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The Effects of Deformation on the Electrical Resistivity of Molybdenum Single Crystals*

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Single crystals of high-purity molybdenum were deformed at temperatures from 195 to 473°K, and the effect of deformation on the electrical resistivity was determined. To separate the resistivity components of point and line defects some crystals were annealed at 473°K. The rate of resistivity increase with strain was nearly linear and was strongly dependent upon the deformation temperature. Point defects are annealed out without any effect on the flow stress. At low temperatures the flow stress is a linear function of the square root of the resistivity increase attributable to dislocations.

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Electrical resistivity measurements have been used successfully to gain information on structural changes in metallic materials. During plastic deformation the electrical resistivity rises because of electron scattering from newly created lattice defects. Such measurements lend themselves, therefore, to corroborating results from direct observation of lattice defects and, to a certain extent, to correlating defect densities and distribution with mechanical properties.

Published information on research with single crystals of the body-centered-cubic metals of Group VI, particularly molybdenum, is still limited. Yet, molybdenum single crystals of relatively high purity can be readily prepared by electron-beam melting techniques. Furthermore, some valuable information on the defect structure of deformed crystals by direct observation is available. Lawley and Gaigher[1], for example, have examined dislocation configurations in deformed molybdenum crystals by means of transmission electron microscopy. Their results revealed that the dislocation density and distribution were strongly dependent upon the deformation temperature. These findings differed from those by Keh and Weissman[2], who found that the average dislocation density in polycrystalline iron deformed between 138 and 298°K depended only on the degree of strain and not on the deformation temperature. Martin[3] and Peiffer[4] showed that point defects in polycrystalline molybdenum can be eliminated by annealing at a relatively low temperature. In view of their work it became apparent that resistivity measurements of suitably annealed crystals could disclose changes in their dislocation structure and contribute to the understanding of the work hardening of molybdenum crystals.

EXPERIMENTAL PROCEDURE

Crystals were grown by electron-beam zone melting[5,6] of 0.062" diameter molybdenum rods (99.99%) supplied by General Electric Lamp and Wire Division, Dover, Ohio. The crystals were prepared by using five zone-refining passes at a speed of about 6 mm/min in a vacuum of about 5×10^{-6} torr. The resistivity ratio of the crystal, $\rho(4.2^{\circ}K)/\rho(273^{\circ}K)$, was generally near 10^{-3}.

These crystals were used as tensile specimens of uniform diameter in the "as-grown" condition. They were oriented for maximum shear on the $(011)[1\bar{1}1]$ slip system (Schmid factor > 0.49). The specimens were held in spherically seated Templin-type grips so as to minimize bending. Samples were deformed in a thermostat on an Instron machine at a strain rate of about 5×10^{-5} sec^{-1} at 195, 273, 373, and 473°K.

Resistance measurements were carried out with a Kelvin double bridge. Current and potential leads were spot welded to the specimens. The distance between the potential leads, about 3", was considered to be the gauge length for the strain measurements. Diameter and gauge length of the samples were measured optically with an error of less than 2%. Resistivity changes were determined from the resistance measurements at 4.2°K, assuming uniform strain and constancy of volume. In the course of a test, the crystal diameter, gauge length, and resistance at 4.2°K were determined first in the initial state and subsequently for various amounts of elongation.

RESULTS AND DISCUSSION

The resistivity increased with elongation in a manner strongly dependent upon the temperature of deformation, Fig. 1. In this figure, ρ_o is the initial resistivity at 4.2°K (Table I), ρ the resistivity at the same temperature after deformation, and ε the tensile strain. The resistivity increase appeared to be linear with strain at all deformation temperatures tested. At 195°K fracture without any noticeable necking prevented the study of strains above 6%. At deformation temperatures higher than 195°K tests were discontinued at the first sign of necking. Slopes of the resistivity-strain curves are

TABLE I

Initial Resistivity of Crystals

Crystal No.	$\frac{\rho_o}{\Omega cm}$
Mo 272	10.23×10^{-9}
Mo 273	8.19×10^{-9}
Mo 282	3.69×10^{-9}
Mo 285	2.25×10^{-9}
Mo 286	2.07×10^{-9}
Mo 301	6.20×10^{-9}
Mo 303	4.50×10^{-9}

given in Column (1) of Table II.

TABLE II

Effect of Deformation Temperature on the Rate of Resistivity Increase

Deformation Temperature $^{\circ}K$	(1) As Deformed $\delta\rho/\delta\varepsilon$ Ωcm/ % Strain	(2) Annealed at 473°K $\delta\rho/\delta\varepsilon$ Ωcm/ % Strain	(3) Resistivity per Dislocation Ωcm^3
195	0.102×10^{-8}	0.065×10^{-8}	5.9×10^{-19}
273	0.063×10^{-8}	0.042×10^{-8}	5.7×10^{-19}
373	0.024×10^{-8}		
473	0.013×10^{-8}		

These results are comparable to those by Cuddy[7] who obtained a value of $\frac{\delta\rho}{\delta\varepsilon} = 0.08 \times 10^{-8}$ Ωcm/ % strain with iron of average grain size of 750 microns at a deformation temperature of 298°K. Working with single crystals of tungsten deformed at 273°K, Shukovsky et al[8] recently found values about one order of magnitude greater than those mentioned above.

