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DEFECT PRODUCTION AND MIGRATION IN COPPER AND NICKEL

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DEFECT PRODUCTION AND MIGRATION IN COPPER AND NICKEL

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ABSTRACT

The recovery of electrical resistivity change of high purity copper, nickel, and gold has been studied over a wide temperature range from 4.2 °K to 870 °K following electron irradiation and cold-work. The following was observed:

1) The electron damage rates for samples simultaneously irradiated below 15 °K were 10.6×10^{-27} ohm-cm per electron/cm^2 in nickel and 3.6×10^{-27} ohm-cm per electron/cm^2 in copper.

2) Copper, nickel and gold pulled at 4.2 °K have similar recovery characteristics up to 100 °K, showing no sharp recovery stage (Stage I).

3) Copper and nickel irradiated by electrons near liquid air temperature show a sharp recovery stage (Stage III) at 25 °C in copper and 125 °C in nickel. These temperatures are equivalent on a reduced temperature scale using the melting temperatures as reference points.

4) Nickel cold worked at room temperature shows three recovery stages: Stage III at 80 °C, Stage IV at 275 °C, and Stage V beginning at 400 °C.

The similarities between copper and nickel in these recovery stages is striking and allows one to make assignments for defect migration in both metals in corresponding temperature ranges.

I. INTRODUCTION

It is well accepted in the field of irradiation effects in metals that it is desirable, if not necessary, to examine the behavior of more than one metal under more than one mode of irradiation to understand the various phenomena taking place in crystal lattices. Copper has been commonly used as a "standard material." The hope has been implicit that other metals would behave more or less similarly depending on how closely their other properties resemble those of copper. In particular, it was expected that silver and gold would be very close to copper in their irradiation effects. To some extent the expectation is realized but the deviations are important. Most conspicuous of the deviations is the relative magnitude of the recovery stages following deuteron bombardment near 40° K[1] and 240° K[2] for these three materials now usually called recovery stages I and III, respectively. In stage I, copper recovers the most, silver is intermediate, gold the least. The situation is just reversed in stage III, suggesting an inter-relationship between the two stages.

We have been examining in some detail the behavior of still another metal, nickel, with particular attention to its similarities to copper. It is obvious that some degree of similarity should be expected. The two atoms are of nearly equal mass; both structures are face-centered cubic. Perhaps more suggestive is the recent data published by the Oak Ridge group[3] that copper doped with as much as 1 per cent nickel shows essentially the same behavior in stages I and II (temperature region between I and III) as pure copper.

There are also reasons to expect possible differences between nickel and copper. The electronic structure is, at first glance, significantly different. Copper has a $3d^{10}\ 4s^{1}$ structure accounting for its simple electronic properties. Metallic nickel has a $3d^{10-0.6}\ 4s^{0.6}$ structure. The hole in the d-band accounts for nickel's ferromagnetic behavior. The fact that nickel is ferromagnetic should be borne in mind in analyzing the following data; at the same time, however, this one characteristic should not be overemphasized.

Experimentally, some peculiarity has been noted in nickel under neutron bombardment. Various investigators[4] have reported an inability to get consistent results. Some suggestions as to the reason will be made later.

II. PREVIOUS INVESTIGATIONS

The reason for investigating nickel in as much detail as we have is to be found in the work of Clarebrough, Hargreaves, Michell, and West[5] in Australia. These investigators made excellent studies of the stored energy release of compressed pure copper, arsenic-doped copper, and moderately pure nickel. Their results are shown in Fig. 1, 2, and 3.

