THE INFLUENCE OF ISOTOPIC MASS ON SOME PHYSICAL PROPERTIES OF IRON

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ABSTRACT

This thesis presents the results of an experimental study to determine whether atomic mass has an appreciable influence on certain physical properties of metals. Iron was chosen for this investigation, several specimens of natural iron of high purity and two specimens of iron enriched in the isotopes Fe^{54} and Fe^{57} being available.

Measurements of the temperature coefficients of electric resistance between 67° and 270°K indicate an isotopic effect in qualitative agreement with deductions from the Gruneisen theory. The previous results of Tuyn may also be interpreted to give agreement with this theory and therefore are preferred to other previous work in disagreement with the theory.

No isotopic influence on thermoelectric power at temperatures between 80° and 270°K is found. If such an influence does exist, however, it is probably less than 0.15 $\mu V/{}^{\circ}K$ for a thermocouple made of Fe^{54} and Fe^{57}.

Measurements of the temperature of the alpha-gamma allotropic transformation do not indicate an isotopic effect on this temperature. A difference of 2.5°C in the transformation temperatures of the isotopes Fe^{54} and Fe^{57}, which is suggested by theoretical considerations, cannot be excluded on the basis of the present measurements, however, because of the hysteresis observed in the present study.

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I. INTRODUCTION.

The existence of isotopes of the chemical elements was established about forty years ago by Soddy and others (1). Subsequent investigations have demonstrated many differences in the physical properties of isotopes. In general, the radioactive properties of matter are profoundly influenced by isotopy; non-radioactive properties, which will be treated henceforth in this thesis, are usually less affected.

The non-radioactive properties which were first studied in this connection were those in which classical theory predicted a dependence on atomic mass -- for example, rates of gaseous diffusion and densities of gases. These classical predictions were soon verified and formed the basis for most of the useful methods of isotopic separation. Somewhat later, the study of isotopic effects anticipated by the quantum mechanics began. These latter effects are more numerous than the classical ones, though often smaller in magnitude and hence more difficult to detect. The knowledge that has been gained from their study, however, has often proved useful. Small variations in natural isotopic abundances, for example, are now used to obtain a variety of geological information (2).

The physical properties of metals have seldom been studied for isotopic effects. Theoretical reasoning suggests that such effects should be small. Furthermore, the materials available for studies in this field are small in amount. Consequently, the field has not been an attractive one for experimental studies. The knowledge that might be gained from such studies, however, is of potential value for the theory of metals, in which atomic mass is a particularly simple parameter.

The purpose of the present investigation is to determine whether atomic mass has an appreciable influence on certain physical properties of solid metals. The decision as to which properties could be studied most profitably was reached after a survey of previous work in this field had been made. This previous work may be discussed conveniently by reference to the following physical properties.

Specific Heat:

The specific heats of crystalline substances can, in many cases, be predicted by the Debye theory of specific heat (3) to very nearly the accuracy of experimental determination. In this theory, only universal constants appear, except for the so-called Debye temperature, Θ, which is characteristic of each particular substance. The theory requires that Θ vary inversely with the square root of atomic mass, so that, in principle, an isotopic effect could be expected in the specific heats of solids. Such an effect has seldom been sought experimentally because of the smallness of the isotopic specimens available. The studies which have been made have dealt with non-metallic solids, but these studies are of interest in the present investigation, since the Debye theory applies equally to metallic and non-metallic solids.

Measurements of the specific heats of the hydrogens between about 11° and 21°K indicate an isotopic effect (4). The observed specific heats of H_2 and D_2 can each be represented in the Debye theory with values of θ equal to 105° and 97°K, respectively. This difference in θ values is in the proper direction, but lesser in amount than the Debye theory predicts. Low temperature properties of the hydrogens are currently being investigated further (5).

The specific heats of H_2O and D_2O have been measured between 15° and 300°K by several investigators, whose results have been compared by Kirshenbaum (6). Although these investigators disagree by as much as 8 per cent, Kirshenbaum concludes that the specific heat of D_2O exceeds that of H_2O, perhaps by as much as 19 per cent at about 200°K.

