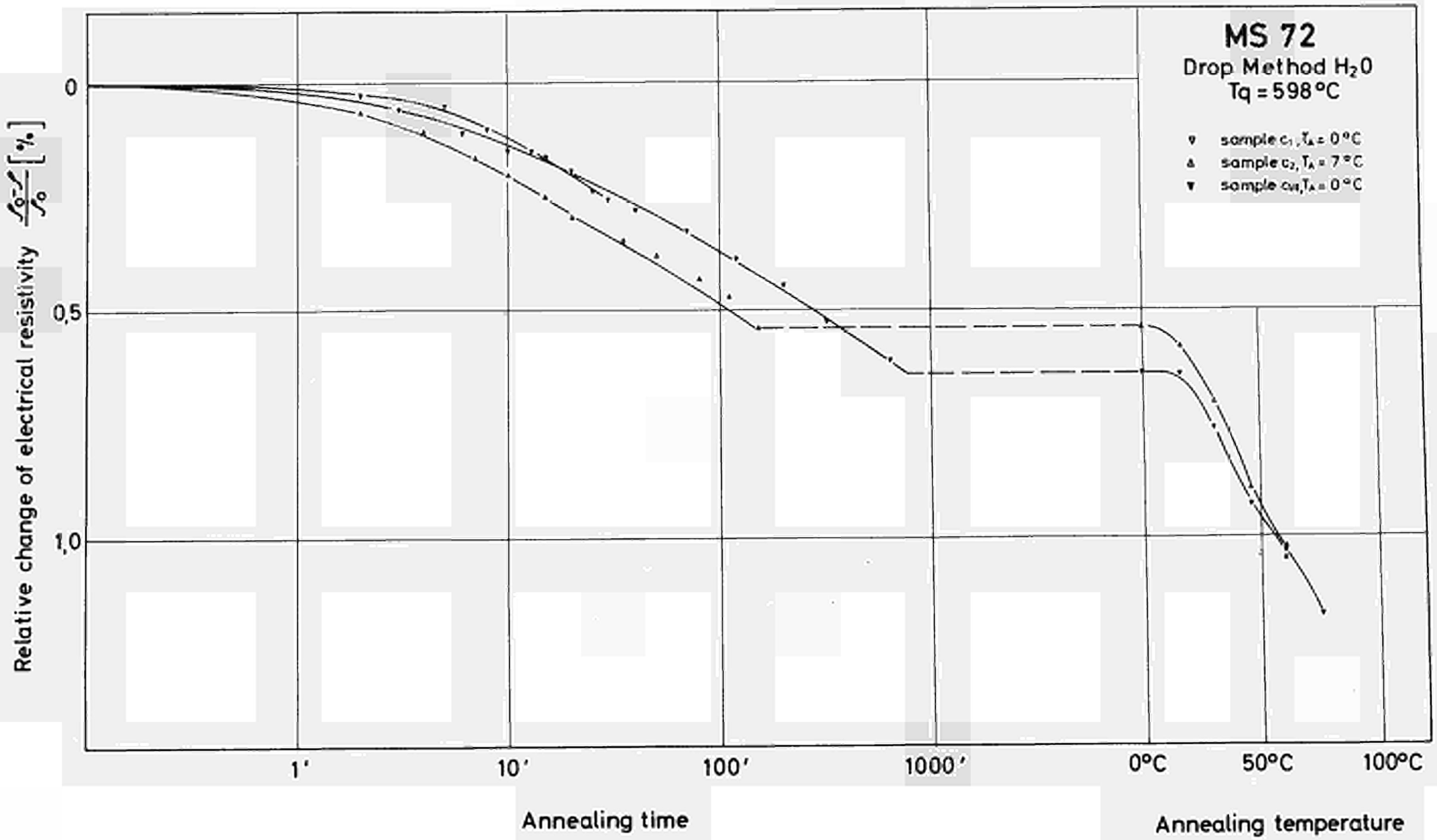


Fig. 30 : Another set of isothermal annealing curves (stage A) of Ms - 72 quenched from 600° C.

