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RESISTOMETRIC OBSERVATION
OF THE ANNEALING CHARACTERISTICS
OF A TENSILE LOADED Cu-Al ALLOY

Ronald Paul Malatesta
(M. S. Thesis)

September 1967

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AEC Contract No. W-7405-eng-48

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CONTENTS

Page

ABSTRACT. v

I. INTRODUCTION. 1

II. EXPERIMENTAL APPARATUS 5

III. EXPERIMENTAL PREPARATIONS 12

IV. EXPERIMENTAL PROCEDURE 14

V. RESULTS 15

VI. DISCUSSION 22

VII. CONCLUSIONS 23

ACKNOWLEDGMENT. 24

REFERENCES. 25

RESISTOMETRIC OBSERVATION OF THE ANNEALING CHARACTERISTICS OF A TENSILE LOADED Cu-Al ALLOY

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September, 1967

ABSTRACT

A highly sensitive resistance measurement apparatus was set up to observe the effect on the electrical resistance of alloying copper with aluminum and to observe recovery at low temperatures after cold work. The electrical resistivity ρ_o was shown to be proportional to the square of the scattering charge z of the alloying element. An increase in resistance was detected in specimens annealed at 90°K and 113°K.

I. INTRODUCTION

The electrical resistance of a material is important in a metallurgical sense because it can be employed to analyze the stages of recovery,[1-4] the purity of a specimen using the resistivity ratio method,[5] the degree of ordering,[6] the degree of cold work[7] and many other properties. Resistance measurement is most commonly used in studying recovery phenomena and is the most effective and reliable method in this most important area, although interpretation of results even with this method can be quite difficult when many processes of annealing are involved simultaneously.

The scattering of electrons resulting in an increase in resistivity can be caused by several types of disturbances of the lattice: by temperature vibration (phonon scattering), by impurities (both substitutional and interstitial) and by mechanical deformation (which produces vacancies, interstitials and dislocations). The object of this study was to measure some of the effects due to the latter two causes of scattering. One method of making a highly sensitive electrical resistance measurement will be presented along with some of the merits and drawbacks of the method.

The additive nature of the several sources of resistivity has been known for some time and is essential to any analysis of resistivity data. Called Mathiessen's Rule it can be written

$$\rho_{total} = \rho_{temperature} + \rho_{impurities} + \rho_{deformation} \qquad (1)$$

If necessary the value for ρ_{total} can be lengthened to include the additional resistivity produced by irradiation and quenching.

The basis for the behavior of metals according to Eq. (1) is contained in the nature of the scattering process itself. This can be shown by closely examining the concept of mean free path of the electron is defined in Eq. (2).

$$\lambda = v(2\tau) \tag{2}$$

where λ is the mean free path of the electron, v is the speed of the electron and τ is the relaxation time between collisions. The mean free path is defined as the average value of the distance between collisions for all trajectories of the electron. For a group of electrons passing through the lattice in the x direction, the number dN(x) that make a collision in some length of path dx at position x is given by

$$dN(x) = -\frac{N(x)dx}{\lambda} \tag{3}$$

where N(x) is the number of electrons which still have to make a collision at position x. λ in Eq. (3) is merely a term used to satisfy dimensional requirements but is actually identical to λ in Eq. (2). Eq. (3) is based on the premise that an electron has the same probability of colliding in each increment dx. Integrating Eq. (3) gives the number of electrons remaining in the group after it has travelled a distance x,

$$N(x) = N_o e^{-x/\lambda}$$

where N_o is the number of electrons in the group initially. Since N(x) drops to (1/e) th of its original value when x takes the value λ,

the parameter λ is the average distance between collisions (i.e. the mean free path).

All independent scattering processes can easily be considered. Suppose the precesses taking place are temperature scattering with a mean free path λ_T, impurity scattering with a mean free path λ_I and deformation scattering with a mean free path λ_D. The number of collisions can be expressed

$$dN(x) = -\frac{N(x)dx}{\lambda_T} - \frac{N(x)dx}{\lambda_I} - \frac{N(x)dx}{\lambda_D} \tag{4}$$

The solution of the equation is

$$N(x) = N_o\, e^{-(1/\lambda_T + 1/\lambda_I + 1/\lambda_o)x} \tag{5}$$

The total mean free path is given by

$$\frac{1}{\lambda} = \frac{1}{\lambda_T} + \frac{1}{\lambda_I} + \frac{1}{\lambda_D} \tag{6}$$

The relaxation time $\tau = \lambda/2v$ can be written

$$\frac{1}{\tau} = 2v\ \{\frac{1}{\lambda_T} + \frac{1}{\lambda_I} + \frac{1}{\lambda_o}\} = \frac{1}{\tau_T} + \frac{1}{\tau_I} + \frac{1}{\tau_D} \tag{7}$$

The resistivity ρ can be expressed

$$\rho = \frac{m^*}{Nq^2\tau} = \frac{m^*}{Nq^2\tau_T} + \frac{m^*}{Nq^2\tau_I} + \frac{m^*}{Nq^2\tau_D} \tag{8}$$

where m^* is the effective mass of the electron and g is the charge on the electron. The terms on the right are, respectively, ρ_T, ρ_I and ρ_D. Thus, the additive nature of the total resistivity is established.

Substituting the appropriate values into Eq. (8) yields a total relaxation time for pure copper at room temperature of about 2×10^{-14} sec. The velocity of the electron in copper is about 1.6×10^8 cm/sec. Substituting these two values into Eq. (2) yields $\lambda \cong 3 \times 10^6$ cm, or about 100X the lattice constant of copper.

II. EXPERIMENTAL APPARATUS

The assembly of the electrical equipment was designed so that a highly sensitive resistance measurement could be made on specimens of various shapes. The instruments used for making measurements of this nature were assembled as seen in Figure 1.