The change in resistivity is attributed to both point and line defects introduced by the deformation. In order to separate resistivity effects of dislocations from those of point defects, deformed crystals were subjected to a recovery treatment at a relatively low annealing temperature. Fig. 2 illustrates the changes in resistivity produced by a 24-hour anneal at 473°K. Annealing times longer than these at 473°K produced no further change in the resistivity. Martin[3] reported that point defects introduced in polycrystalline molybdenum by deformation anneal out with an activation energy of 1.26 ev. Later tests by Peiffer[4] indicated that no further decrease in the resistivity was produced by annealing at 473°K after recovery at 318°K appeared complete. While Peiffer was able to recover about 26% of the resistivity introduced by elongation at room temperature by means of prolonged annealing at 318°K, present results revealed relative recoveries after room-temperature deformation of varying magnitudes. These increased with strain and reached values up to 60%.

The flow stress remained unaffected by the recovery of the resistivity, and no yield points were observed during deformation subsequent to the anneals, Fig. 2. Similar results were reported by Martin[3]. On the other hand, the recovery of resistivity at about 325°K after irradiation of molybdenum was accompanied by hardening[3,10]. The loss of point defects without any rearrangement of the dislocation structure is undoubtedly responsible for the drop in resistivity during low-temperature annealing treatments. The rate of increase of resistivity with strain was always independent of the annealing treatment preceding the strain increment, Fig. 2. This indicated that the resistivity increased in a manner unrelated to the concentration of point defects.

When the crystals were deformed in steps and subjected to low-temperature annealing treatments after each increment, the residual resistivities at 4.2°K, $\rho_a - \rho_o$, shown in Fig. 3, were obtained. The point-defect resistivity corresponds to the difference between the "not-annealed" curves in Fig 1 and the "annealed" curves in Fig. 3 and follows the equation, Fig. 4,

$$\Delta\rho_{p.d.} = \Delta\rho_o \, \varepsilon^m ,$$

with

$$m = \begin{cases} 1.0 \text{ for a deformation temperature of } 195^{o}\text{K} \\ 1.3 \text{ for a deformation temperature of } 273^{o}\text{K}. \end{cases}$$

A relationship of this kind was predicted by van Bueren[11] with m = 1.25 for the case of single glide and m = 2 for multiple glide. Peiffer[4], however, found a linear relation, i.e., m = 1, with polycrystalline molybdenum deformed at room temperature. Recently, Shukovsky et al[8], who used tungsten single crystals strained at 273°K, also found the above exponential form with m = 0.9 up to tensile strains of 2% and m = 1.9 for higher strains up to 8%. It appears that present understanding of the generation of point defects by deformation of body-centered cubic crystals is insufficient for a meaningful quantitative interpretation of the results. The observed change in the exponent m may be indicative of an increased contribution of screw dislocations to the strain at 273°K.

The resistivities observed after low-temperature annealing, Fig. 3, are representative of the dislocation densities of the deformed crystals. Estimates of the specific resistivity of dislocations in molybdenum, Column (3) of Table II were obtained from the initial slopes of the curves, $\frac{\delta\rho}{\delta\varepsilon}$, listed in Column (2), and the dislocation densities determined by Lawley and Gaigher[1]. The value of ~5.8 x 10^{-19} Ωcm^3 is consistent with the value for iron of ~10 x 10^{-19} Ωcm^3 suggested by Cuddy[7]. It is also comparable to the value of 11 x 10^{-19} Ωcm^3 computed for tungsten by Basinski et al[12] and to their estimate of ~19 x 10^{-19} Ωcm^3, which was based on resistivity data for polycrystalline tungsten by Schultz[13].

Shukovsky et al[8], however, reported recently the substantially greater value of 6.7×10^{-17} Ωcm^3 for deformed tungsten crystals. A comparison of resistivity increases resulting from deformation[14] revealed significantly higher values for tungsten than for molybdenum. In Fig. 3 the resistivity at a deformation temperature of 273°K has a slope that decreases with strain. Since Lawley and Gaigher found a linear rise of the dislocation density with strain in molybdenum crystals at 300°K, it is likely that the resistivity is affected by both dislocation distribution and density. Indeed, the above authors have shown that strain at relatively low temperatures generates a fairly uniform distribution of individual dislocations which with rising deformation temperatures gives way to a cellular, clustered arrangement. The latter may well result in a relaxation of strains accompanied by a lower resistivity per dislocation.