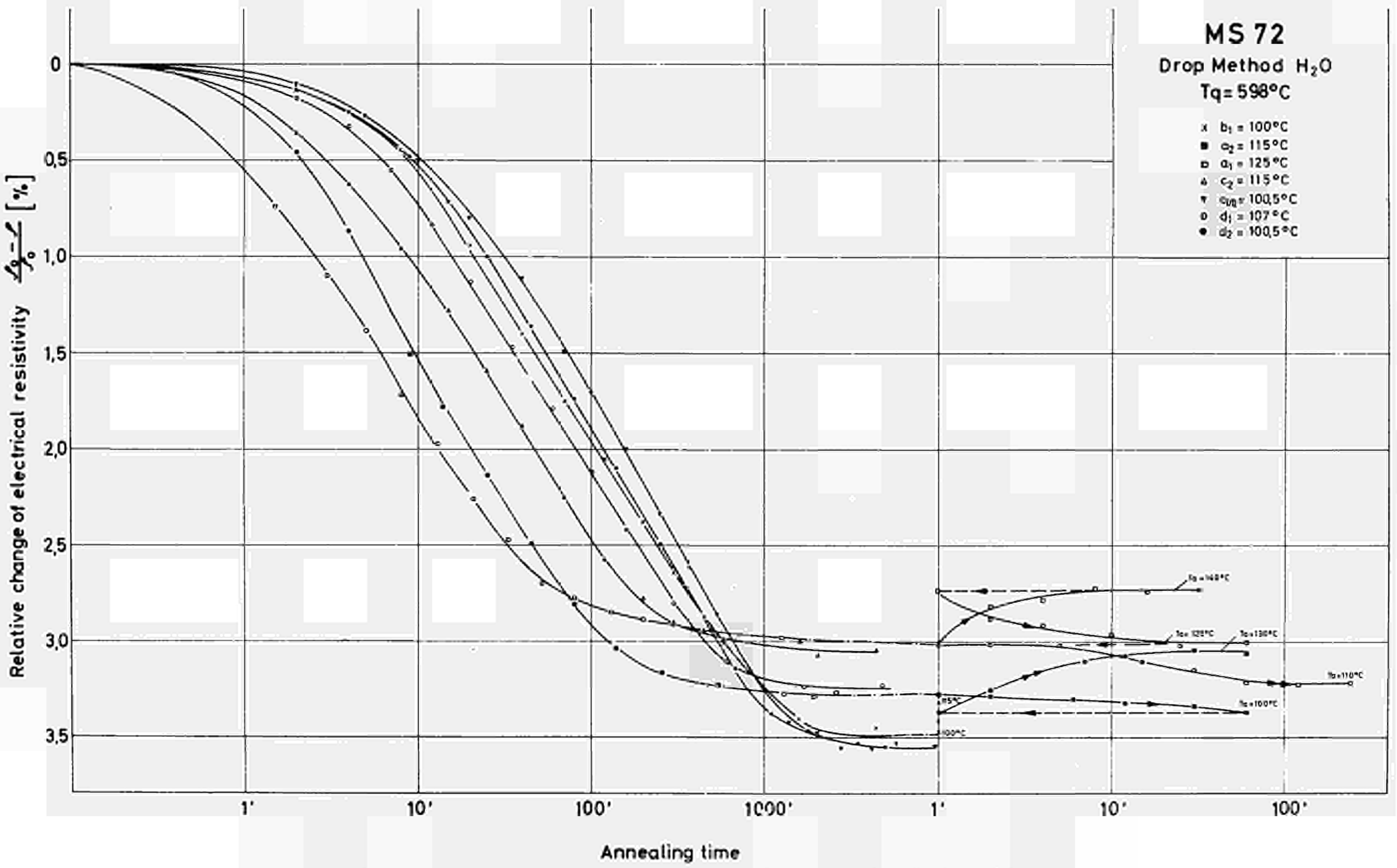


Fig. 31 : Isothermal annealing curves (stage B) of Ms - 72 upon quenching from 600° C into water by the drop method. It is plotted the relative resistivity change $(\rho_o - \rho) / \rho_o$.

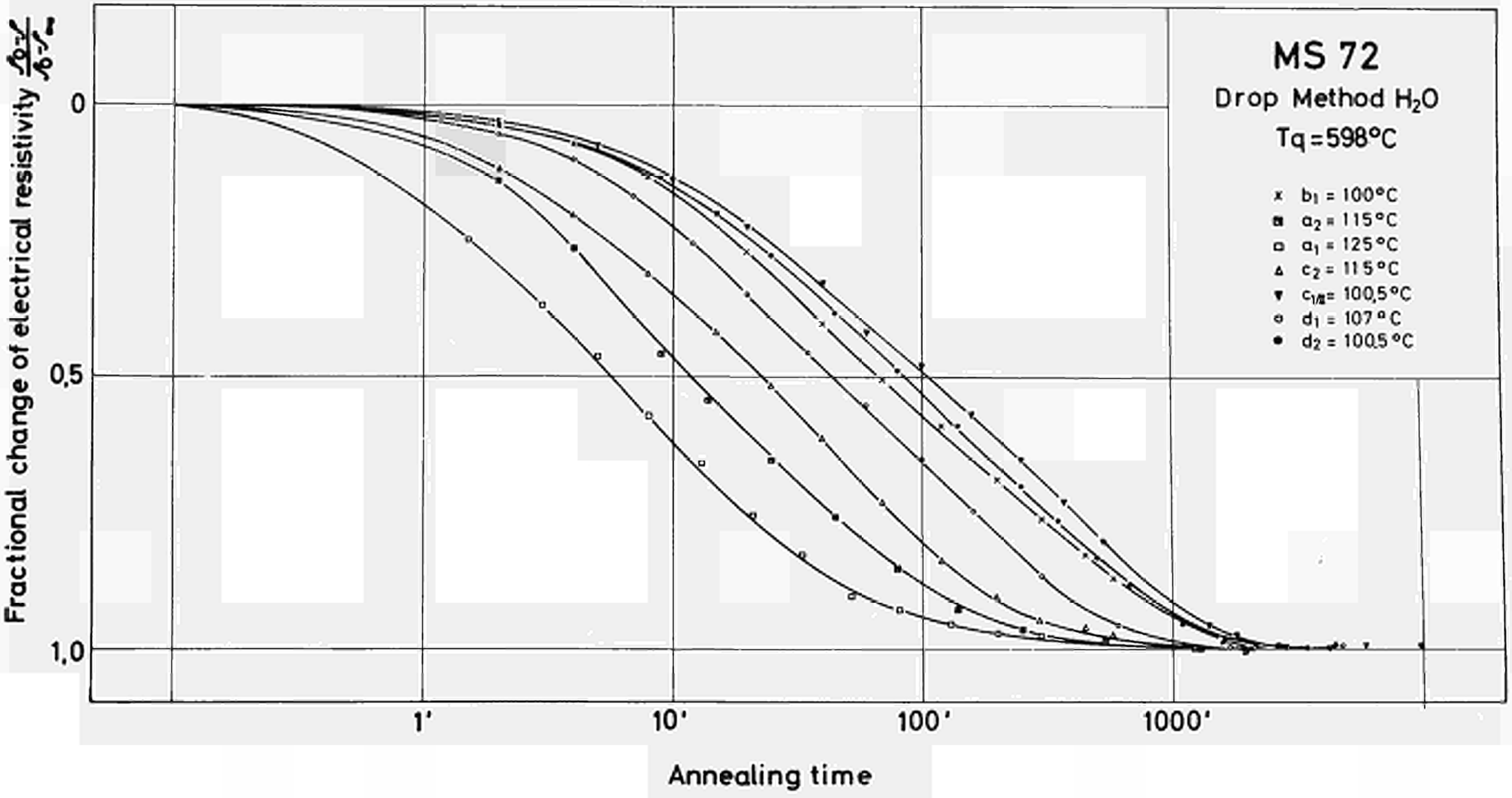


Fig. 32 : The isotherms of Fig. 31 are plotted in the normalized form (p_o - p)/(p_o - p_∞) for determination of the activation energy.