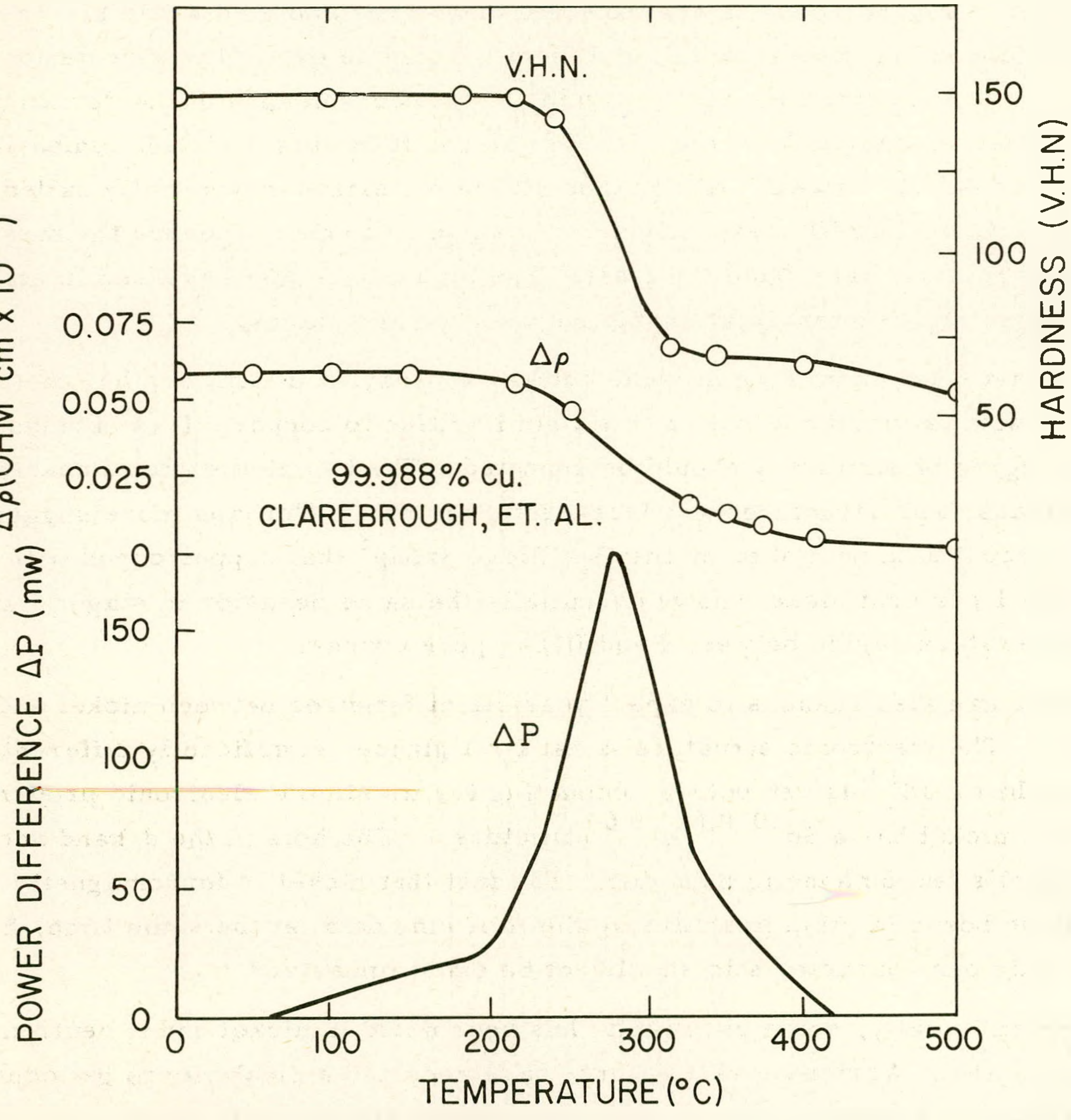

Fig. 1. Stored Energy Release, Resistivity Recovery and Vickers Hardness Recovery of Cold-Worked Copper

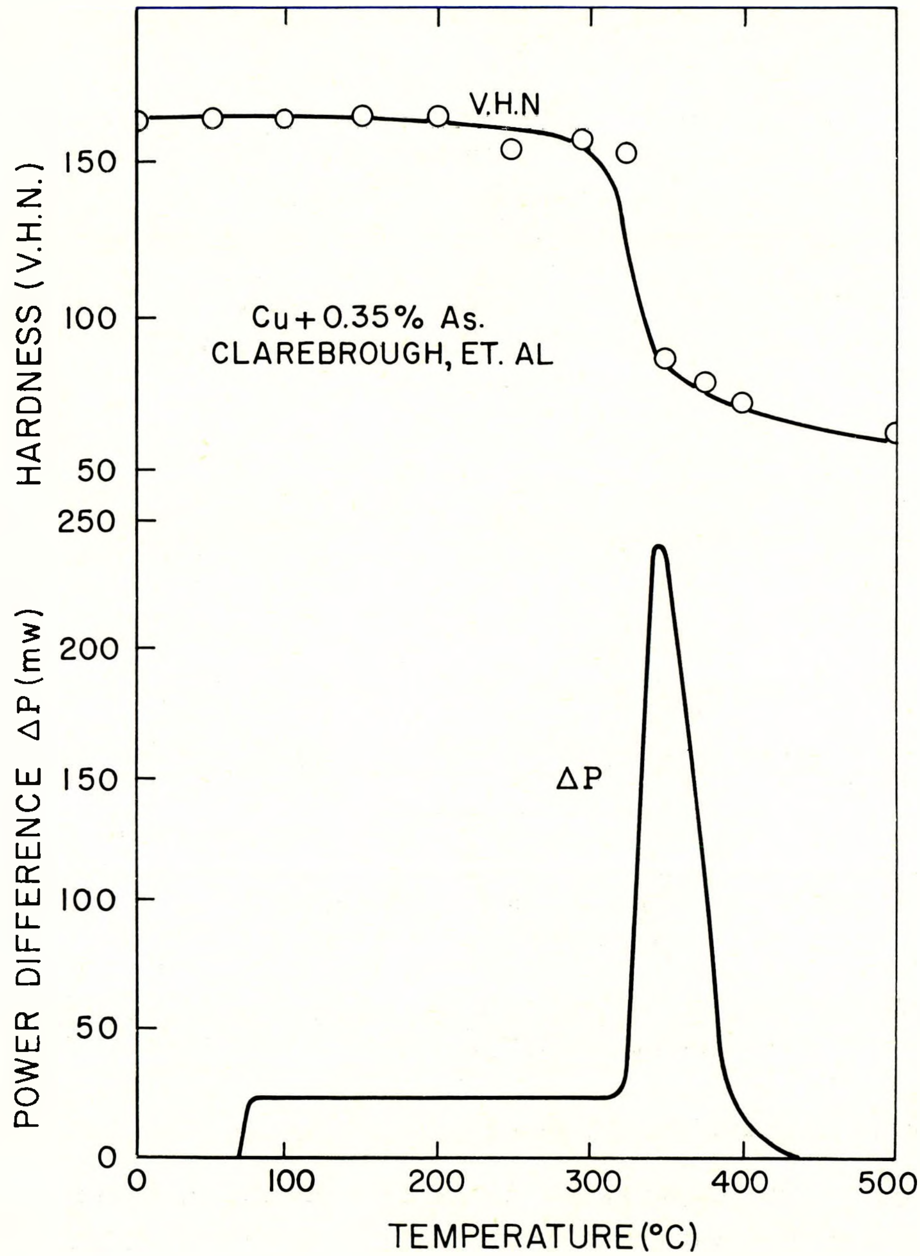

Fig. 2. Stored Energy Release, Resistivity Recovery and Vickers Hardness Recovery of Arsenical-Copper