Melting Point:

The theory of the metallic state has not been sufficiently perfected to enable the temperatures of allotropic transformation, melting, and boiling to be predicted with accuracy. These properties are known accurately only from experiment. This situation is generally true of non-metallic substances as well.

In 1919 Richards (7) reported that ordinary lead and uranium-lead do not differ in their melting temperatures by more than about 0.06°C, which was the uncertainty of his experimental measurements. Subsequently the more favorable case of the hydrogens was studied with the conclusion that the melting point of deuterium exceeds that of ordinary hydrogen by roughly 10 per cent (8). Thus the characteristic temperature, Θ, and the melting point are affected in opposite senses by the isotopy of hydrogen. Other experiments (6) have shown that the melting point of D_2O exceeds that of H_2O by about 3.81°C.

Specific Volume:

Measurements of the densities of several isotopic species of lead (9) indicate that the specific atomic volume is independent of atomic mass to within an experimental accuracy of about 3 parts in 10,000. Deuterium, however, has been reported to have a specific volume about 13 per cent less than that of ordinary hydrogen, on the basis of density measurements (8,10). This difference has been attributed to the relatively large anharmonicity of the hydrogen bond compared to the bonds of other chemical elements (8).

Comparative x-ray investigations of H_2O and D_2O single crystals suggest some small differences in the dimensions of the unit cell of crystal structure (11). While the height of this unit cell is apparently the same for both substances, at 0°C the basal dimension of the D_2O cell is reported to be 4.5165 ± 0.0014 Å, compared to 4.5135 ± 0.0014 Å for the H_2O cell. Thus the difference in cell dimension, if any, is quite small, though a "real difference" in the opinion of the investigator. The ratio of the molecular volumes of crystalline D_2O and H_2O estimated from these x-ray measurements is 1.0014.

Diffusion Rate:

Johnson (12) has proposed that the diffusion rate in solid metals should be influenced by atomic mass. His experiments show that the relative abundance of the various isotopes of nickel is altered by diffusion into copper in approximately the way that would be expected if the diffusion rate varies inversely with the square root of atomic mass. Recently Chemla and Sue (13) have proposed that the isotopic enrichment obtainable by solid state diffusion can be enhanced by the presence of an electric field.

Superconductivity:

The first search for an isotopic effect in superconductivity was reported by Onnes and Tuyn (14) in 1920. Two specimens of ordinary lead, atomic weight 207.20, and one specimen of uranium-lead, atomic weight 206.06, were studied. Within an experimental error of 1/40°C, all specimens were observed to undergo the superconducting transition at the same temperature. Some twenty years later the problem was reinvestigated by Justi (15), who claimed temperature measurements accurate to within a few 1/1000°K, but again with negative results.

In 1950, an isotopic effect on the transition temperature of mercury was discovered independently by Maxwell (16) at the National Bureau of Standards and by Reynolds, Serin, Wright, and Nesbitt (17) at Rutgers University. At first the quantitative nature of the effect was uncertain (18); however, subsequent measurements (19,20) as well as theoretical considerations (21,22) now strongly favor the relation $m^{0.5}T_c$ = constant, where m is the atomic mass and T_c is the transition temperature for superconductivity. Furthermore this relation appears to apply, at least approximately, to the superconductors tin (23,24,25,26,27,28) and lead (24,29). The latter case is of particular interest in view of the early negative results of Onnes and others. According to the relation $m^{0.5}T_c$ = constant, the isotopic shift of the transition temperature in lead should be about 0.025°K, which is the uncertainty of Onnes measurements (14), but significantly larger then the resolution claimed by Justi (15).

The experimental evidence for an isotopic effect in superconductivity has stimulated several theoretical discussions (18,21,22, 30,31,32), one conclusion of which is that the interaction of electrons and lattice vibrations in the superconducting material must be of primary importance in any theory of superconductivity.