The work by Keh[15] with iron crystals suggests a study of the dislocation resistivity as a function of stress. When the square root of the resistivity increase of molybdenum crystals, that were subjected to low-temperature annealing, is plotted as a function of the applied shear stress, the resulting relationship for deformation at

$195^{o}K$ is linear, except at very low stresses, Fig. 5. Keh found also from electron microscopy of iron crystals that the applied shear stress, τ, was related to the average dislocation density, N, by

$$\tau = \tau_o + \alpha G b \sqrt{N},$$

where $\alpha = 0.31$, G = shear modulus, and b = the magnitude of the Burgers vector. Using the present resistivity data for molybdenum with $b = |\frac{a}{2}\langle 111\rangle|$ and the specific dislocation resistivity determined here, i.e., $\frac{d\rho}{dN} = 5.8 \times 10^{-19}\ \Omega cm^3$, the non-dimensional constant α is 0.4. Lawley and Gaigher[1] find a similar dependence of stress on dislocation density in molybdenum with α varying from 0.44 to 1.27. The deviation from the simple square-root relation observed at low stresses suggests that the net stress, $\bar{\tau}$, acting at points of activation of the dislocations, varies significantly in the low-strain region but remains nearly constant at higher strains. For deformation at $273^{o}K$ the results in Fig. 5 are somewhat less conclusive possibly because of the effect of dislocation distribution on the resistivity mentioned earlier or as a result of undetected necking at higher strains. Fig. 6 is an attempt to derive from the resistivity data the net stress $\bar{\tau}$, and the internal stress τ_g, where $\tau = \tau_g + \bar{\tau}$. This plot is highly speculative because of the assumptions involved in computing τ_g.

CONCLUSIONS

1. The point-defect resistivity as a function of strain is given by

$$\Delta\rho_{p.d.} = \Delta\rho_o \varepsilon^m, \qquad m = \begin{cases} 1.0 \text{ at } 195^\circ K \\ 1.3 \text{ at } 273^\circ K \end{cases}.$$

The annealing of these point defects does not affect the flow stress.

2. The specific resistivity of dislocations in molybdenum crystals based on the dislocation density measurements by Lawley and Gaigher[1] is

$$\sim 5.8 \times 10^{-19} \ \Omega cm^3.$$

This value tends to decrease with strain at higher deformation temperatures.

3. The applied stress at low temperatures and sufficiently high strains is linear with the square root of the dislocation density, as was observed by electron microscopy in iron crystals[15], i.e.,

$$\tau = \tau_o + \alpha Gb \sqrt{N},$$

with $\alpha \doteqdot 0.4$.

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Captions to Figures

1. Resistivity increase, measured at 4.2°K, as a function of tensile strain for molybdenum single crystals at various temperatures of deformation.
2. Comparison of resistivity increase, measured at 4.2°K, with flow stress for a molybdenum crystal deformed at 195°K and subjected to annealing treatments for 24 hours at 473°K.
3. Resistivity increase, measured at 4.2°K, as a function of tensile strain for molybdenum single crystals at two temperatures of deformation. The crystals were subjected to annealing treatments for 24 hours at 473°K after each strain increment.
4. Resistivity increase due to point defects, measured at 4.2°K, as a function of tensile strain at two temperatures of deformation.
5. Relationship between resistivity increase, measured at 4.2°K, after annealing treatments for 24 hours at 473°K and flow stress at two temperatures of deformation.
6. Internal stress, τ_g, and net stress, $\bar{\tau}$, estimated from resistivity data for deformation of a molybdenum crystal at 195°K.