The layout of the equipment was designed so that one potentiometer could be used to measure the voltage drop across both the specimen and the standard resistor. The advantages of using one potentiometer are a more easily portable set-up and a more economical one. Using two potentiometers makes it possible to make more rapid readings because one potentiometer can be set to the voltage drop across the standard resistor, which fluctuates only slightly from reading to reading or not at all. Since current deviations were, at most, only slight, the voltage drop across the standard resistor need be measured only every 5 minutes, thus, allowing between this measurement, a constant monitoring of the voltage drop across the specimen.

A thermal compensator (see Figure 2) was used to cancel any thermal EMF produced in the potential leads extending from the specimen to the potentiometer. Low thermal solder was used at all connections and high purity copper wire (99.999%) was used in the circuitry. Its maximum output is 10 $\mu\Omega$ sufficient to cancel any thermal EMF's encountered provided care is taken in attaching the potential leads to the specimen.

No thermal compensator was employed in the leads from the standard resistor to the potentiometer because of the relatively good stability of the environment of the standard resistor as compared to that of the

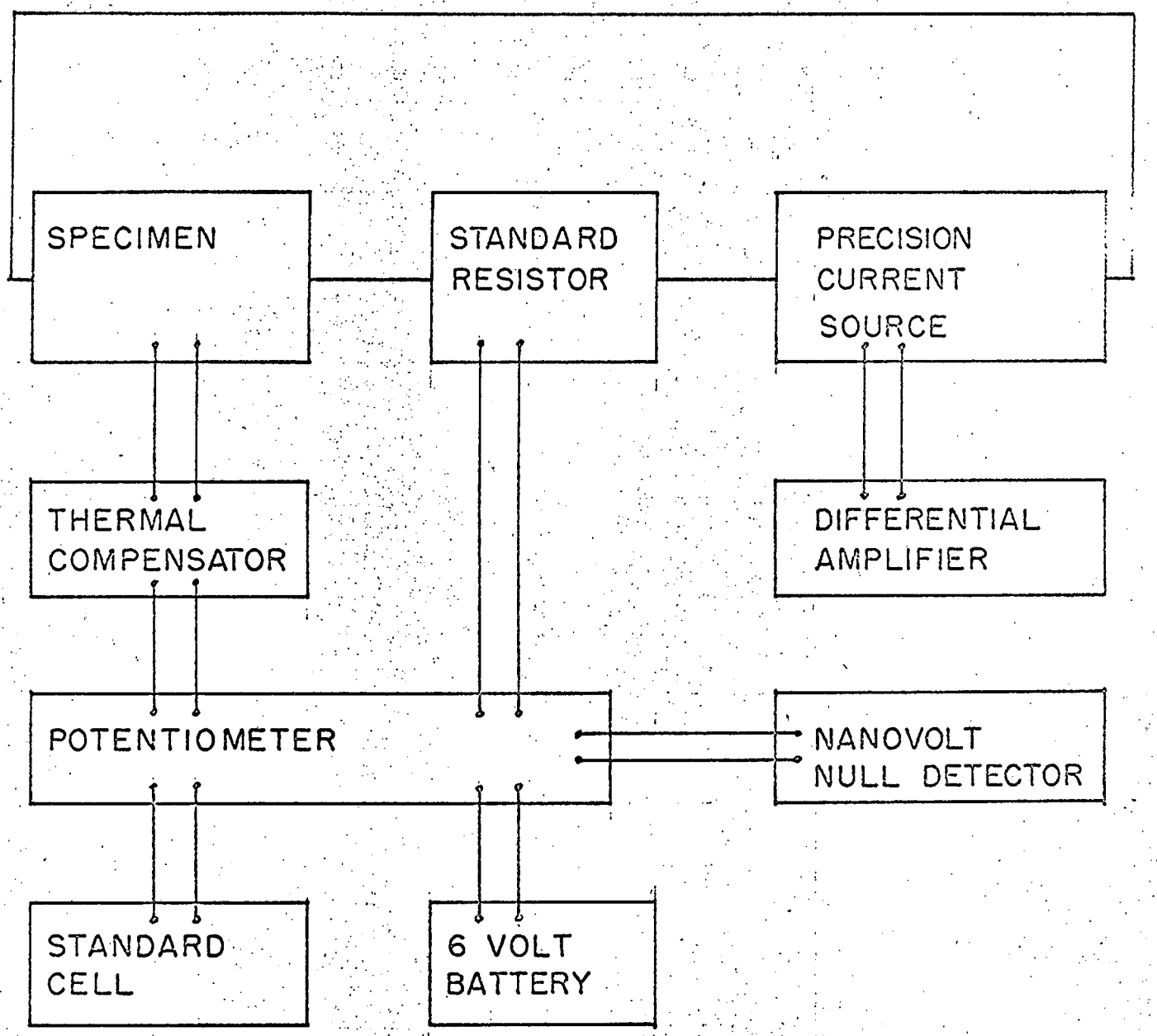


FIG 1 Block diagram of components used in making a resistance measurement

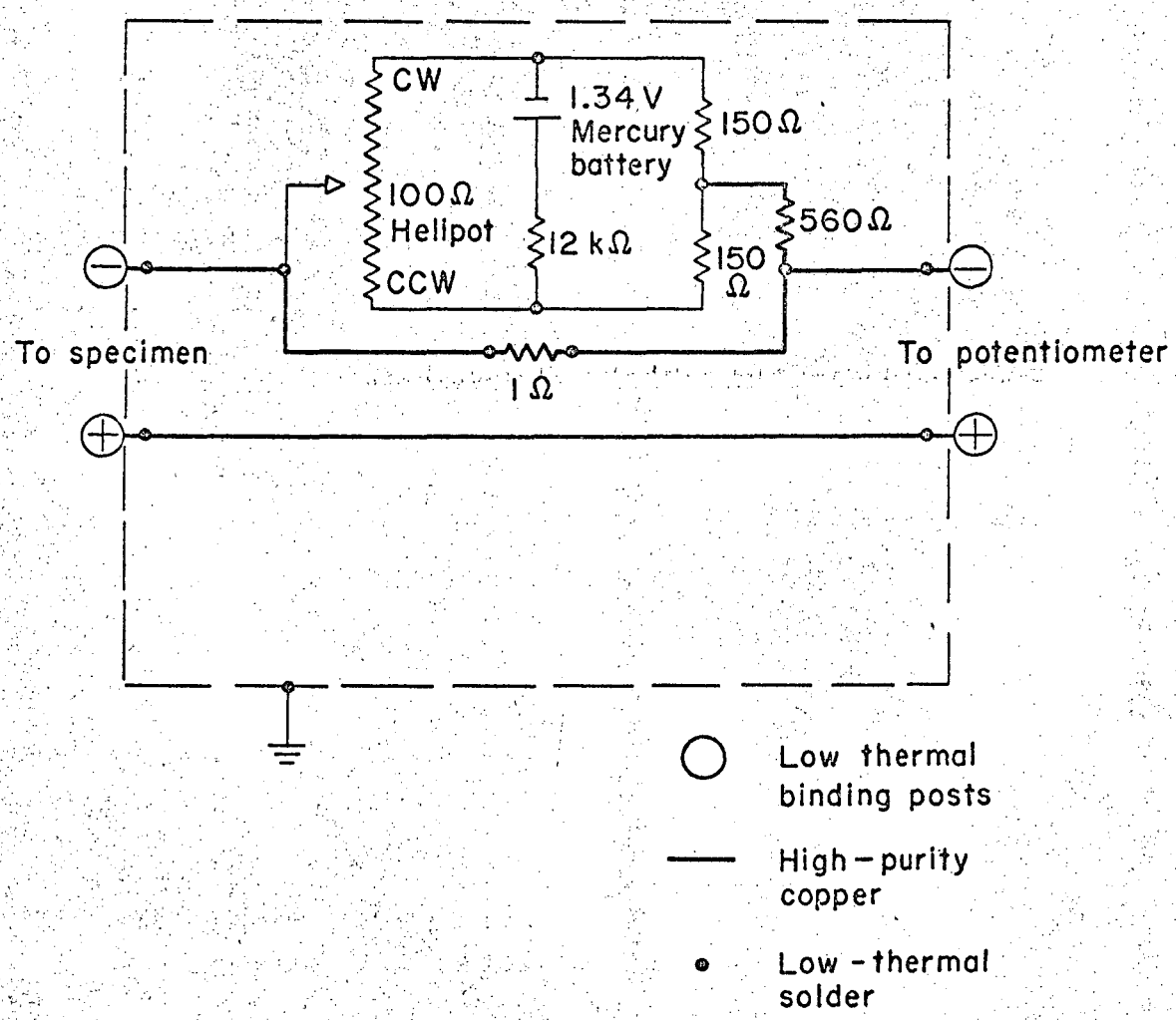


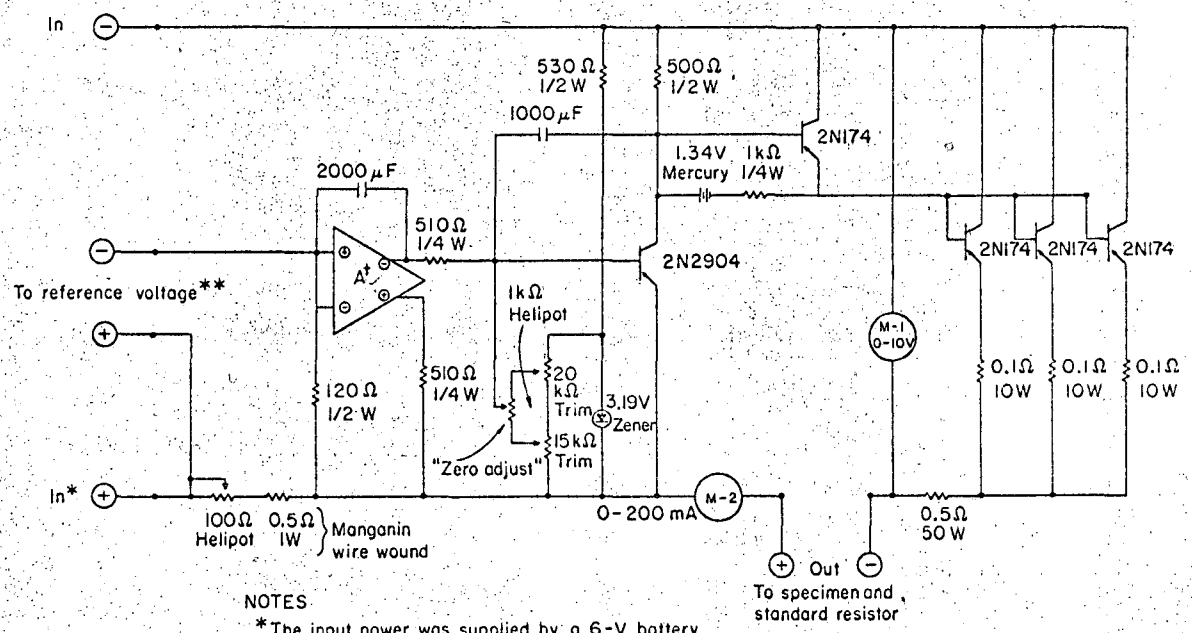
Fig. 2 Circuit diagram of precision thermal compensator

specimen. The environment of the standard resistor was set up once and then was not altered whereas the surroundings of the specimen were altered each time a new specimen was used, thus, necessitating the need for the thermal compensator. The standard resistor was housed in an oil bath to minimize thermal fluctuations in its environment. The bath temperature varied < 0.1°C in 10 hours.