Electric Resistance:

In 1922 Onnes and Tuyn (14) measured the electrical resistances at temperatures between 7° and 14°K of the same specimens as were used in their study of the superconductivity of lead isotopes. No difference was observed between the relative resistances* of these specimens. Subsequently Tuyn and Onnes (33) reinvestigated the relative

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* The relative resistance, r_t, is defined as R_t/R_o, where R_t is the resistance measured at temperature t and R_o is the resistance measured at 0°C. Thus the relative resistance is independent of specimen geometry.

resistances of the same specimens with greater precision. The differences then observed between the uranium-lead and either of the normal leads were not markedly larger than the differences observed between the two normal leads. In 1929 Tuyn (34) repeated some of these measurements and extended the range of temperatures at which observations were made (see Fig. 17).

At about the same time Jaeger and Steinwehr (35) sought a difference in the electrical resistivities of mercury isotopes at room temperature. The difference they observed, approximately 0.0003 per cent, was of the same magnitude as their experimental error. Their work was handicapped by the low degree of enrichment of the mercury isotopes available to them (about one per cent of the enrichment available to contemporary investigators (36)). Their use of a capillary tube into which each specimen could in turn be poured, however, had the advantage of imposing the same geometry on all specimens, so that the relationship between resistance and resistivity was the same for all specimens. Thus their technique permits the direct comparison of electrical resistivities, in contrast to the other resistance measurements discussed here.

In 1941 the question of the relative resistances of normal and uranium-lead was again raised, this time by Justi (15). Measurements were limited to one specimen of each of these isotopic forms of lead, so that no direct indication of experimental errors is available in Justi's work. Justi observed a larger difference in relative resistance between the two lead isotopes than had been reported by Onnes et al. (14,33,34). His results can be interpreted to indicate an isotopic effect opposite in sign to that which would be expected on the basis of the widely accepted Gruneisen theory (37) of resistivity.

Thus the above researches established the likelihood that an isotopic effect on electrical resistance, if any, would be small. In addition, the possibility was introduced that the resistance is influenced by atomic mass in a way opposite to the expectations of the Gruneisen and similar theories.

It is evident from this discussion of previous work that there are some outstanding problems associated with isotopic effects in solid metals. One of the most attractive of these problems appeared to the present investigator to be that of the effect of atomic mass on electric resistance. Theories of the electric resistance indicate an isotopic effect on this property over a considerable range of temperatures. Furthermore, the dependence of the transition temperature for superconductivity on atomic mass suggests a similar dependence of the electric resistance at low temperatures. Considerably greater differences in isotopic mass are available at present than has been the case in earlier investigations of this problem, so that a more satisfactory comparison of experiment with theory may be possible in the present investigation than has been obtained heretofore.

Further investigation of isotopic effects on the specific volumes and diffusion rates of metals does not appear promising to the present investigator in view of technical problems that are associated with experimental studies of these properties. The same objection applies to an experimental study of isotopic effects on specific heat. Previous studies of the influence of atomic mass on melting points, however, suggest a related problem particularly pertinent to metallurgy, namely, that of the influence of atomic mass on the temperatures of allotropic transformations. This latter problem is treated in the present investigation, as is another problem not previously studied, namely, that of the influence of atomic mass on thermoelectric power.

The selection of a metal for the present investigation depends upon considerations of experimental technique. Iron was selected therefore, since it is available in the form of oxide of high purity, which can be reduced readily, and the techniques of melting and forming are well known. In principle, lithium would be more attractive for this study, since its stable isotopes, Li^6 and Li^7, exhibit the largest percentage difference in mass of any metal, but the technical problems associated with the preparation of small specimens of these isotopes of high purity were considered to be too difficult.

II. DESCRIPTION OF THE SPECIMENS.

The experimental work described in this thesis was performed on several specimens of natural iron* and two specimens of isotopically enriched iron. The materials from which these specimens were prepared are described in Table 1.