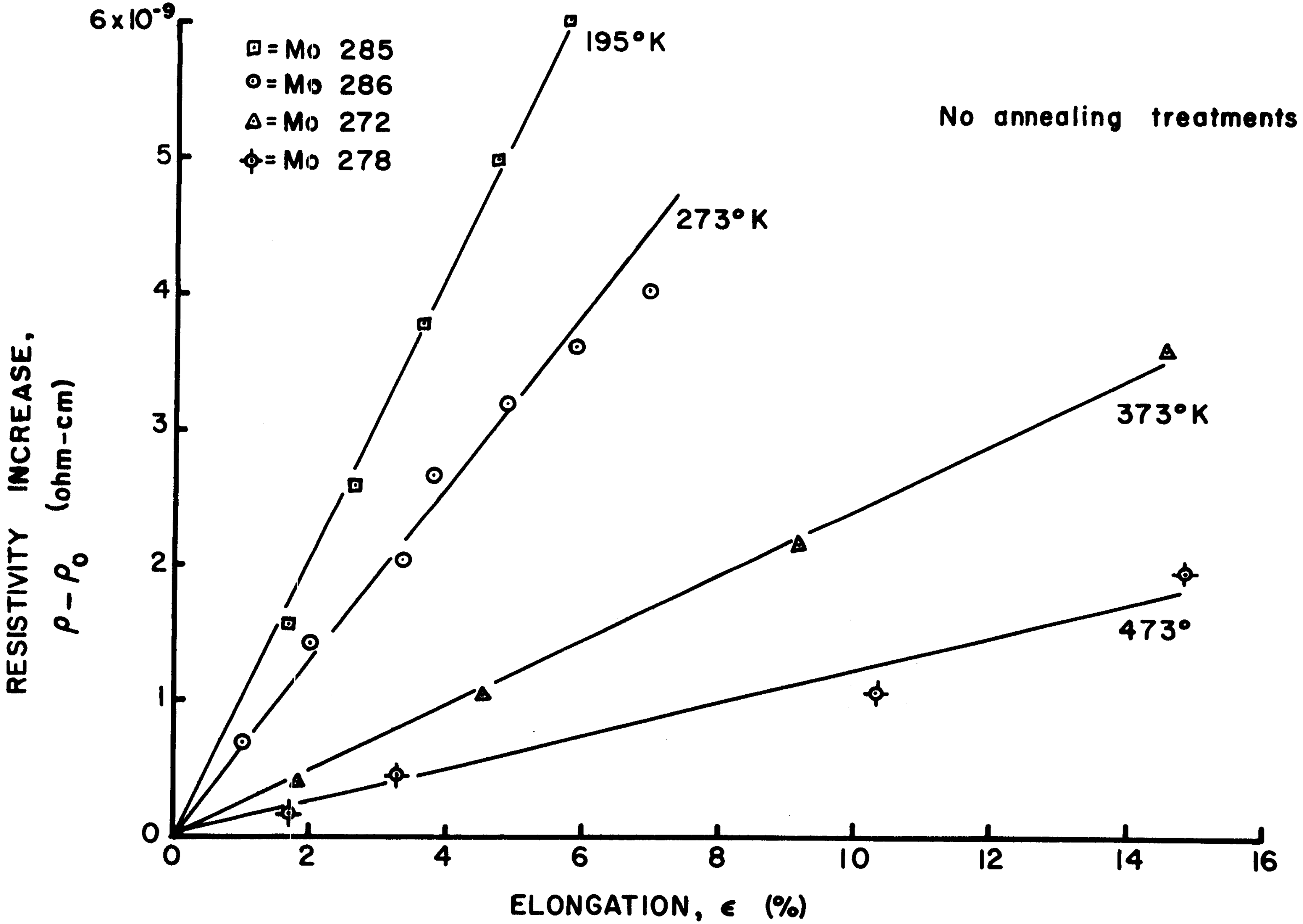

6x10^-9
5
4
3
2
1
0
□ = Mo 285
⊙ = Mo 286
△ = Mo 272
⌖ = Mo 278
195°K
273°K
373°K
473°
No annealing treatments
RESISTIVITY INCREASE,
ρ − ρ0 (ohm-cm)
0
2
4
6
8
10
12
14
16
ELONGATION, ε (%)