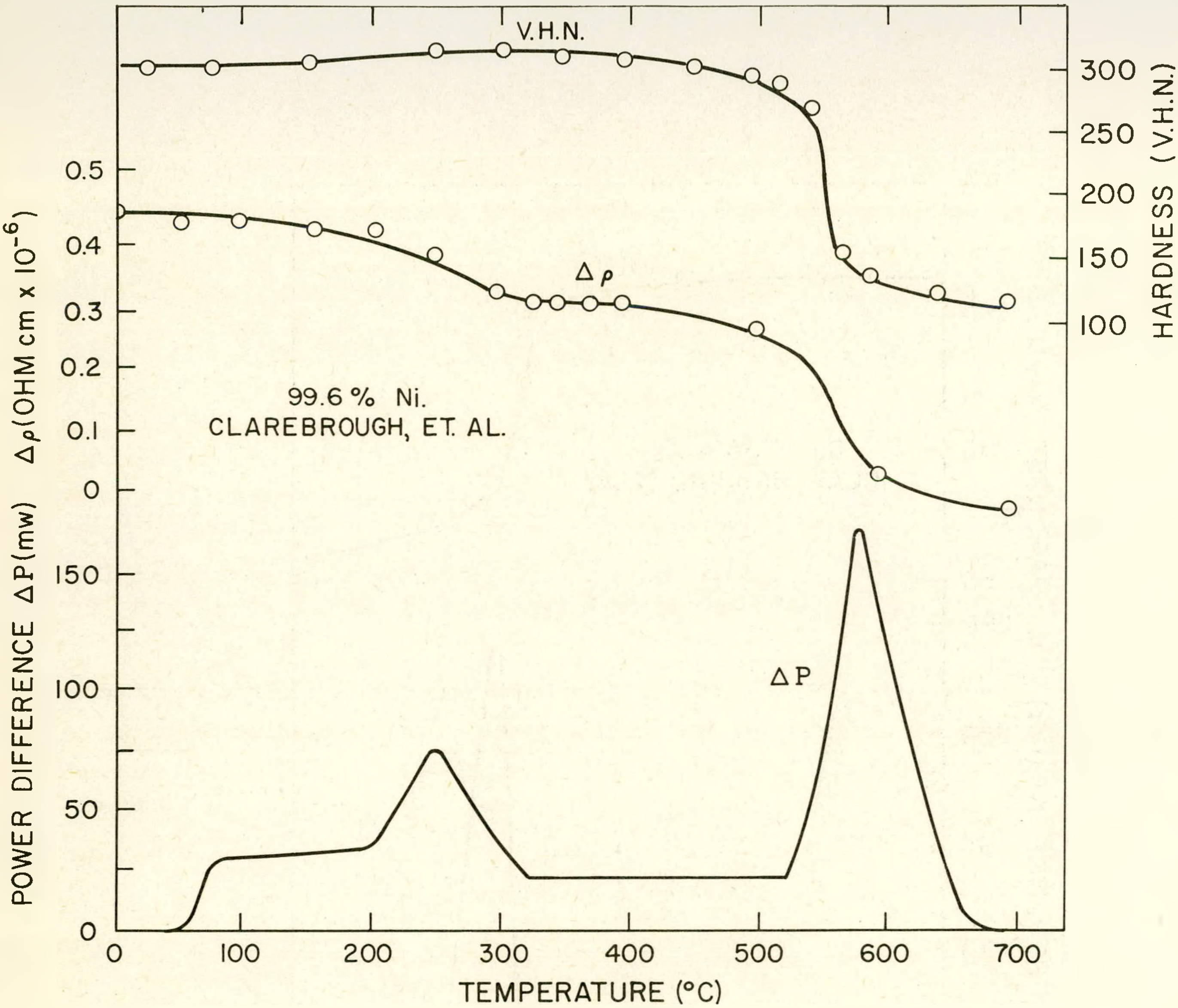

Fig. 3. Stored Energy Release, Resistivity Recovery and Vickers Hardness Recovery of Nickel

The points to be noted here are the following:

1) In pure copper, the majority of the energy released in the recovery stage centered at about 290° C is associated with recrystallization. There is, however, a definite skewness in the peak indicating more than one recovery process is operating.

2) In arsenical copper, the recrystallization peak is quite clearly defined and centered at about 330° C.

3) In nickel, *two distinct recovery stages exist*. The investigators have concluded, on the basis of associated study of density changes and other measurements, that the lower stage is associated with the migration and subsequent annihilation of vacancies; the upper stage is due to recrystallization. This interpretation seems widely accepted and we shall follow suit.

As these figures show, the investigators also measured hardness and resistivity. In all measurements, the samples were 3/4-inch diameter bars. The hardness results are also of interest. Looking back on our work, we regard the resistivity results with somewhat less confidence, as will be discussed later.

III. PRESENT INVESTIGATIONS

Now let us examine our comparison of nickel and copper. Figure 4 shows the results of a simultaneous 1-Mev electron-irradiation of 0.0045-inch copper and nickel wires below 15° K. The copper is 99.999-plus per cent pure; the nickel is 99.98 per cent pure. These materials are used throughout this study unless otherwise specified. Resistivity measurements throughout this study were always made at 4.2° K. As shown, the slopes of the damage vs flux curves are 10.6×10^{-27} ohm-cm/e/cm^2 for nickel and 3.6×10^{-27} ohm-cm/e/cm^2 for copper. The ratio of these slopes is approximately three, although some reservation should be made in considering the difference in threshhold energies for the two metals. The fractional amount of recovery is approximately equal, particularly if reference is made to some reduced temperature scale. The above irradiation was made in a low temperature target box which has been redesigned since these data were taken. The recovery shown was achieved merely by warming up to 60° K, then quenching back to 4° K. The new apparatus will permit a more detailed study of recovery.