During a series of measurements the thermal compensator was initially adjusted to balance out any thermal EMF's and then was kept constant. Since nothing was done to change the potential measuring circuitry after connecting the specimen, any additional EMF measured after the initial adjustment of the compensator was a result of the alteration of the specimens internal structure.

A "make before break" switch was included in the circuitry so that the current through the specimen could be switched to zero and the check for thermal EMF's could be made. The "make before break" provision was necessary in order to maintain a relatively constant output level for the precision current source. This was accomplished by diverting the current flow through copper wiring of approximately the same resistance as the specimen.

The precision current source (Figure 3) can be set to maintain a current in the range 0 - 2 amps. Higher currents up to 10 amps are possible but cause excessive heating of the transistors in the source and an accompanying decrease in the constancy of output. The current source was set to maintain a current of approximately 1 ampere and at this output the precision was ± 10 p.p.m. Its ability to level out



NOTES

*The input power was supplied by a 6-V battery

**The reference voltage source was a Evenvot Zener diode (Model 203-05)

†The operational amplifier, A, was a modified Brown Electronik Null-Indicator

MUB-10691

Fig. 3 Circuit diagram of precision direct current source.

deviations in current to a constant value was aided by employing a differential amplifier. The amplifiers function was to equalize any differences in voltage between the reference voltage and the bank of resistors (see Figure 3).

An electronic nanovolt null detector with excellent damping ability and quick response was used for null detection.

The sensitivity of any measurement of resistance was ± 0.1 uv providing the specimen was housed in a constant temperature environment. The stability of a reading is heavily dependent on thermal fluctuations of the specimen (e.g. a Cu-Al alloy, 0.1 At.% Al, 10 cm long, 0.056 cm in diameter, varied approximately 30 $\mu\Omega/°C$).

The best environments for maintaining good sensitivity were found to be baths which boil at room temperature (liquid oxygen or liquid nitrogen) and inert gas environments in which a range of temperatures are produced by resistance heating the specimen. Maher[8] has employed the latter technique successfully by using the dependence of the resistance on temperature to achieve a certain temperature of quench or anneal. However, this technique is limited to materials that have their temperature vs. resistance dependence accurately known. Therefore, the Cu-Al alloy mentioned earlier could not be annealed in this manner until its temperature vs. resistance dependence was determined.

Baths composed of two phases of a material in equilibrium at the solid → liquid transition temperature were found to be inadequate. With the exception of isopentane mixed with liquid nitrogen the temperature would fluctuate ± 2°C even with vigorous stirring and was sensitive to

the additions of liquid nitrogen. The liquid nitrogen was used to cool the bath down from room temperature to the transition temperature.

The most critical step in maintaining low thermal EMF effects and high sensitivity is the attachment of the potential leads to the specimen. Care was taken to avoid junctions of dissimilar metals and metal to metal oxides.

Spot welding was found to be the most successful method for joining the leads to the specimen. No problems with thermal EMF's were encountered providing the leads were stripped of their oxide coating. The leads were 99.999% copper, 0.016 in. diameter and they extended from the thermal compensator to the specimen in order to avoid any unnecessary junctions. All external wiring was shielded and grounding points were carefully chosen. The thermal compensator and all connections in the measuring circuit were housed in styrofoam and the room temperature fluctuations were controlled to within ± 2°C.

III. EXPERIMENTAL PREPARATIONS

The specimens used in the investigation were 0.016 in. diameter hard drawn copper wire (99.999%) and 0.023 in. diameter annealed Cu-Al alloy (0.1 At.% Al) prepared by melting 99.999% Cu with 99.999% Al in an induction furnace. The alloy was fabricated into wire form by swaging from 1/4 in. rod as obtained from the graphite mold down to the 0.023 in diameter of the specimen. No intermediate anneal during swaging was necessary. After the final swaging the specimens were cut into 12 cm lengths, placed in an evacuated quartz tube under 1×10^{-6} mm Hg, and annealed for 1 hour at 450°C.

The specimens were mounted on an Instron tensile testing machine as shown in Figure 4. The lower grip was designed so that it would hang free from any contact with the frame when the load was removed after elongation. This development eliminated any change in the electrical resistance due to a varying load on the specimen. The current and potential leads were coiled near the ends to eliminate any possibility of them contributing to the stress on the specimen. Polyvinylchloride was used in the support frame to minimize the thermal shock to the annealing bath when the temperature of deformation was changed to the annealing temperature.