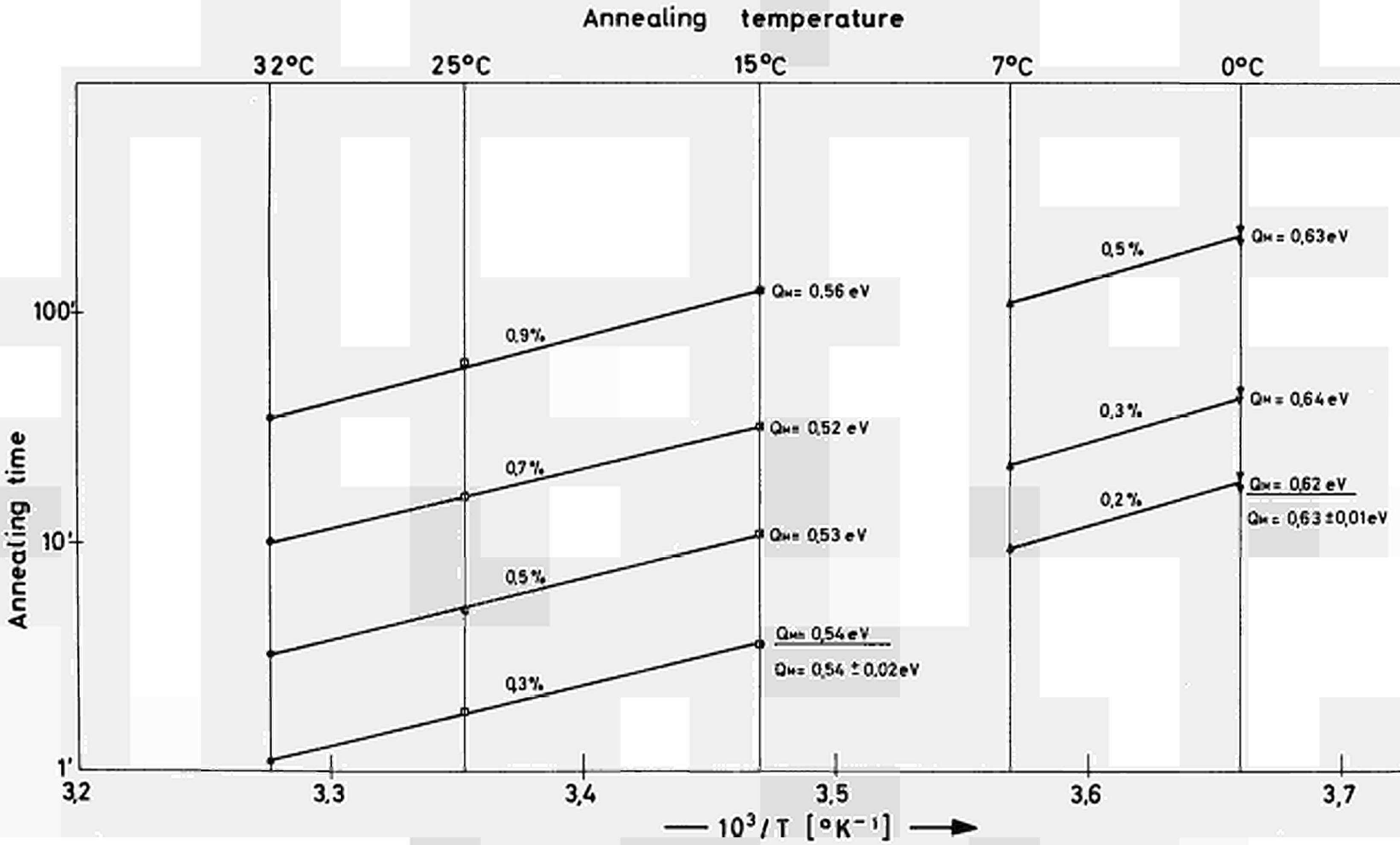


Fig. 33 : Determination of the activation energy of the isothermal annealing curves (stage A) of Ms - 72 quenched from 600° (Fig. 29/30) by the cross-cut method.

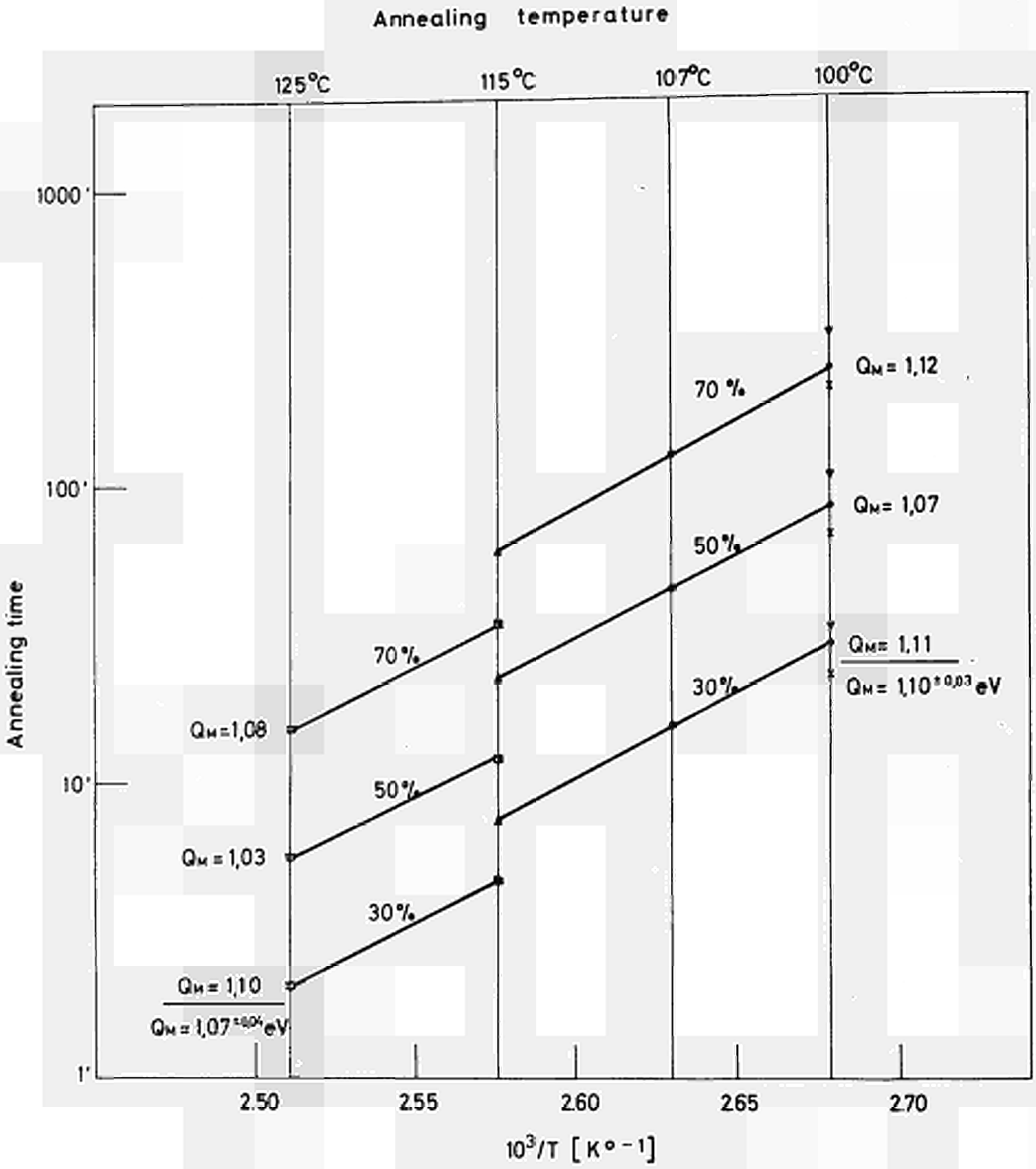


Fig. 34 : Determination of the activation energy of the isothermal annealing curves (stage B) of Ms - 72 quenched from 600° C (Fig. 32) by the cross-cut method.