We have also examined the recovery of copper, nickel, and 99.999-plus per cent gold following cold work in a liquid-helium bath. The apparatus used to make these measurements is shown in Fig. 5. The sample is cold-worked in a

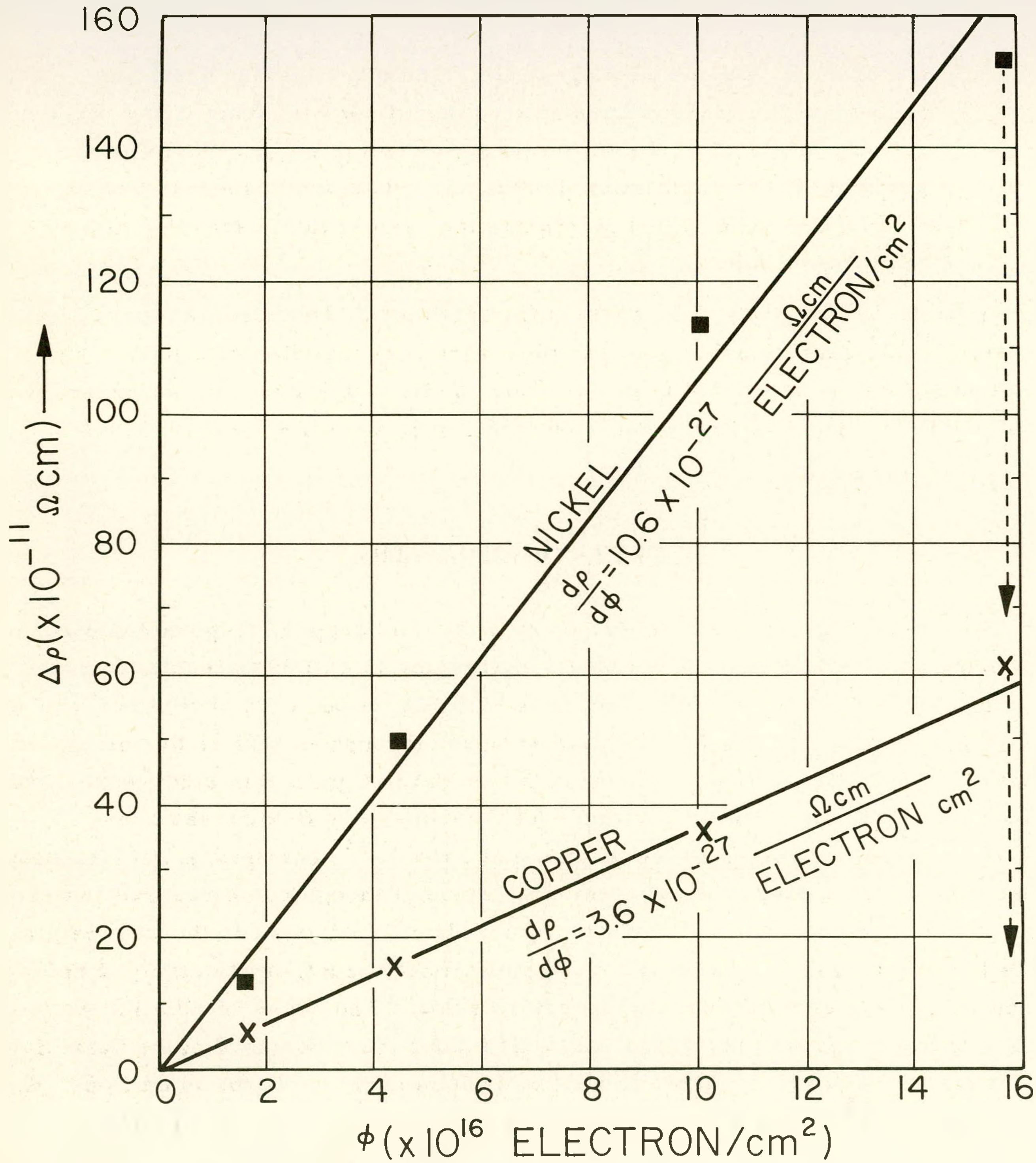

Fig. 4. 1-Mev Electron Bombardment of Copper and Nickel Below 15° K

1. SPECIMEN
2. COPPER ENDS WITH SOLDER JOINT
3. PHENOLIC TUBING
4. HEATER
5. INSULATION
6. COPPER CHAMBER
7. PHENOLIC TUBING SUPPORT
8. ACCESS HOLES FOR LIQUID HELIUM
9. THERMOCOUPLES AND LEAD WIRES
10. EXTENSION NUT
11. LIQUID HELIUM