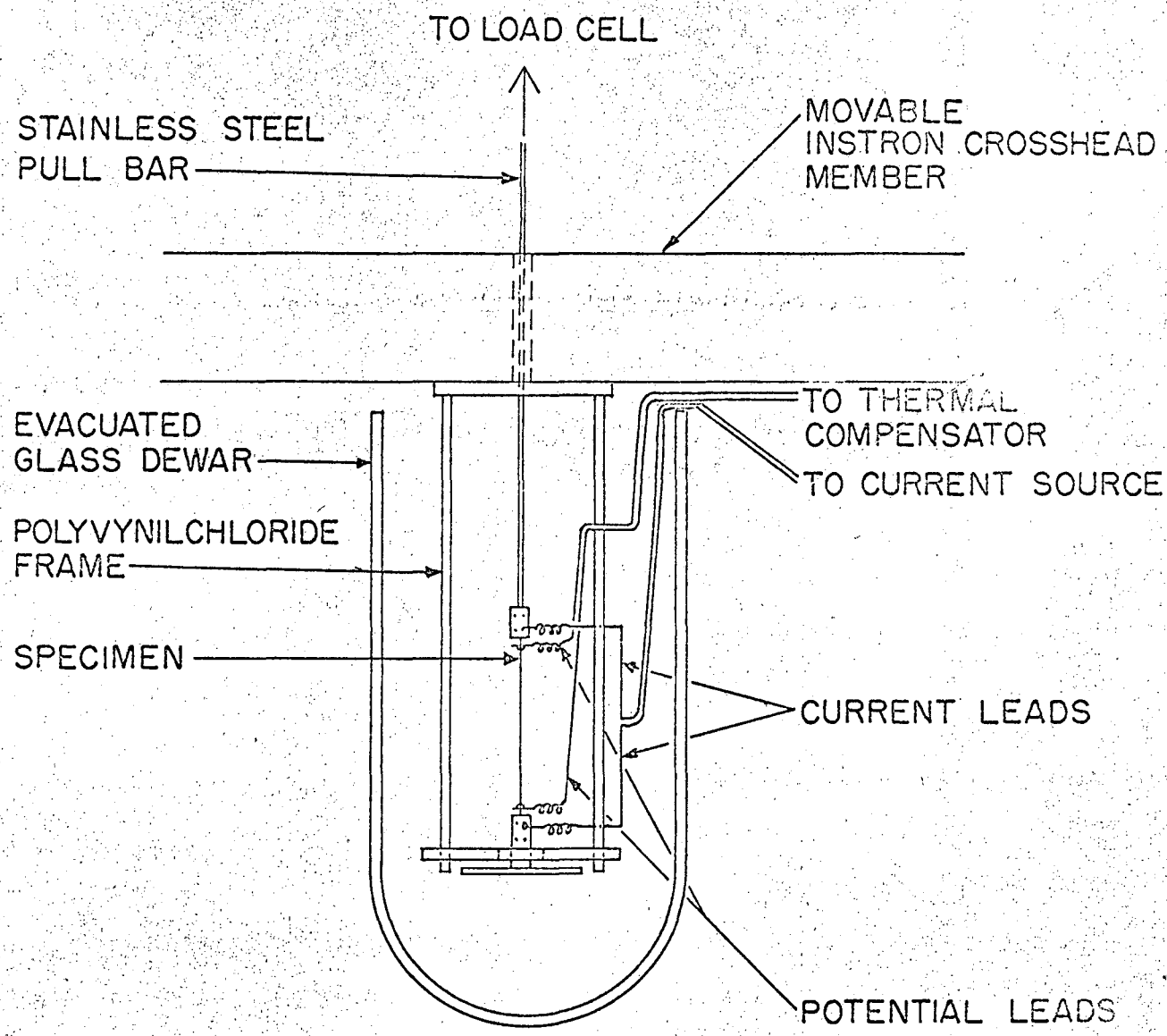


FIG 4 Instron experimental apparatus

IV. EXPERIMENTAL PROCEDURE

The specimens were elongated 10% in tension at 77°K. After elongation the load was completely removed except for the small tensile load exerted by the lower grip. The specimen was then held for at least 5 minutes at 77°K to see if any annealing occurred and then was submerged in the annealing bath.

The electrical resistance was measured at least once per minute and more often if time allowed. During the experiment some of the bath liquid would evaporate and so small additions had to be made to the bath to keep the level constant. The thermal compensator was adjusted before deformation and immediately after submersion in the annealing bath.

V. RESULTS

In all cases measurements made in the interval from 30 sec to 25 minutes after removal of the stress show no annealing taking place at 77°K.

A pure copper specimen was annealed at 0°C (see Figure 6) to observe if any change was produced in the residual resistance by the deformation at 77°K. An increase in the resistance of about 2% was introduced by the deformation. The recovery curve has a uniform decline and a leveling off after 40 minutes. After returning the specimen to 77°K, 50% of the resistance change introduced by the deformation had recovered.

The isothermal recovery curve for the Cu-Al alloy at 90°K presented in Figure 5 exhibits a peak occurring at about 9 minutes and then a rather uniform decline to a constant value after 125 minutes. The recovery curve at 113°K also shows a peak occurring this time at 3-1/2 minutes. Again the decline of the resistance occurs without the presence of any significant plateaus. The peak value is much larger in the case of the 113°K anneal and at about 100 minutes recovery is complete. Recovery of the additional resistance of cold work is about 6% complete after the annealing at 113°K and less than 1% complete after the annealing at 90°K.

Slight temperature variations (± 0.1°C) were observed during the annealing at 113°K resulting in some scatter in the curve. These variations were probably caused by the slight additions of liquid nitrogen to the bath. During all tests rapid movements in the vicinity of the measuring apparatus would result in slight shifts in the reading.