FIG. 1

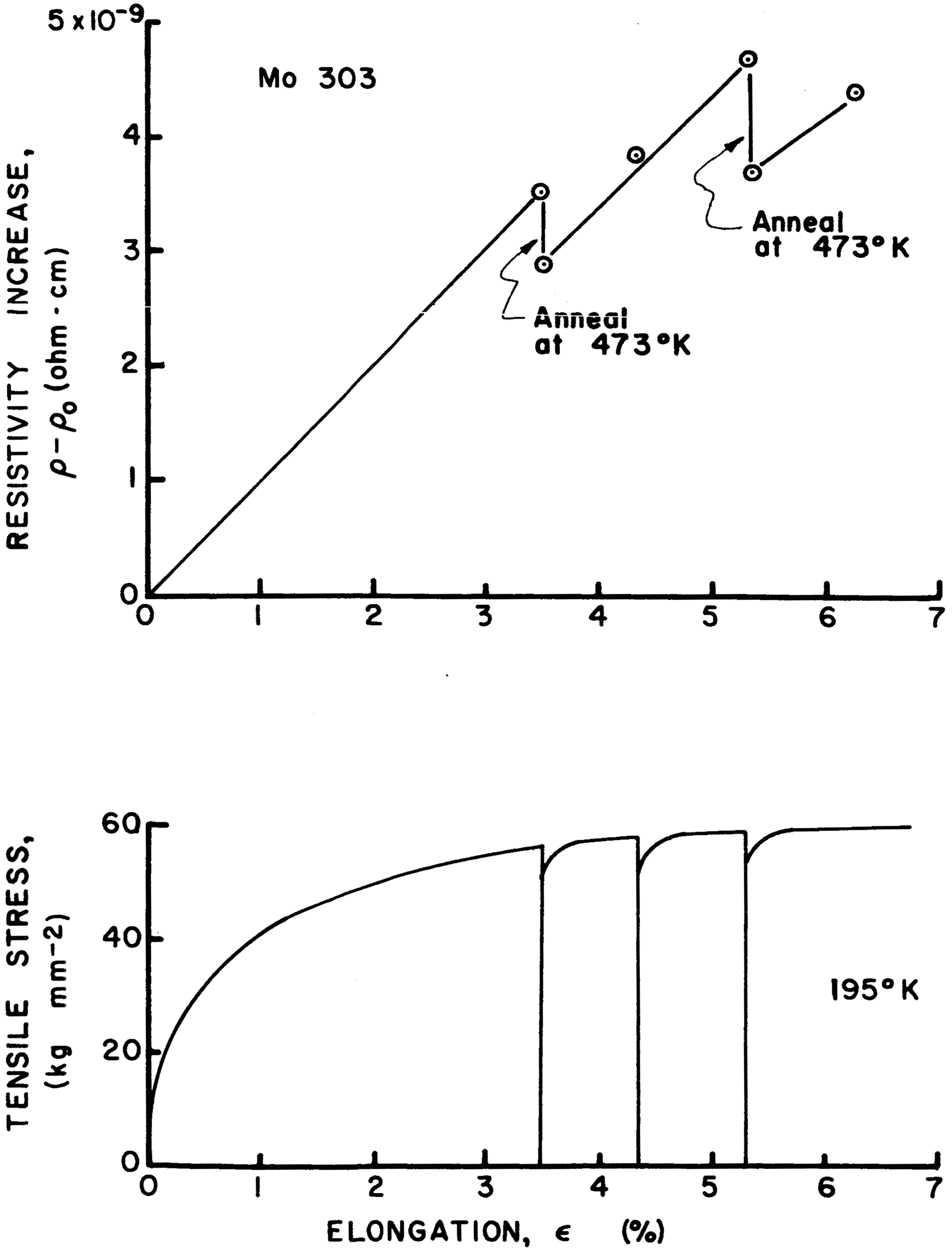

Mo 303
RESISTIVITY INCREASE, $\rho-\rho_0$ (ohm · cm)
5×10^{-9}
4
3
2
1
0
Anneal at 473°K
Anneal at 473°K
0
1
2
3
4
5
6
7
TENSILE STRESS, (kg mm^{-2})
60
40
20
0
195°K
0
1
2
3
4
5
6
7
ELONGATION, ϵ (%)