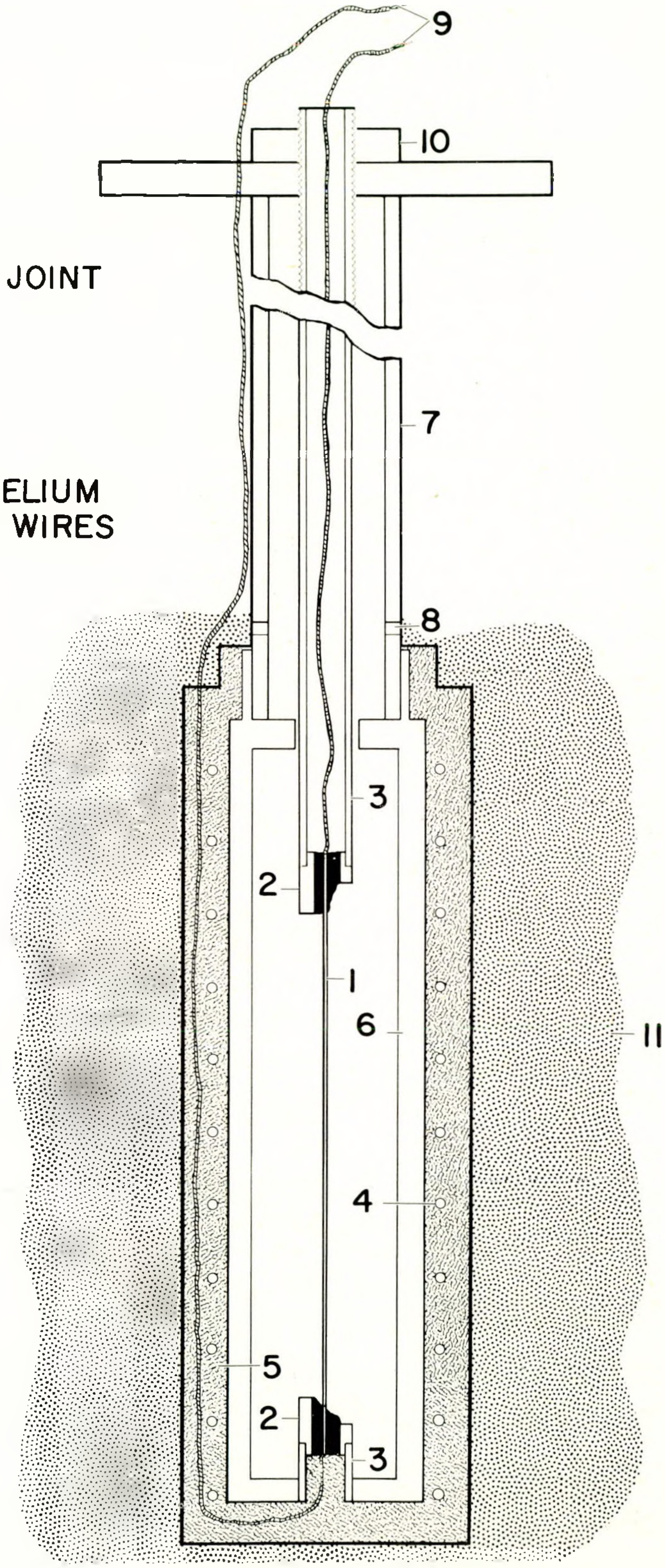

Fig. 5. Apparatus for Cold Working at 4° K

liquid-helium bath. The sample and its surrounding isothermal enclosure is then raised above the bath and a heater turned on to bring the sample to a desired temperature for annealing. After annealing, the sample is quenched back into the liquid helium for measurement. The results are shown in Fig. 6. The samples again were wires with diameters between 0.0045 inches and 0.008 inches. Samples A, B, and C were pulled in tension to about 15 per cent elongation. The actual amounts are as shown. Sample D was first pulled in tension to 8 per cent elongation, then twisted so that the total resistivity change was almost the same as that of Sample A (both samples are copper). The following points are to be noted:

1) It is definitely established that no stage I recovery exists in these metals up to 100° K. The curves for copper seem to fit very nicely onto those obtained by Eggleston[7] indicating that the first well-defined resistivity recovery stage following cold-work in copper is stage III.

2) The shapes of the recovery curves for all three metals are quite similar. Again, if account is taken of the difference in total strain, the ratio of resistivity increases for nickel and copper is about 2-1/2.

3) There seems to be no significant difference between the pulled and twisted wires as far as low temperature resistivity recovery is concerned.

Another detail not revealed by these figures is the dependence of fractional recovery up to some temperature, such as 80° K, on amount of strain. For the 15 per cent elongation shown in the figures, there was about 2 per cent recovery. For a 30 per cent elongation, 6 per cent recovery was found.

We have also made an investigation[8, 9] of copper and nickel irradiated somewhat above liquid air temperature by 1.25 Mev electrons and the subsequent recovery. These results are shown in Fig. 7. The temperature scale is a reduced one to emphasize the large amount of similarity between the two metals. The actual positions of the dominant recovery stages are approximately 25° C for copper and 125° C for nickel. Once again the damage rates as measured here are in a ratio between 2-1/2 and 3.

The last results to be presented are those of a limited study made of the recovery of nickel following cold-working at or below room temperature.