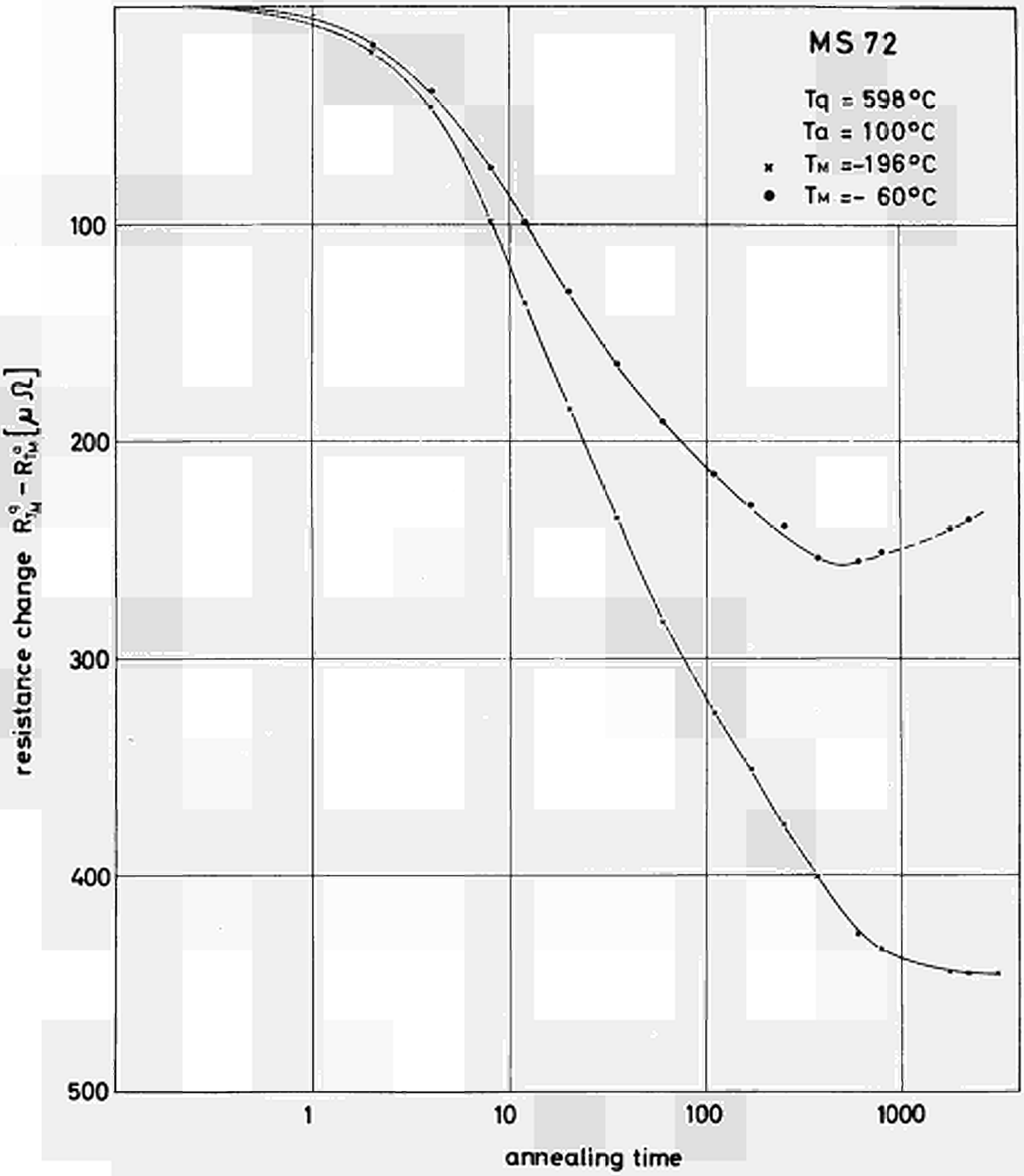


Fig. 35 : Isothermal annealing (stage B) of Ms - 72 quenched by the drop method from 600° C into water. The relative resistivity change has been measured at LN_2 - temperature and at - 60° C.