FIG 2

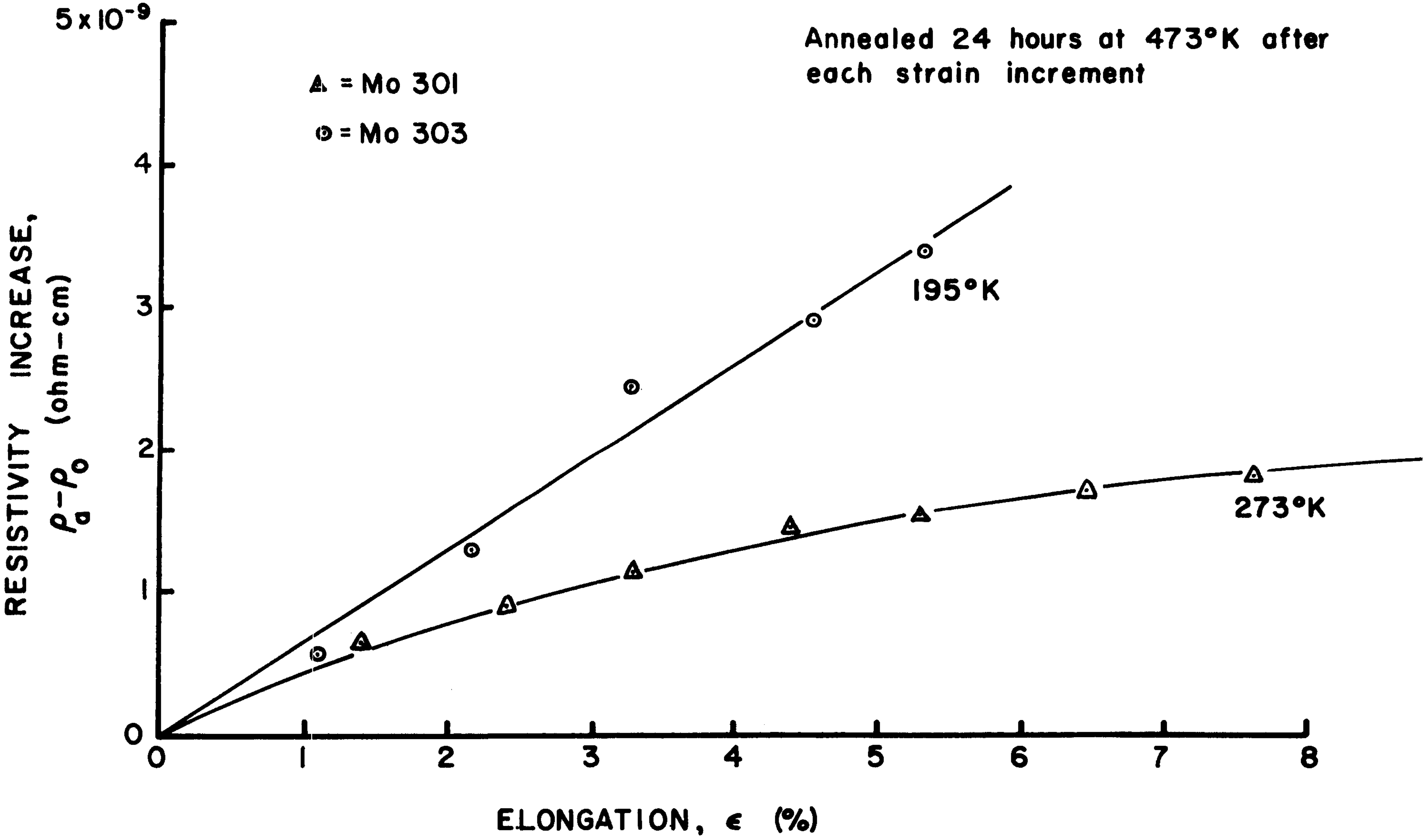

5 x 10⁻⁹
4
3
2
1
0
RESISTIVITY INCREASE,
ρa−ρo (ohm-cm)
0
1
2
3
4
5
6
7
8
ELONGATION, ϵ (%)
△ = Mo 301
⊙ = Mo 303
Annealed 24 hours at 473°K after each strain increment
195°K
273°K