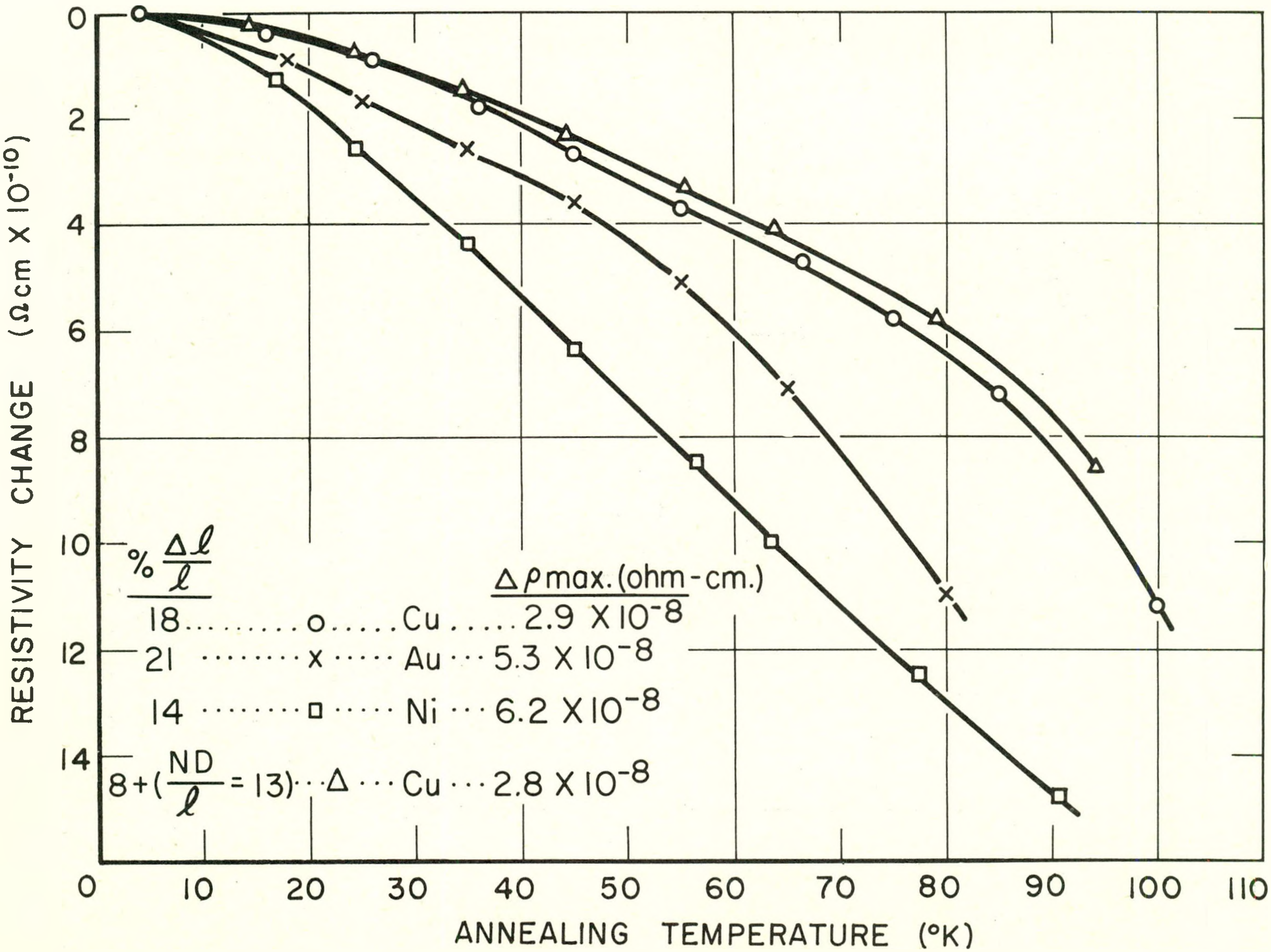

Fig. 6. Recovery of Electrical Resistivity of Cu, Au, and Ni Following Cold Work at 4° K

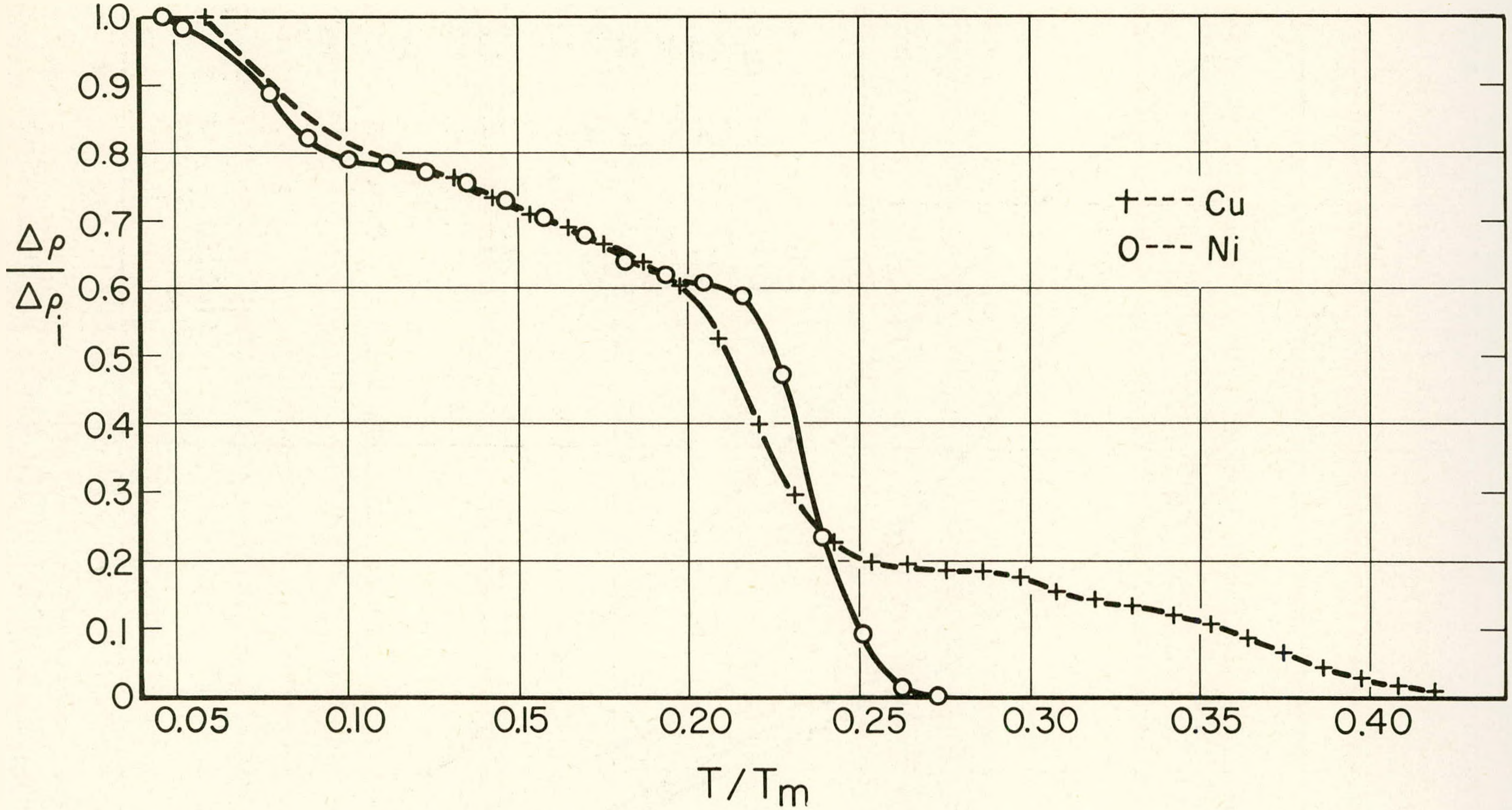

Fig. 7. Recovery of Electrical Resistivity Change in Cu and Ni Irradiated at 80° K With 1.25-Mev Electrons

Figure 8 gives the results of two nickel wires which were each reduced approximately 40 per cent in area, then tempered through the recrystallization temperature region. Figure 9 gives similar results for a wire which was merely pulled about 10 per cent in tension. Heating rates were between 3° and 6° C per minute.

The main fact to be noted here is a definite resistivity recovery stage in all cases at about 100° C. In the case of the more heavily cold-worked wires, the stage is shifted to lower temperatures, as would be expected for a higher concentration of defects. Referring back to Fig. 3, it will be seen that there is no evidence for this recovery stage in the work of Clarebrough, et. al.[5]. The reason for this apparent discrepancy is not known but several possibilities suggest themselves.

1) The resistivity measurements were made on a sample whose geometry is far from ideal for these measurements, although excellent for the other measurements made: stored energy, hardness, X-ray line breadth, and density. Furthermore, the measurements were made at 20° C. Our measurements, as stated previously, were made in a liquid-helium bath where the thermal resistivity is greatly reduced.