Estimates of the chemical impurities present in the materials used for the present investigation are listed in Tables 2 and 3. The estimates for specimens "54" and "57" are quoted from a spectrographic analysis supplied by Dr. C.P. Keim, Isotope Research and Production Division, Atomic Energy Commission, Oak Ridge, Tennessee, to which the following comment was appended: "Impurities other than those listed were not detected". Impurity estimates for specimens "BS" and all "NR" specimens are quoted from Moore (38), and for specimen "Ph" are based on verbal statements of Dr. J.D. Fast, Philips Lamp Company, Eindhoven, Holland. In the case of the Fe_2O_3 powder from which specimen "CP" was prepared, J.T. Baker and Company, Phillipsburg, New Jersey, supplied the impurity estimates.

The estimated isotopic compositions of the specimens are listed in Table 4. These estimates are quoted from Keim, Normand, and Weaver (36) in the case of natural iron and from a mass analysis supplied by Dr. C.P. Keim in the cases of specimens "54" and "57".

Specimens in the form of pellets were required for the first experiment performed in these investigations. Specimens "54",

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* Iron with the isotopic composition found in nature.

"57", "CP", and "NR1" in the form of metallic powders were compacted at a pressure of about 40,000 lb/in^2. in a non-magnetic die made of beryllium copper, thus forming pellets about 0.17 in. in diameter and 0.08 in. in height. These pellets were sufficiently coherent so that with careful handling they could be transferred to a sintering furnace without crumbling. Sintering was accomplished by heating at 1600°F in pure hydrogen for four hours. While the porosity of the sintered pellets was about 20 per cent, they were strong enough to permit handling without difficulty.

The experiments described in Parts IV and V of this thesis required specimens in the form of wires about 0.020 in. in diameter and 4 in. long. Specimens "54", "57" and "NR1" in pellet form were melted into ingots in the following manner. An alumina crucible was formed from a piece of Alundum tubing of 1/16 in. ID, 1/8 in. OD, and 3/4 in. length by closing one end of the tubing in an oxygen-hydrogen flame. The open end of the tubing was then flared by grinding with a conical abrasive wheel. The crucible was placed vertically in the furnace shown in Fig. 1. The pellet to be melted was placed on top of the crucible and the assembly heated in a chamber evacuated to a pressure of 10^{-5} mm. Hg. until the pellet melted. The melted pellet formed into a sphere as a result of surface tension and remained on the flared mouth of the crucible. Pure helium was suddenly admitted to the vacuum chamber, forcing the molten iron down into the crucible. The ingots produced in this manner were about 1/16 in. in diameter and 7/16 in.

long and were separated from the crucibles by fracturing the latter.

Each of the ingots was then drawn into wire, as described below, using wire-drawing dies and a lathe equipped with collet chucks. One end of the ingot to be drawn was swaged by compression in the collet chuck so that this end could be started through the die. The die was secured to the tool carriage of the lathe and the swaged end of the ingot gripped in the collet chuck. The ingot was then drawn through the die by causing the tool carriage to travel away from the collet. Drawing in this manner was repeated until a wire diameter of about 0.021 in. was obtained.

Specimens "BS" and "Ph", which were received as wires of 0.080 in. and 0.040 in. diameter respectively, were drawn to diameters of about 0.021 in.

TABLE 1.

Sources of the Specimens.

Specimen Designation	Source
"54"	Isotope Division, Atomic Energy Commission, Oak Ridge, Tennessee loaned for the present investigations approximately 285 milligrams of Fe_2O_3 powder, the iron content of which was enriched in the isotope Fe^{54}. The present author reduced this oxide to a metallic powder by heating at 1200°F in pure hydrogen for four hours. The metal prepared in this way is designated specimen "54".
"57"	Isotope Division, Atomic Energy Commission, Oak Ridge, Tennessee loaned for the present investigations approximately 287 milligrams of Fe_2O_3 powder, the iron content of which was enriched in the isotope Fe^{57}. The present author reduced this oxide to a metallic powder by heating at 1200°F in pure hydrogen for four hours. The metal prepared in this way is designated specimen "57".
"BS"	A 0.080 in. diameter wire of high purity iron from the ingot designated no. 8 by Cleaves and Hiegel (39) was obtained from the National Bureau of Standards, Washington, D.C. This metal is designated specimen "BS".
"Ph"	A 0.040 in. diameter wire of high purity iron was obtained from the Philips Lamp Company*, Eindhoven, Holland. This metal is designated specimen "Ph".