FIG 3

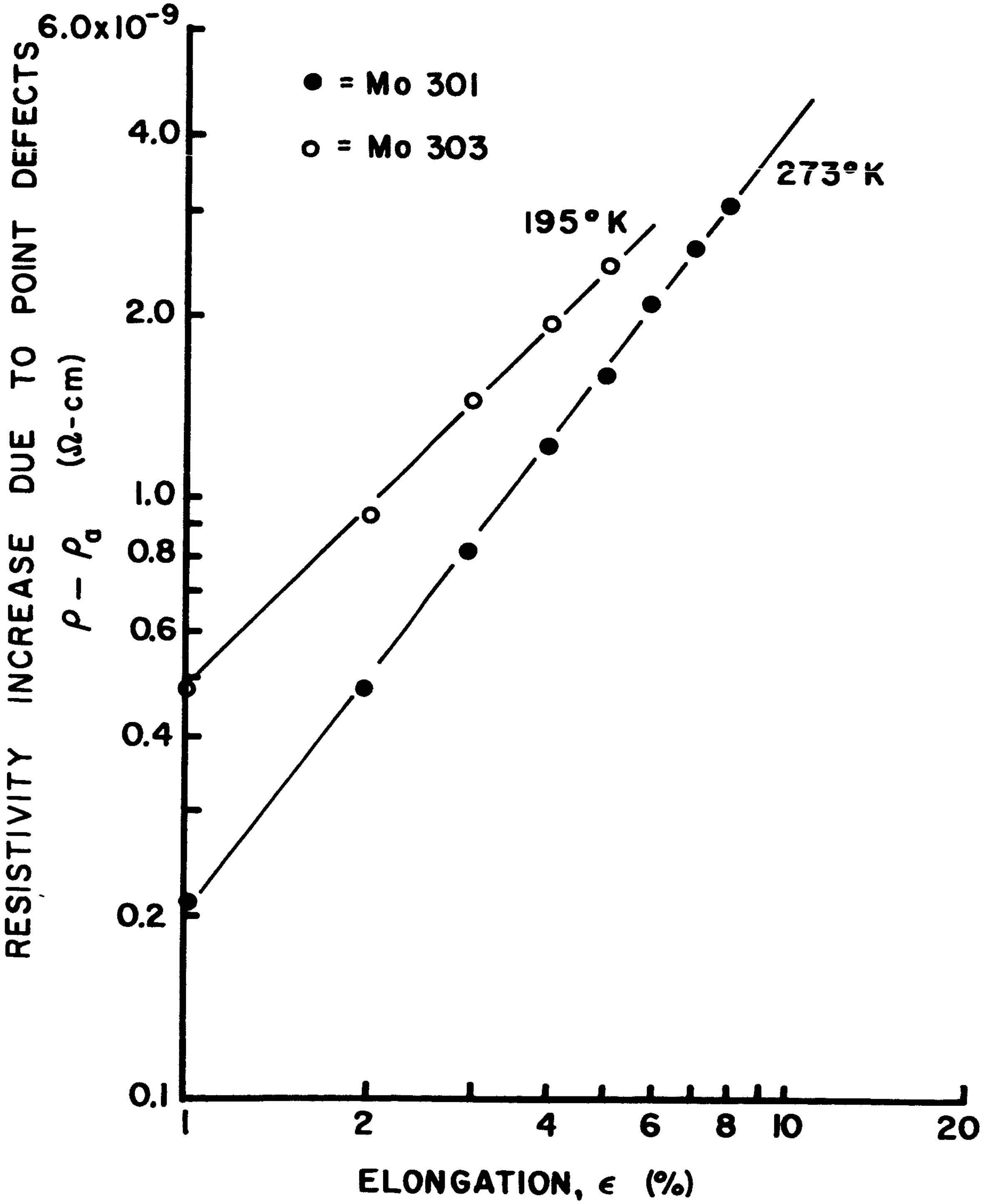

● = Mo 301
○ = Mo 303
195° K
273° K
RESISTIVITY INCREASE DUE TO POINT DEFECTS
$\rho - \rho_a$ (Ω-cm)
6.0x10^{-9}
4.0
2.0
1.0
0.8
0.6
0.4
0.2
0.1
1
2
4
6
8
10
20
ELONGATION, ε (%)