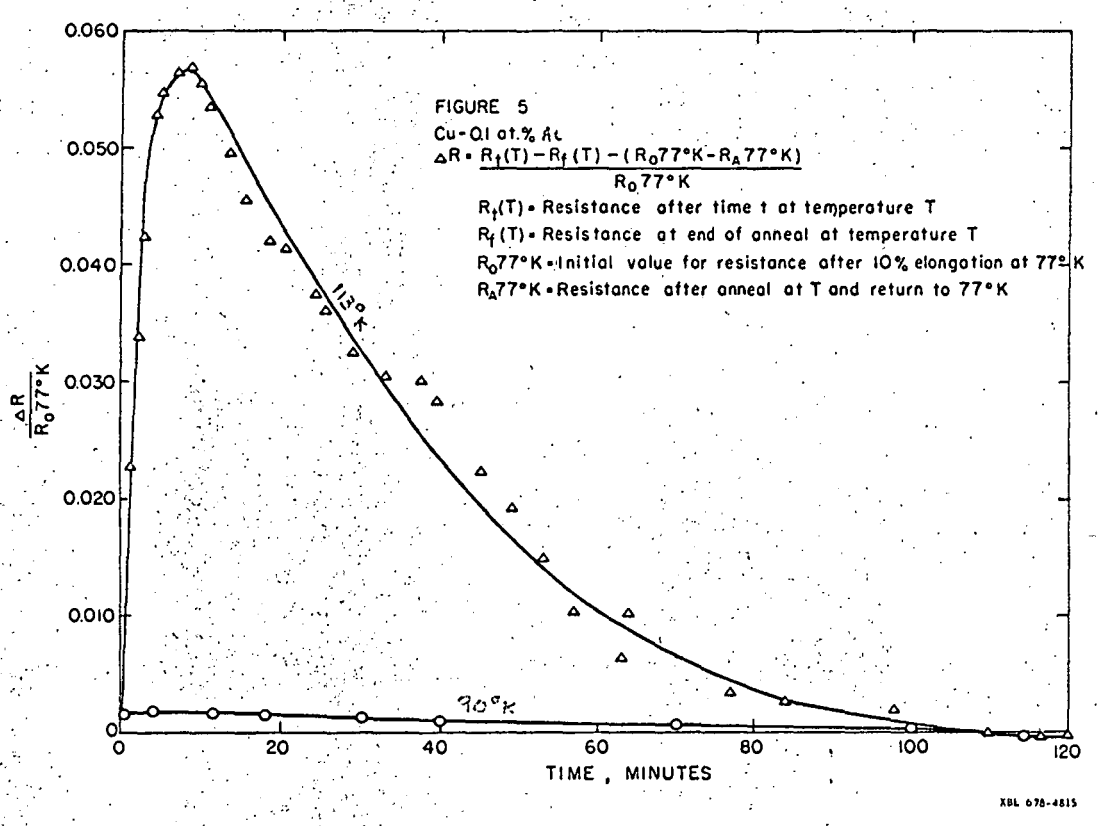


Fig. 5 Annealing curves after 10% elongation

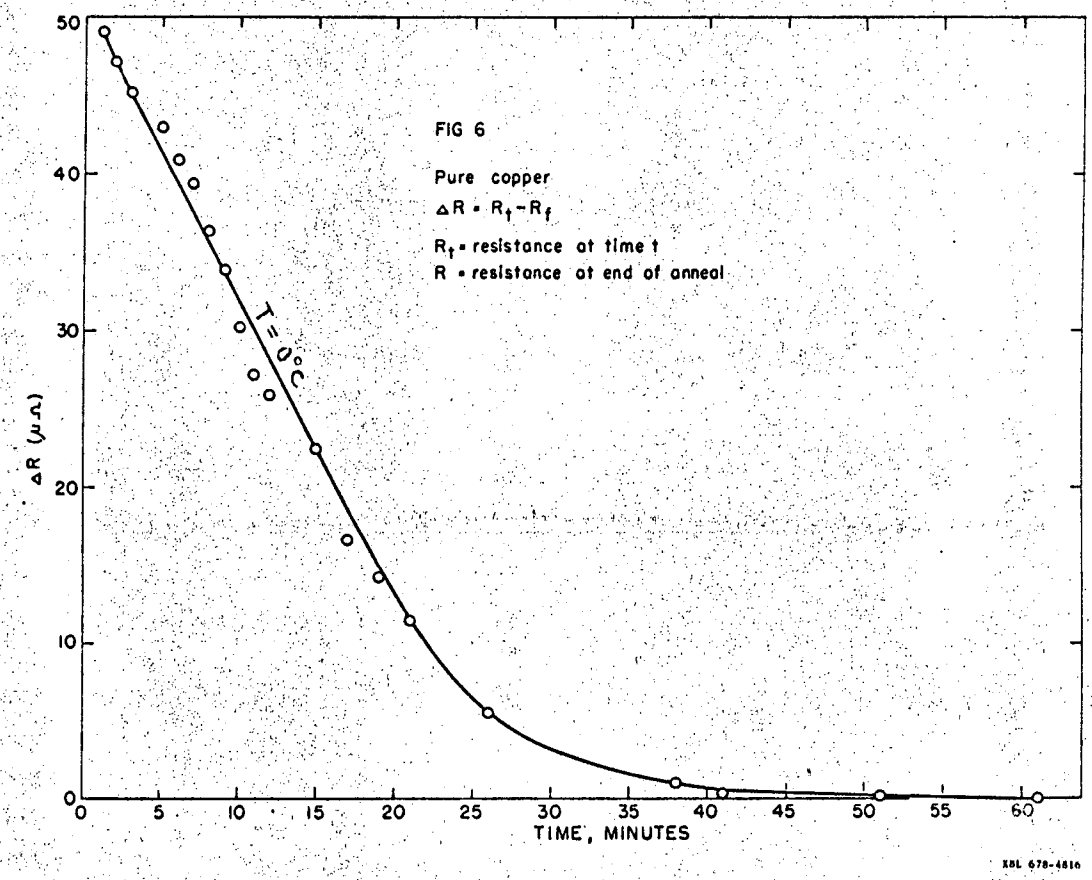


Fig. 6 Annealing curve for pure copper elongated 10% (T = 0°C)

The figures cited for the amount of recovered resistance of cold work were arrived at by first subtracting the resistance increase, ΔR_D, due to the increase in length and the decrease in cross sectional area of the specimen from the total resistance increase, ΔR_T, due to 10% elongation, then finding the percentage of this value which remained after annealing. The error in this value could be as large as ± 25% due to the inaccuracy in the measurements of the gage lengths and the diameter of the specimen.

Linde[9,10] has found a correlation between the incrase in resistivity, ρ_o, of noble metals caused by the mixing of 1% of an alloying element and the valency of the latter (see Figures 7 and 8). Linde finds that ρ_o is proportional to z^2 where z + 1 is the number of electrons outside of a closed d shell in the alloying element.