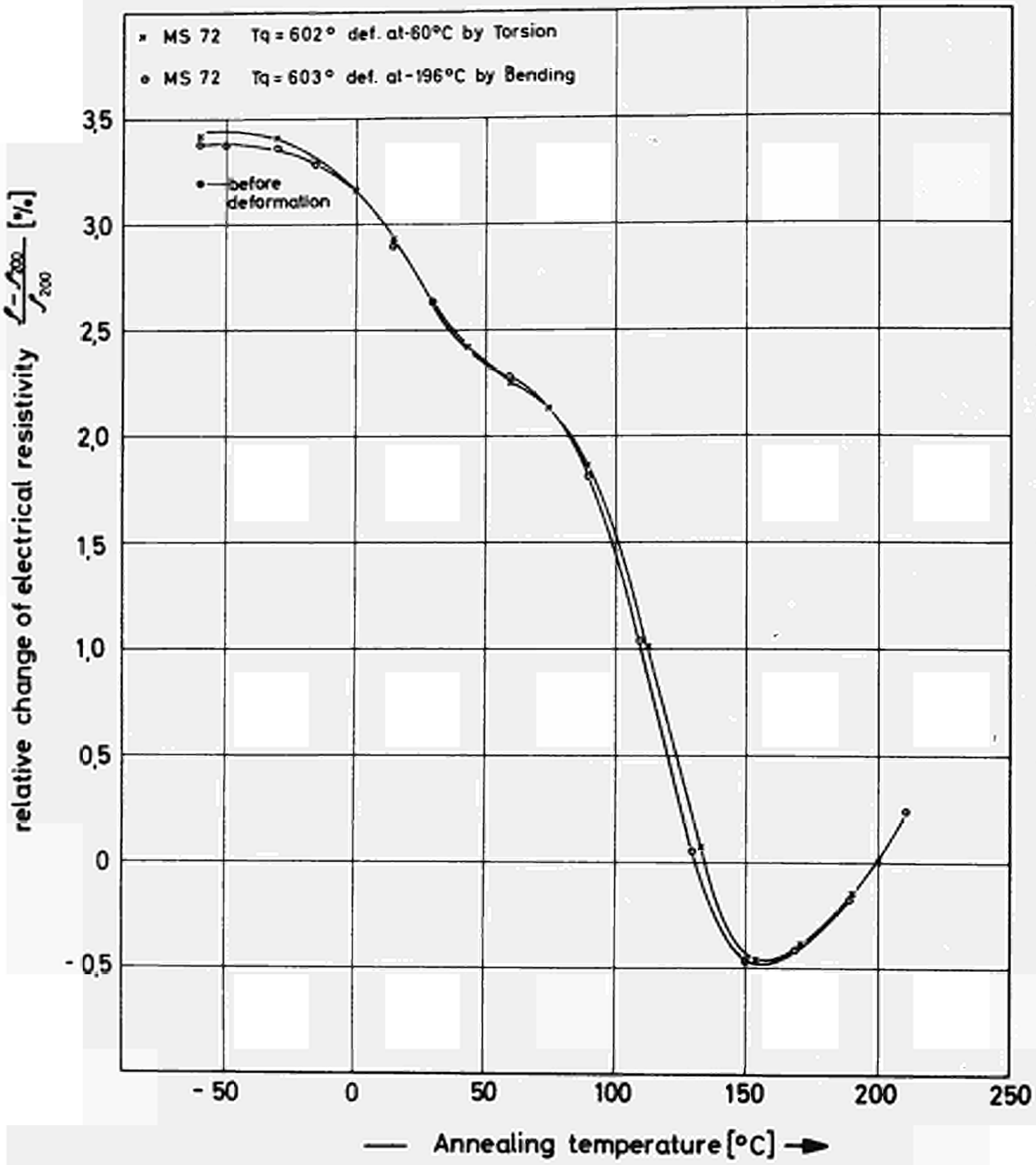


Fig. 36 : Isochronal annealing curves of two Ms - samples after quenching from 600° C and subsequent cold-deformation. One sample was deformed at - 60° C by torsion and the other one by bending in LN_2.

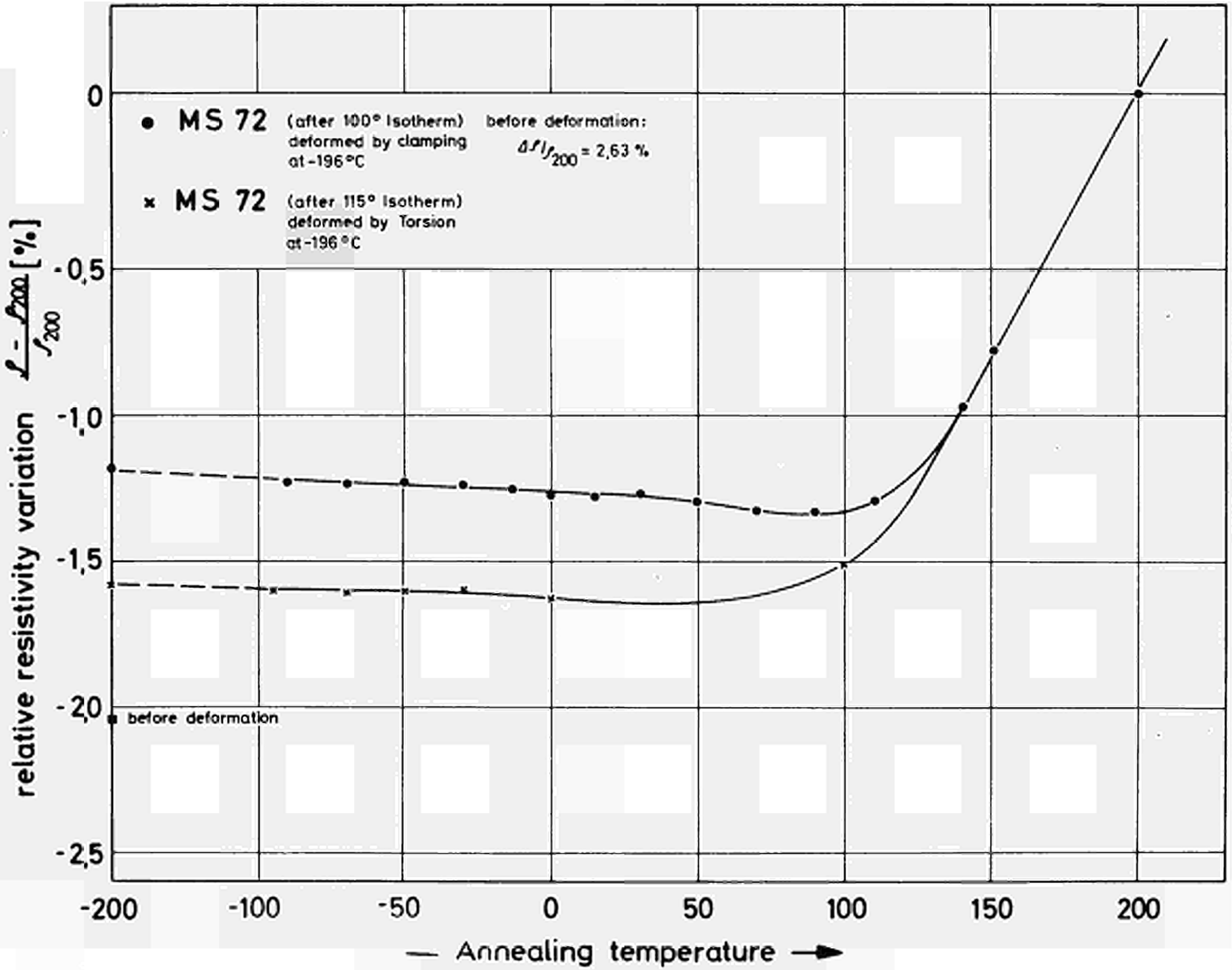


Fig. 37 : Isochronal annealing curves of two Ms - 72 samples cold-worked at LN$_2$ - temperature by torsion and clamping, respectively. The specimens had been previously annealed isothermally after quenching from 600° C.