* Courtesy of Dr. J.D. Fast in 1951.

TABLE 1 (continued).

Sources of the Specimens.

Specimen Designation	Source
"CP"	Fe_2O_3 powder, of grade "chemically pure", was obtained from J.T. Baker and Company, Phillipsburg, New Jersey. The present author reduced this oxide to a metallic powder by heating at 1200°F in pure hydrogen for four hours. The metal produced in this way is designated specimen "CP".
All specimens with the designation "NR" followed by an arabic numeral originated from a 10 lb. vacuum cast ingot of high purity iron supplied by National Research Corporation, Boston, Massachusetts.	
"NR1"	A coarse powder was obtained by filing the ingot. This metal is designated specimen "NR1".
"NR2"	A cylinder about 0.17 in. in diameter and 0.08 in. high was machined from the ingot. This metal is designated specimen "NR2".
"NR3"	A cylinder about 0.17 in. in diameter and 0.08 in. high was machined from the ingot. This metal is designated specimen "NR3".
"NR4"	A wire of about 0.021 in. diameter was drawn from the ingot. This metal is designated specimen "NR4".

TABLE 2.

Estimated Chemical Impurities of the Specimens (in atoms per million atoms).

Impurity	Specimen "Ph"	"BS"	"54"	"57"	All "NR"
Al	10	1	...	<400	50-60
Ag	...	...	<400	...	...
Be	...	2	...	...	...
Ca	...	<1	...	...	...
Co	<5	...	...	...	90
Cr	...	<1	...	...	<20
Cu	<5	<20	400	400	<20
Mg	<16	<1	<200	<200	...
Mn	...	...	...	<400	<100
Mo	...	...	<400	<400	<20
Ni	<30	<1	800	800	140-400
Sb	...	0.01	...	...	...
Si	~20	9	...	...	300
Sn	...	<1	...	...	<30
Ti	...	...	...	...	80
V	...	...	...	...	<50
C	<10	10	...	...	60-100
H	...	2	...	...	1.7
N	<10	2	...	...	1-10
O	<10	27	...	...	26-80
P	...	<5	...	...	10-20
S	<10	19	...	...	20
Estimated Total Impurities	...	<98	...	...	~1150

TABLE 3.

Estimated Chemical Impurities of the Fe_2O_3 Powder Supplied by J.T. Baker and Company.

NO_3 . . .	0.02%	Cu . . .	0.01%
SO_4 . . .	0.10%	Mn . . .	0.02%
PO_4 . . .	0.00%	Zn . . .	0.01%
SiO_2 . . .	0.04%	As . . .	0.0000%
Substances not precipitated by $NH_4(OH)$ . . .			0.16%

TABLE 4.

Isotopic Composition of the Specimens.

Isotope	Specimen		
	Natural Iron Atom %	"54" Atom %	"57" Atom %
Fe^{54}	5.90	93.06 ± 0.05	0.458 ± 0.005
Fe^{56}	91.52	6.62 ± 0.05	15.92 ± 0.06
Fe^{57}	2.24	0.248 ± 0.012	83.44 ± 0.06
Fe^{58}	0.34	0.079 ± 0.019	0.177 ± 0.010
Average Atomic Wt.	55.91	54.15	56.83
Mass Difference from Natural Iron	....	-3.1^5%	$+1.6^5$%