2) The samples may have been heated during deformation or subsequent drilling.

3) The nickel used may have been too impure to show this stage. In fact, there is direct evidence for this possibility. To see if this possibility has any credence, we also tempered a cold-worked nickel wire prepared from a commercial stock of undetermined purity. The 100° C stage was definitely absent. The tempering curve was followed up to about 250° C and showed a large resistivity drop beginning at somewhat over 100° C and continuing up to the highest temperature of measurement with no suggestion of a defined recovery stage. We have since found a plot of some measurements made by J. E. Wilson and L. Thomassen[10] showing recovery following 75 per cent forging. Their resistivity recovery behaves quite similar to ours when using the commercial purity. It is tentatively believed that varying impurity content is the reason for the apparent discrepancy as well as the lack of reproducibility found by the other investigators mentioned previously.

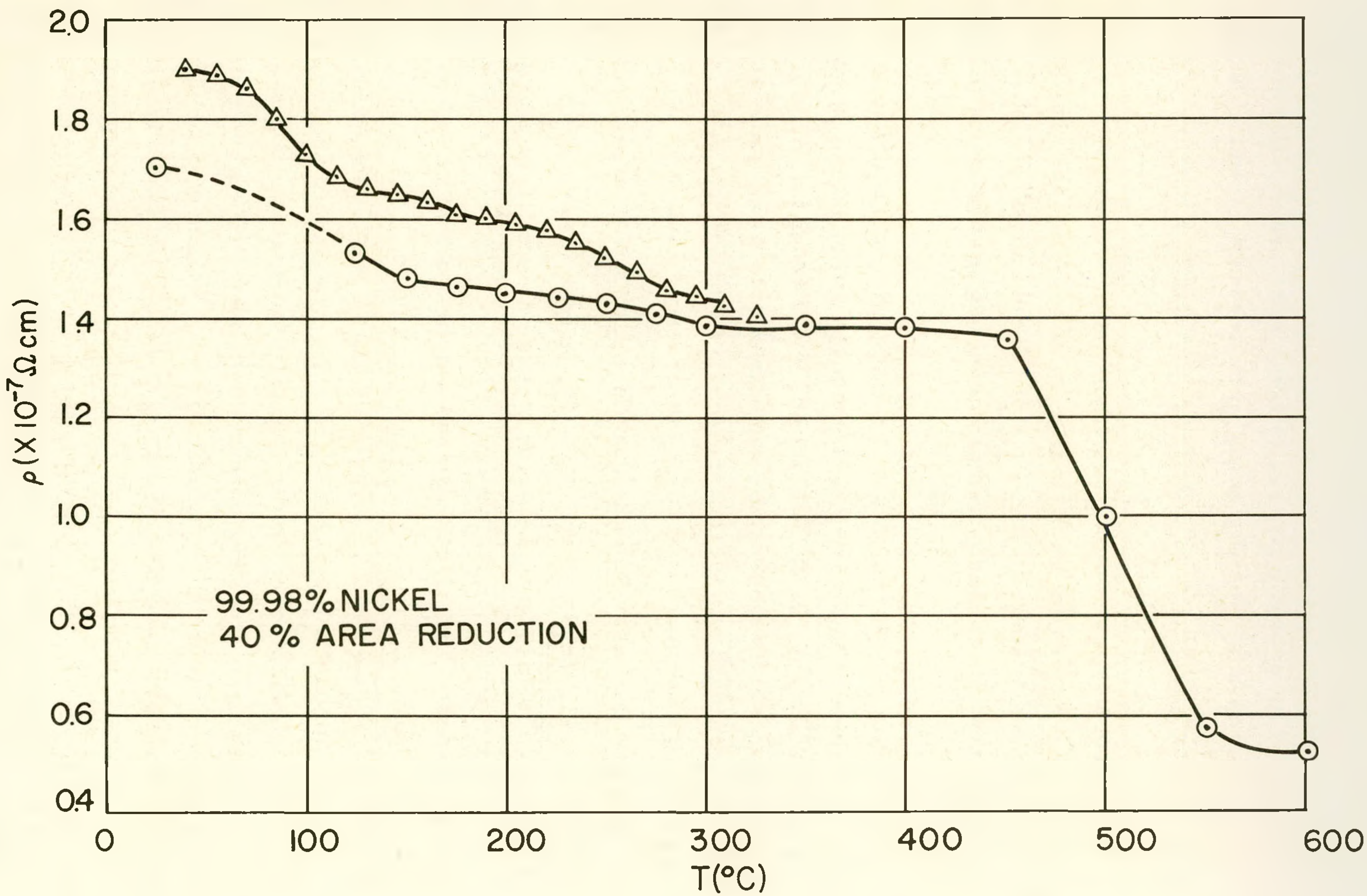

Fig. 8. Recovery of Nickel Following Cold Work Near Room Temperature on Two Drawn Wires