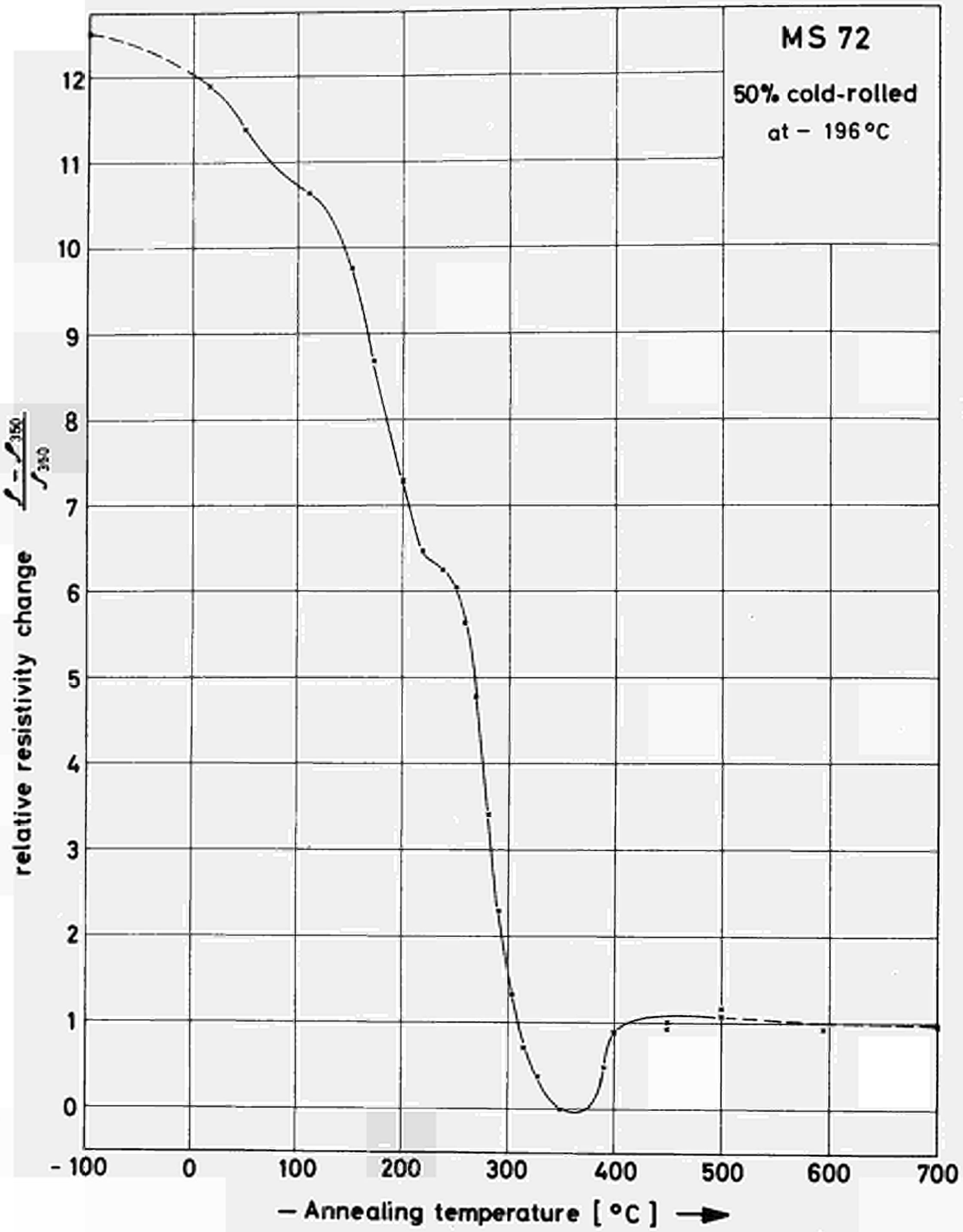


Fig. 38 : Isochronal annealing curve of a Ms - 72 sample cold-worked by 50 % reduction in cross-section by rolling at - 196° C.