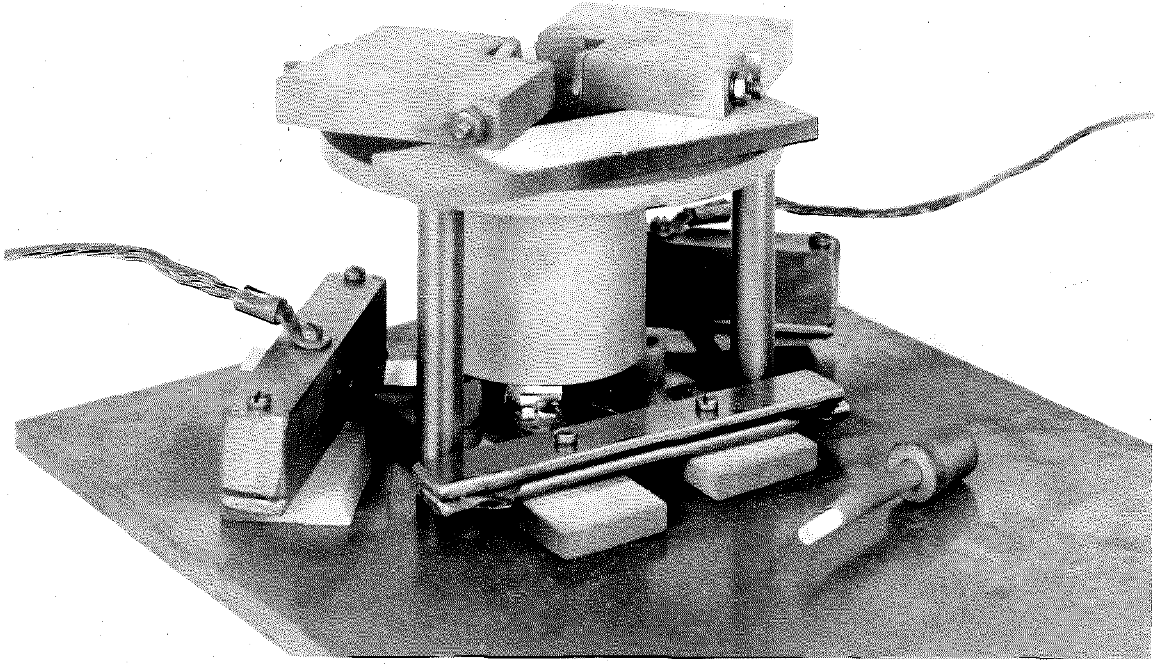

Figure 1. Radiation Furnace used for Vacuum Melting. An alumina crucible may be seen in the right foreground.

III. THE TEMPERATURE OF THE ALPHA-GAMMA ALLOTROPIC TRANSFORMATION IN IRON ISOTOPES.

The allotropic transformations exhibited by some metals are of fundamental importance in many metallurgical processes. The alpha-gamma transformation in iron and many of its alloys, for example, is perhaps the most important factor in the heat treatment of steel. The influence of chemical composition on this transformation has been studied extensively. In the present investigation, an influence of isotopic composition on the equilibrium temperature of the transformation is sought. If such an influence can be measured, it may afford a means of evaluating the relative importance of electronic and lattice energies in this transformation.

An isotopic effect may be predicted in the present case from theories of the lattice vibrations of crystalline substances. In general, the most successful of these theories is that due to Debye (3), and this theory will be adopted in the following analysis. The thermodynamic properties of metals cannot be described completely in terms of the lattice vibrations treated in the Debye theory, however, so that other factors, which, in themselves, would not be affected by atomic mass, must nevertheless be taken into account. In particular, the electronic contribution to the specific heats of ferromagnetic elements like iron cannot be neglected.

Certain assumptions common to theories of the solid state will be indicated before presenting an analysis of the present problem.