These results of Linde have been given a rather simple theoretical explanation by Mott.[11] The nucleus of a solvent atoms has a positive charge +e. The nucleus of the dissolved atom has a positive charge +(z+1)e, greater by ze than for an atom of the solvent element. The extra resistivity ρ_o must be regarded as being caused by the field of this extra charge producing the scattering of the electrons. The Rutherford scattering law states that the intensity of scattering is proportional to the square of the scattering charge and, hence, to z^2. From this proportionality of ρ_o to z^2 follows.

Included in Figures 7 and 8 are the results for aluminum in copper. Of course the value for z of aluminum could not be evaluated strictly according to Linde's verbal definition. However, his numerical definition,

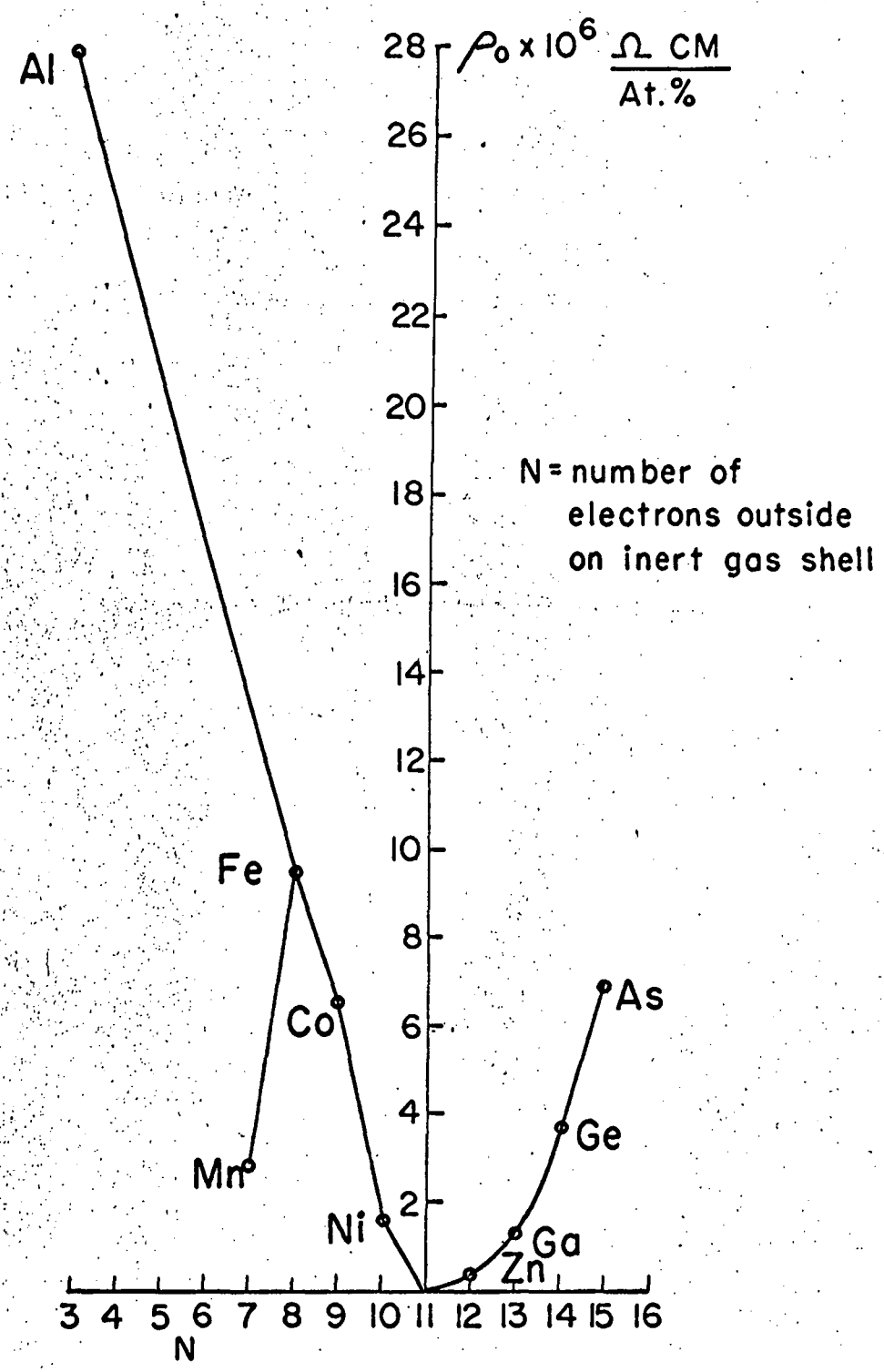


FIG 7 Additional resistivity due to 1 at.% of alloying element vs. the number of electrons outside an inert gas shell of the alloying element .