Fig 4

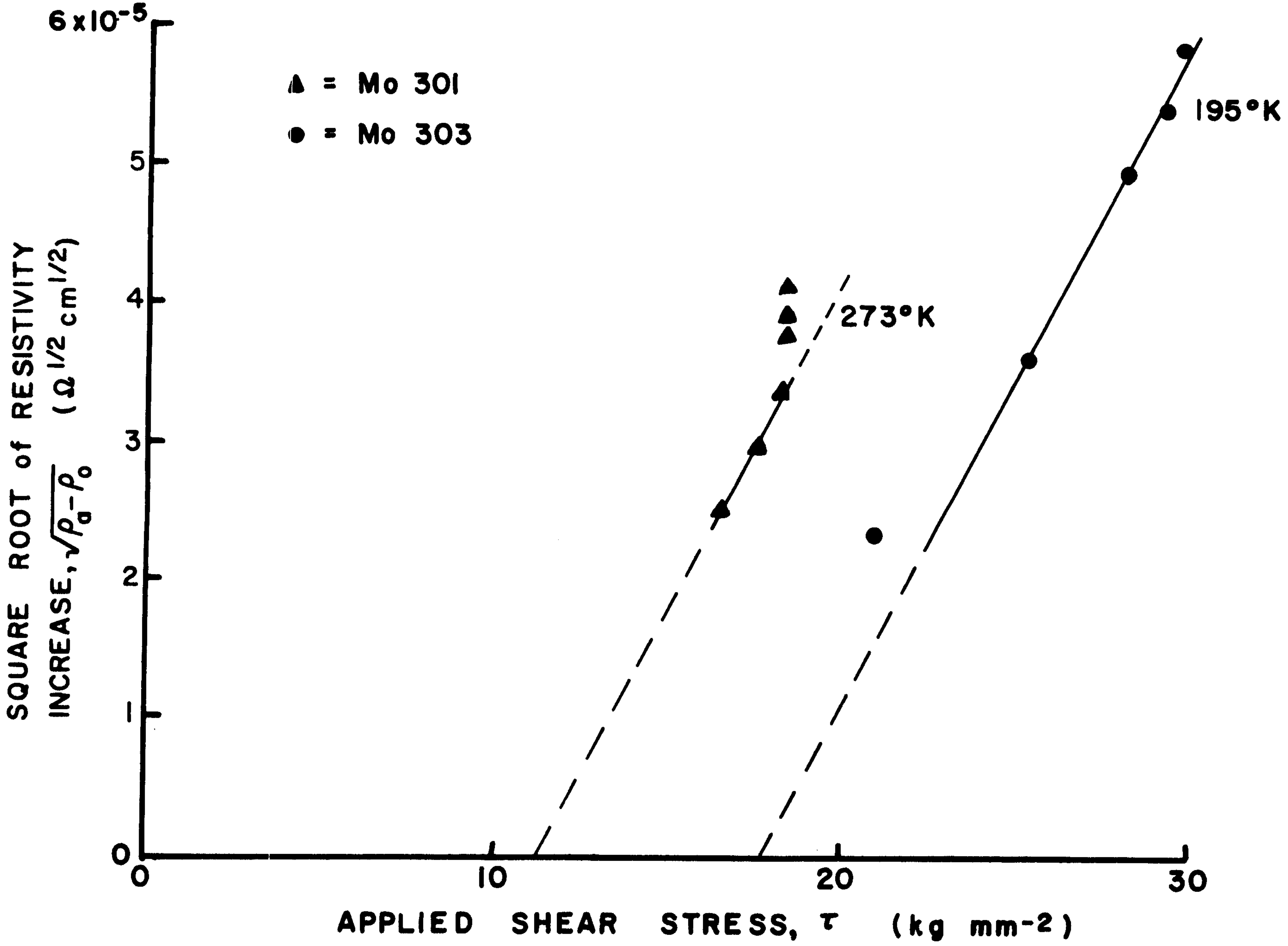
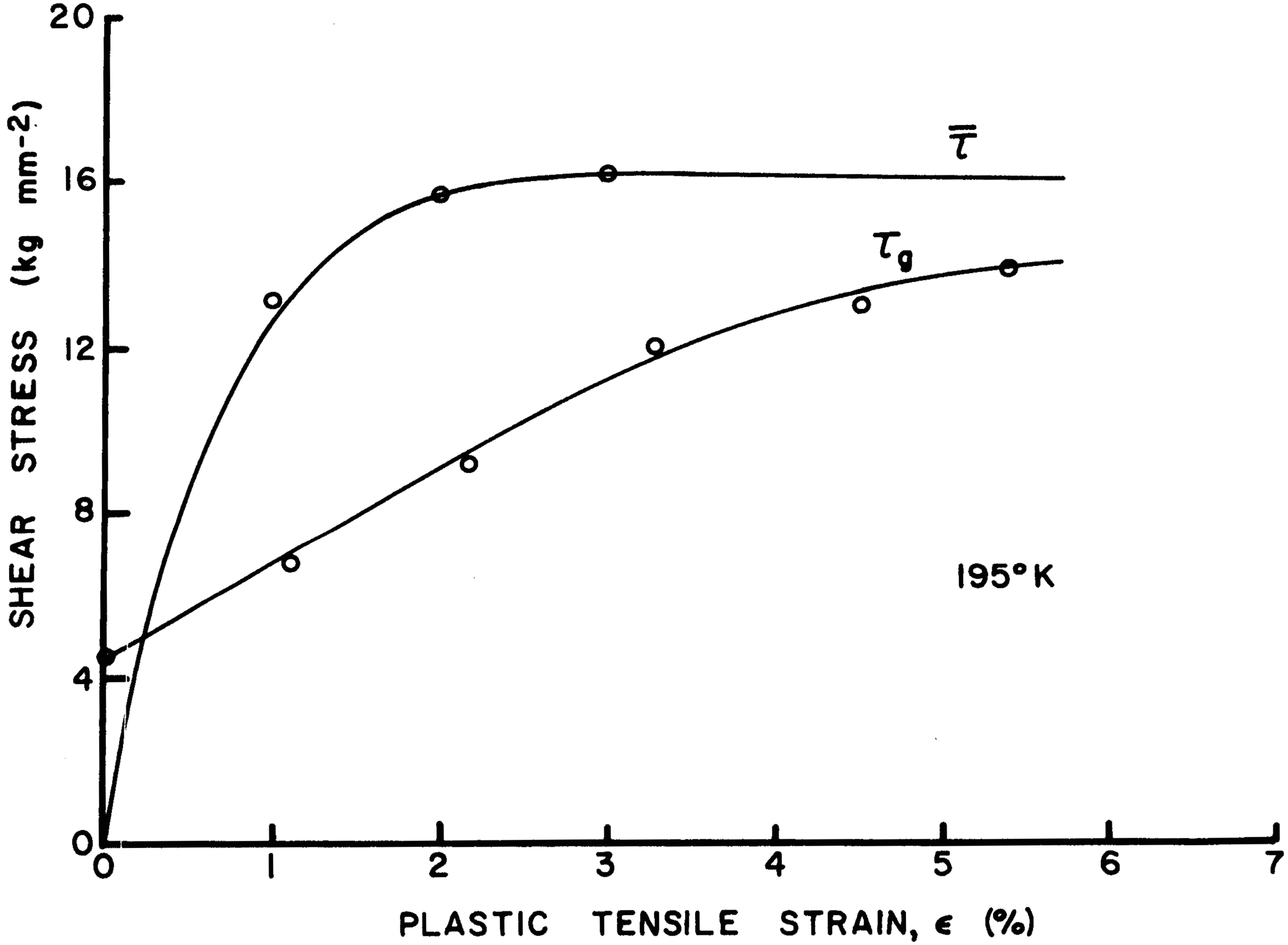

6 x10-5
5
4
3
2
1
0
0
10
20
30
SQUARE ROOT of RESISTIVITY INCREASE, $\sqrt{\rho_a - \rho_o}$ ($\Omega^{1/2}$ cm$^{1/2}$)
APPLIED SHEAR STRESS, τ (kg mm-2)
▲ = Mo 301
● = Mo 303
273°K
195°K

Fig 5



20
16
12
8
4
0
SHEAR STRESS (kg mm-2)
0
1
2
3
4
5
6
7
PLASTIC TENSILE STRAIN, ϵ (%)
$\bar{\tau}$
τ_g
195°K

Fig. 6