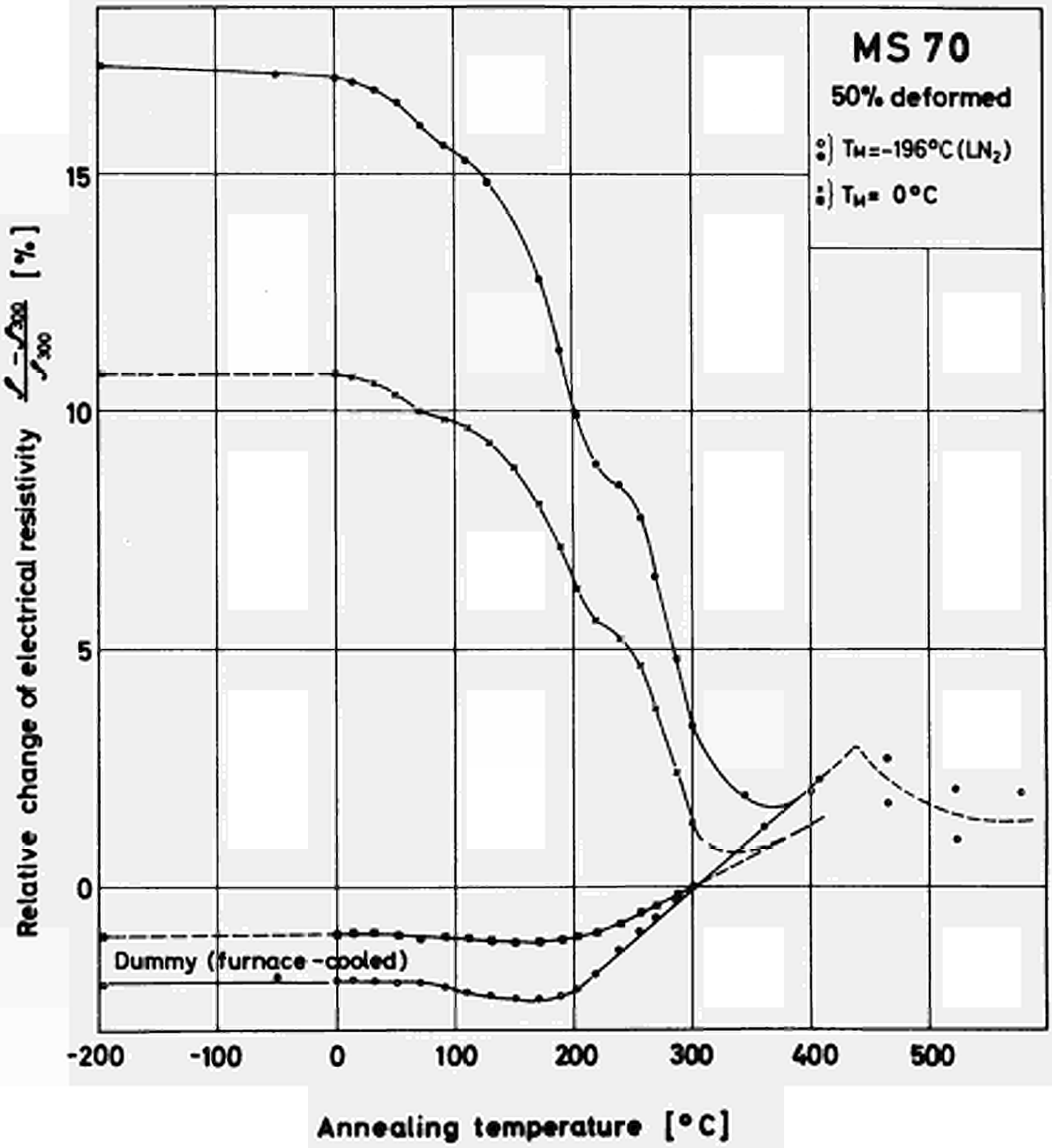


Fig. 39 : Isochronal annealing curves of two Ms - 70 samples. Both samples were recovered for 1^h at 560° C and furnace-cooled. Then one sample was deformed by 50 % at low temperature by rolling an annealed with the other one which served as dummy specimen. Measurements were made at - 196° and 0° C.

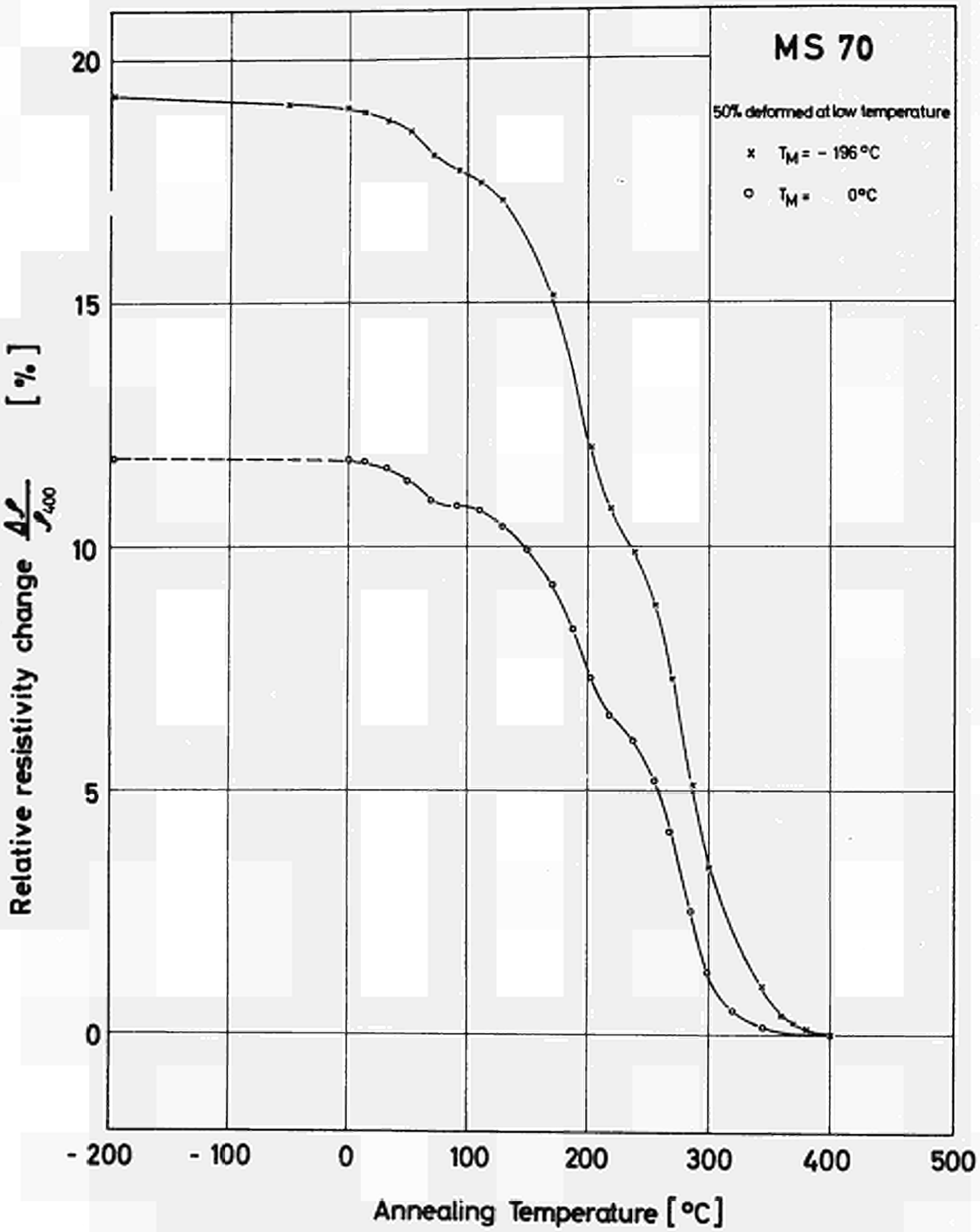


Fig. 40 : Isochronal annealing curve of the same experiment as in Fig. 39 measured at LN_2- temperature and 0° C. It is plotted the difference between the relative resistivity change of the deformed and the dummy specimen.