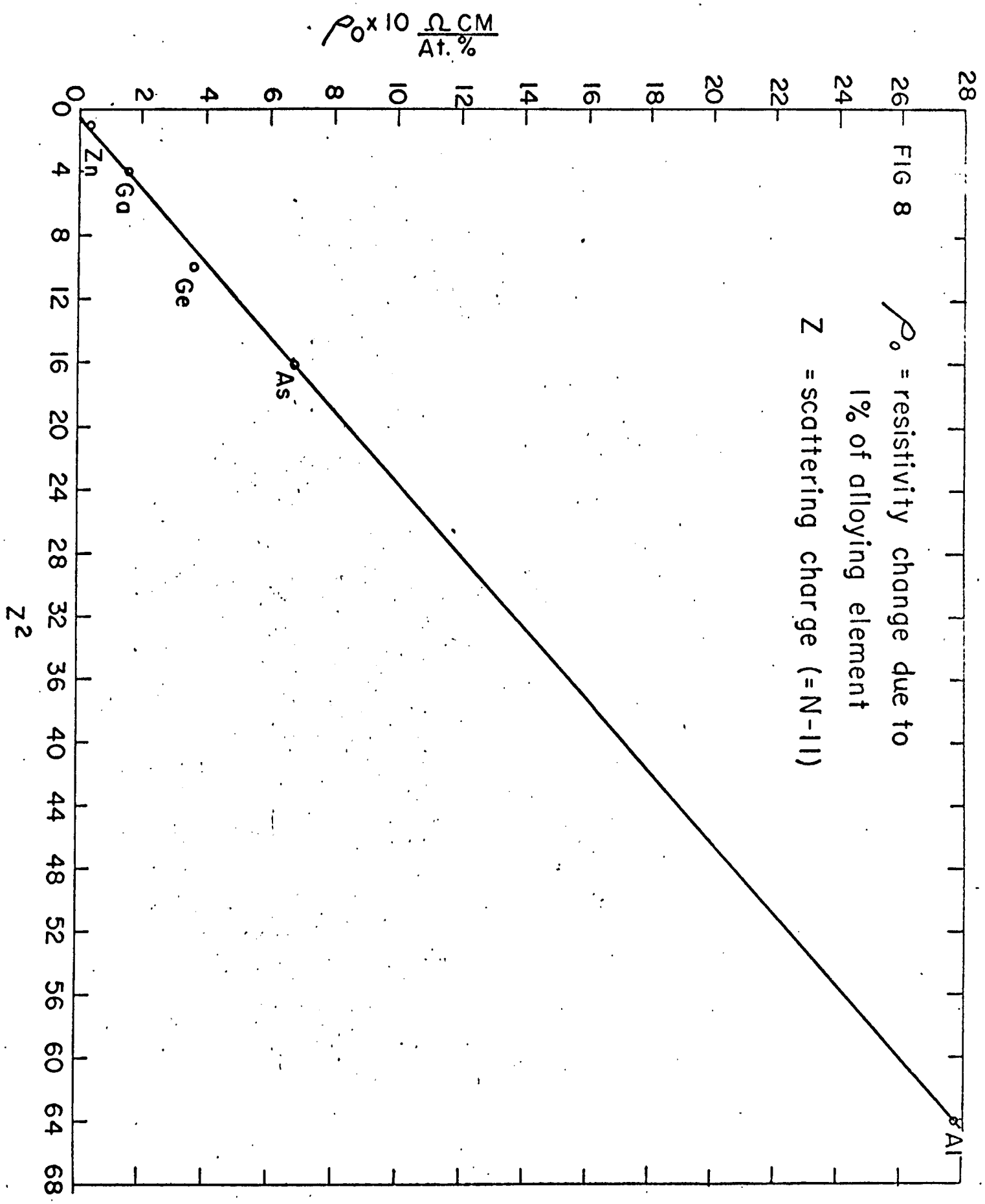


Fig. 8 Resistivity change due to 1 at.% alloying element vs. the square of the scattering charge

$z = N - 11$ where N is the number of electrons outside an inert gas shell, could be used yielding a value of 8 for the z of aluminum.

The Cu-Al alloy used in this investigation had only 0.1% Al but by employing the realtionship of Mott and Jones[10] showing a linear dependence of resistivity on percent alloying element the values for 1% aluminum could be determined.

VI. DISCUSSION

The initial resistivity increase upon annealing at 126°C observed by Cattaneo and Germagnoli[12] in a quenched gold-nickel alloy has been explained as being caused by an impurity-vacancy interaction. Another possibility is that the increase was caused by vacancies clustering about the impurity atoms. Still another explanation is the breakup of vacancy clusters into single vacancies. If this were the case then the resistivity rise should be observed in pure metals also. Since the resistivity of multiple vacancy clusters and vacancy-impurity complexes is not known, and since few experiments have been carried out on the kinetics of these effects, further discussion is not possible at this time.

The increase in resistivity has also been observed by Dawson in a gold + 4.64 at.% copper alloy. The rise begins at 20°C and peaks at about 125°C for a 5 min isochronal anneal. This rise has been attributed to an increase in short range order. The limited sensitivity of the equipment used did not allow careful observation of the annealing at temperatures slightly above 77°K and, thus, Dawson reports no evidence of any rise in resistivity at 113°K. The higher activation energy required for short range ordering would rule out the possibility of it being the rate controlling process at 113°K. A more likely explanation would be the breakup of multiple vacancy clusters or impurity-vacancy complexes.

The additional resistivity introduced by the addition of 0.1 at.% Al to copper is in good agreement with the previous work on the effects of small percentages of alloying elements.

VII. CONCLUSIONS

Much work remains to be done in identifying the annealing processes of cold work induced point defects in both pure metals and alloys. The annealing of interstitials is usually too rapid to be detected. But, with only a small difference between the deformation temperature and the annealing temperature and a method which will rapidly heat the specimen to the annealing temperature, the interstitials might be detected. The resistance heating anneal offers the best chance to observe the annealing of interstitials.

Much controversy exists over which vacancy mechanism is dominant at any particular time. Many investigators have detected a resistance rise in the annealing curves of alloys which is said to be due to an increase in short range order but which has not been systematically investigated. Careful work might possibly show that the breakup of vacancy clusters is accounting for the rise in resistance. A good constant temperature annealing environment with the ability to rapidly change from temperature to temperature used in conjunction with a resistance measuring unit similar to the one described herein could help identify some of the processes of anneal.

For the Cu-Al alloy the annealing at 90°K and 113°K shows a resistance rise before a fairly uniform decline to a constant value. The annealing of pure copper at 273°K was too rapid to detect the rise in resistance. The annealing was uniform and was 50% completed after 1 hour.

The addition of 0.1% aluminum to copper follows Rutherford's scattering law which states ρ_o is proportional to z^2.

ACKNOWLEDGMENT

This research was conducted as part of the activities of the Inorganic Materials Research Division of the Lawrence Radiation Laboratory of the University of California, Berkeley, and was done under the auspices of the U. S. Atomic Energy Commission.

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