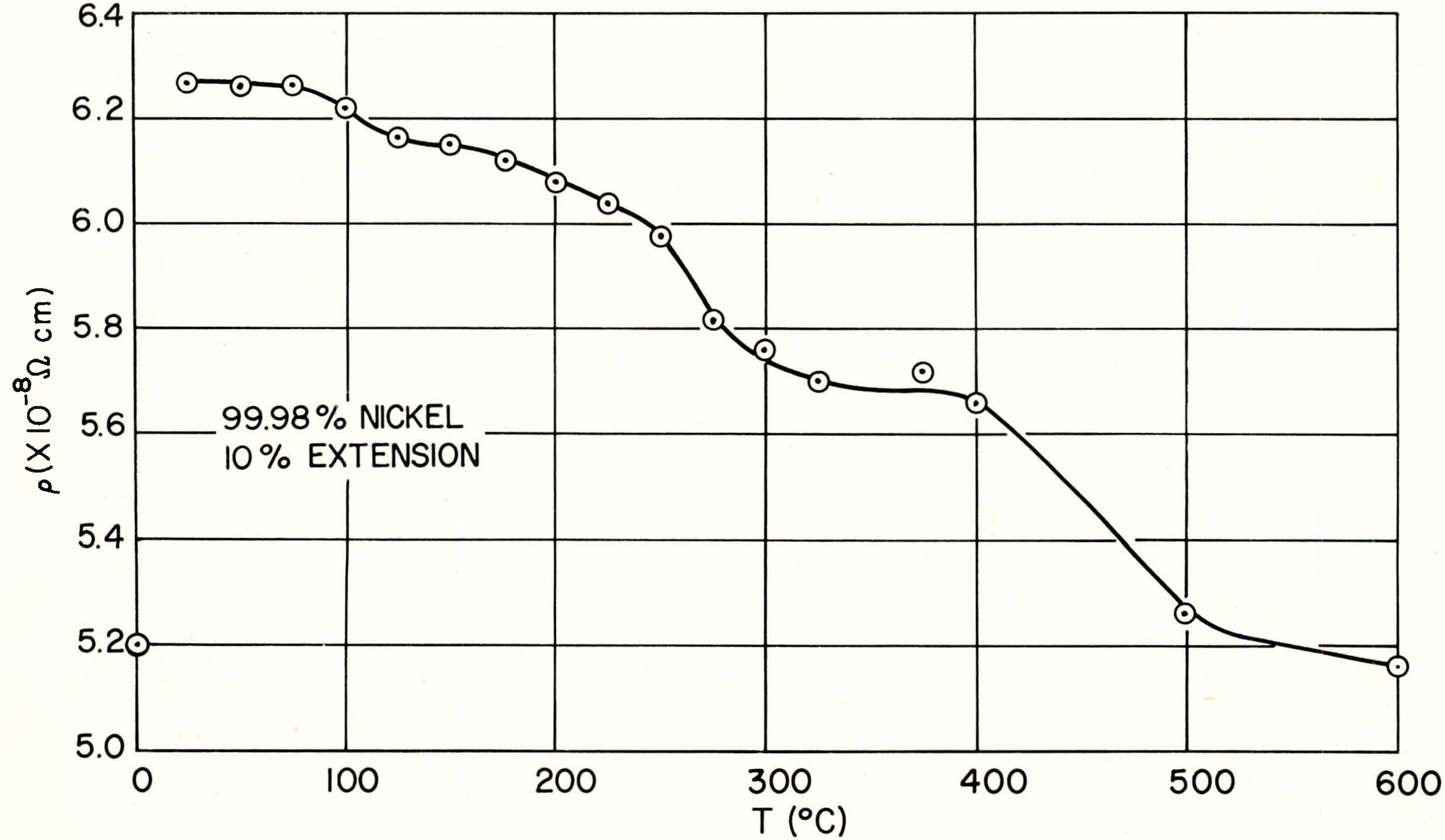

Fig. 9. Recovery of Nickel Following Cold Work Near Room Temperature on One Sample in Tension

IV. CONCLUSIONS

To sum up, we would like to re-emphasize the following findings and our interpretations:

1) The recovery of nickel and copper is amazingly similar. If we make the obvious conclusion that the skewness of the stored energy peak in copper is due to two recovery processes and that the smaller process is the same as that occurring in nickel at about 250° C, we have a one-to-one correspondence for all the recovery data. These conclusions are given further credence by the calculations of A. Seeger, as will be discussed shortly.

2) The 2-1/2 or 3 to 1 ratio of damage and recovery for nickel and copper seems to be quite universal. This suggests that the electron scattering due to all major defects in nickel and copper is the same except for this numerical factor. This same factor can be found in data on deuteron bombardment at Illinois[2] and neutron bombardment at Oak Ridge.[11] This is supported by the theoretical calculations of A. Seeger. Professor Seeger has pointed out that the resistivity in nickel is primarily determined by the s-electrons with spin anti-parallel to the hole in the d-band. These electrons "short" the resistivity of the other s-electrons. Thus the conduction of nickel is determined by a concentration of "free electrons," similar to those in copper, but reduced in number in the ratio of 0.3 to 1.0. Allowing some contribution to the conductivity from the "non-free" electron, one estimates a factor of about three between nickel and copper for any defect scattering.

3) We are led to assign the two recovery stages near 100° C and 300° C in nickel (stages III and IV) to interstitial migration and vacancy migration respectively, in view of the following:

   a) The recovery of electron bombardment damage at 125° C as measured by resistivity-measurements

   b) The recovery of cold-work damage at 275° C as measured by stored energy

c) The recovery of cold-work damage at 100° C and at 275° C as measured by resistivity-measurements

d) Taking into account a defect-concentration effect responsible for the differences between 100° C and 125° C, mentioned above

e) Accepting the interpretation of Clarebrough, et. al.

4) Extrapolating from nickel to copper, we assign stage III (at about 0° C) to interstitial migration, and stage IV (at about 150° C) to vacancy migration in copper. This is, of course, not a new assignment. There exists a large body of data to support these assignments. Note that the ratio of the characteristic temperature of a recovery stage to the melting temperature in both copper and nickel is the same in stages III and IV. We regard our work as new confirmation for copper and a first assignment for nickel.

5) The absence of any stage-I recovery in cold-worked copper, nickel and gold is regarded as evidence against interstitialcy migration in this stage, since cold-working is expected to produce a sizable concentration of interstitials. This argument would seem to apply to all types of interstitialcy migration.

6) It still remains to be decided what accounts for the "garbage" type of recovery observed in stage II. All that can be said from the data presented here is that a close-pair recombination model is not inconsistent if one takes some number such as three atoms separation as defining a close-pair. The dependence of relative amount of recovery on total strain fits into this scheme.

A number of experiments is suggested.

1) Further exploration of the low temperature "garbage" recovery would be desirable.

2) Since the vacancy stage in nickel seems to be well accepted, and since nickel and copper bear such a large degree of similarity, quenching experiments on nickel would help separate single and multiple vacancy migration.

3) A detailed study of the recovery kinetics in irradiated and, perhaps, cold-worked nickel in stages III and IV could be decisive in testing the assignments made in this paper.

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