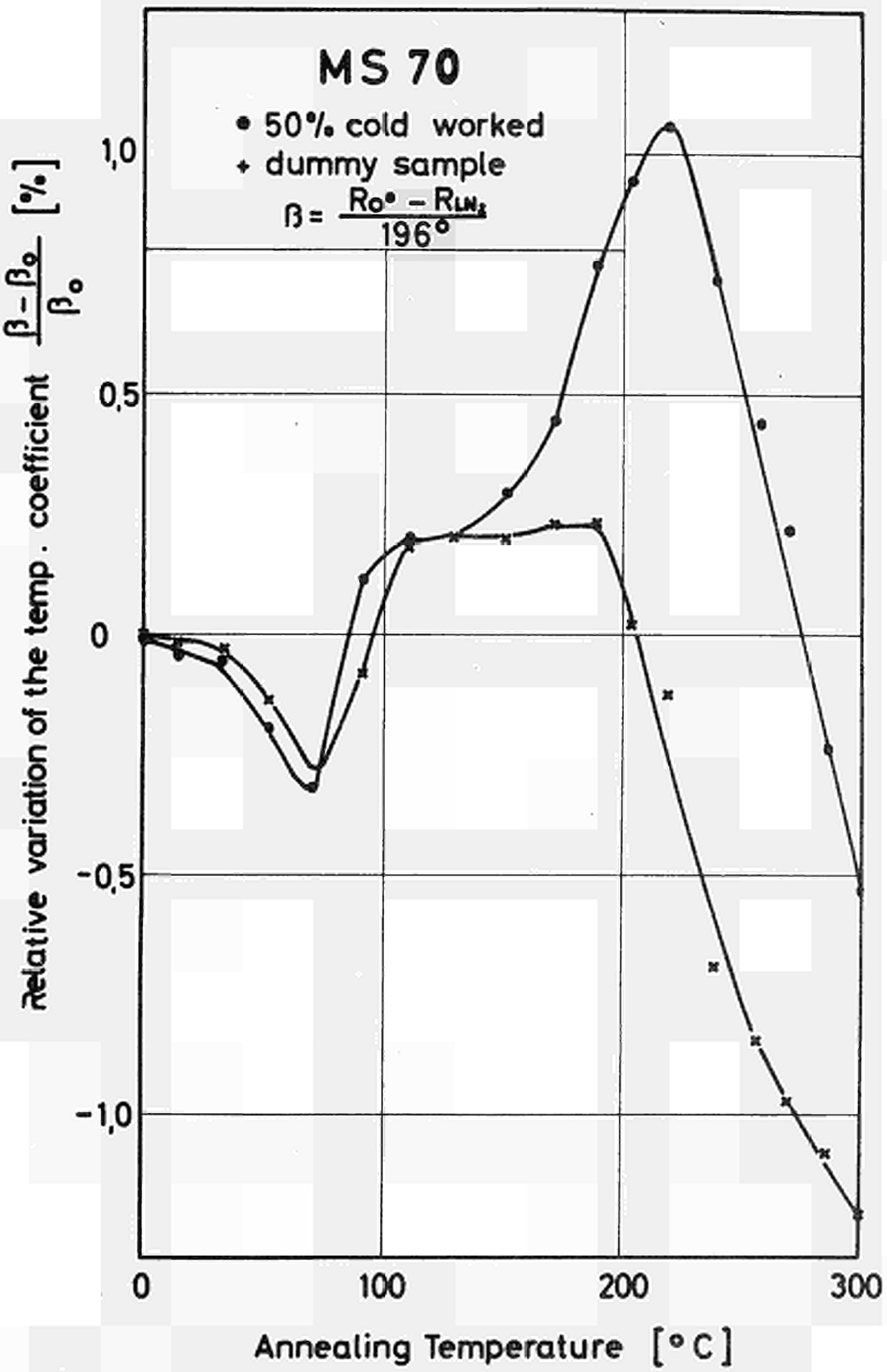


Fig. 41 : Relative variations of the temperature coefficient of the electrical resistivity during isochronal annealing of a 50 % cold-worked and a furnace-cooled Ms - 70 sample as calculated from the curves in Fig. 39.

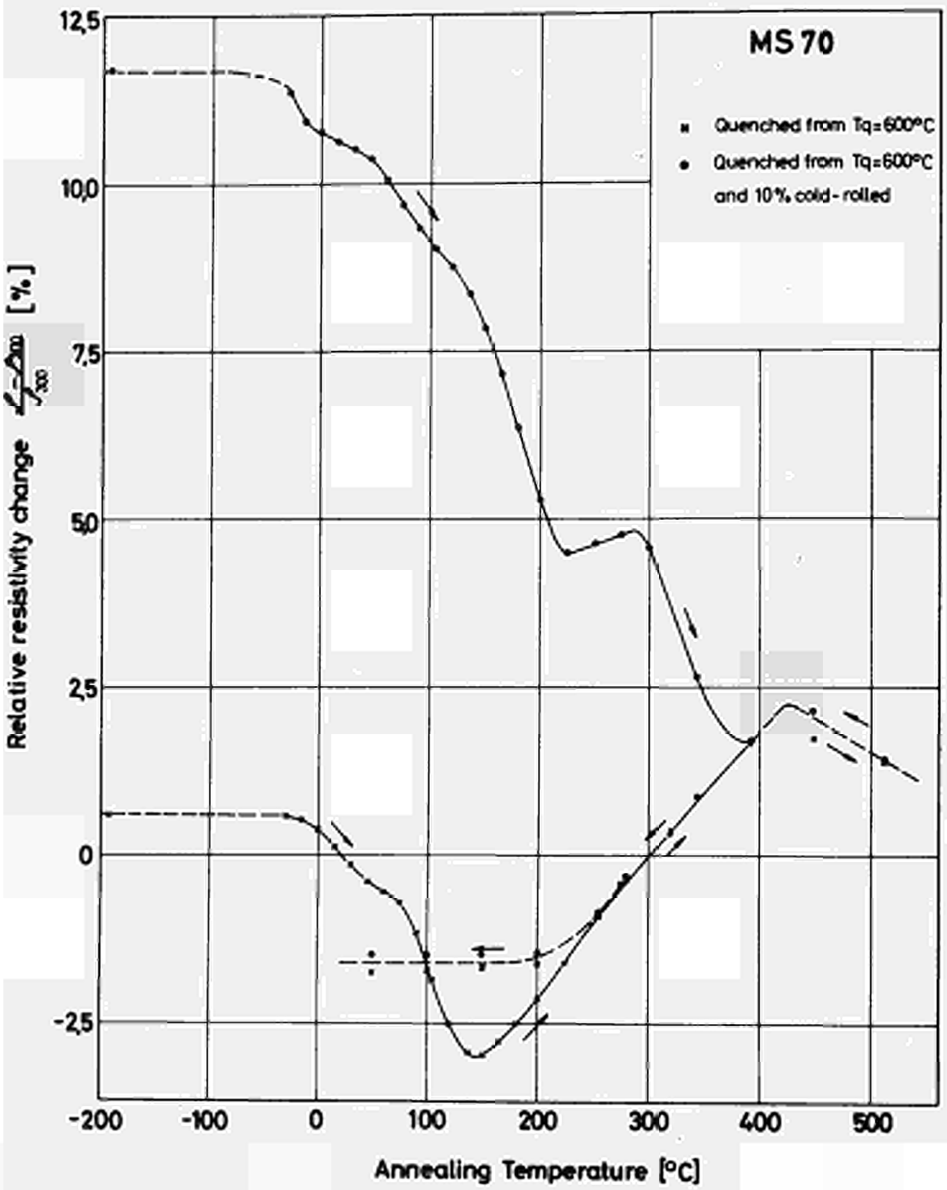


Fig. 42 : Isochronal annealing curves of two Ms - 70 samples. Both samples have been quenched from 600° C into water, thereafter one of them has been cold-rolled (10 % r.c.s.) at low temperature.

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>
> Alfred Nobel

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