These assumptions are discussed in detail in treatises on the solid state, for example, the works of Mott and Jones (40), Cottrell (41), and Kittel (42). The specific heat, C, entropy, S, internal energy, E, and free energy, F, of a solid metallic element may be written*,

$$\begin{aligned} C &= C_{\ell} + C_r \\ S &= S_{\ell} + S_r \\ E &= E_{\ell} + E_r \\ F &= F_{\ell} + F_r \end{aligned} \qquad \text{III-1}$$

where the subscript ℓ denotes the contribution toward the given property arising from lattice vibrations and the subscript r refers to all other contributions to the property. Thus a superposition principle for these properties is implied in relations III-1. In addition, the following assumptions are commonly made:

(a) The properties with subscript r are not influenced by atomic mass.

(b) The binding forces between the atoms of the crystal are unaffected by atomic mass.

(c) Where a metallic element is composed of a variety of isotopic species, each atom is considered to possess a mass equal to the average mass of the isotopic composition.

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* Constant pressure and constant volume conditions are usually not distinguished in analyses of the thermodynamics of metals (see, for example, Cottrell (41)). Such a distinction is not necessary in those theories of lattice vibrations which assume linear binding forces between the atoms, for example, the Debye theory.

As a result of these assumptions, the isotopic effect indicated by the Debye functions for lattice vibrations may be related to the equilibrium of phases at the allotropic transformation temperature.

The Debye functions for free energy and internal energy may be written*

$$F = \frac{9}{8} R\theta + 3RT \left[\ln(1 - e^{-\theta/T}) - (\frac{T}{\theta})^3 \int_0^{\theta/T} \frac{y^3\, dy}{e^y - 1} \right] \qquad \text{III-2}$$

$$E = \frac{9}{8} R\theta + \frac{9RT^4}{\theta^3} \int_0^{\theta/T} \frac{y^3\, dy}{e^y - 1} \qquad \text{III-3}$$

where

θ = Debye characteristic temperature.

R = Gas constant.

T = Temperature.

According to relation III-2, the variation in free energy due to a variation in characteristic temperature is

$$\delta F_\ell = \frac{\delta \theta}{\theta} E_\ell \, . \qquad \text{III-4}$$

According to the Debye theory, the characteristic temperature, θ, depends on the lattice binding forces and atomic mass, being inversely proportional to the square root of the latter. Thus, in view of

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* The zero-point energy, which is sometimes omitted in descriptions of the Debye functions, must be taken into account in the present discussion.

assumption (b),

$$\frac{\delta\theta}{\theta} = -\frac{1}{2}\frac{\delta m}{m} \qquad \text{III-5}$$

for a small variation in atomic mass. Combining relations III-4 and III-5,

$$\delta F_\ell = -\frac{1}{2}\frac{\delta m}{m} E_\ell \; . \qquad \text{III-6}$$

According to assumption (a), the dependence of free energy on atomic mass is described completely by relation III-6, which may now be related to the temperature of the allotropic transformation. At this temperature, the free energies of the two phases in equilibrium are equal,

$${}_\alpha F = {}_\Gamma F \qquad \text{III-7}$$

and vary with temperature according to the relation

$$\frac{\partial F}{\partial T} = -S. \qquad \text{III-8}$$

For a combined variation in temperature and mass, the variation in free energy of the alpha phase is

$$\delta\,{}_\alpha F = -\,{}_\alpha S\,\delta T - \frac{1}{2}\frac{\delta m}{m}\;{}_\alpha E_\ell \qquad \text{III-9}$$

and similarly for the gamma phase. Hence, the amount by which the free energy of the alpha phase exceeds that of the gamma phase, for the variations δT and δm, is

$$({}_\Gamma S - {}_\alpha S)\,\delta T + \frac{1}{2}\frac{\delta m}{m}\,({}_\Gamma E_\ell - {}_\alpha E_\ell) \qquad \text{III-10}$$

which must be zero at the new phase change temperature associated with atoms of mass $(m + \delta m)$. Consequently the variation, δm, in atomic mass entails the corresponding variation in phase change temperature

$$\delta T = -\frac{1}{2}\frac{\delta m}{m}\frac{{}_{\Gamma}E_{\ell} - {}_{\alpha}E_{\ell}}{{}_{\Gamma}S - {}_{\alpha}S}. \qquad \text{III-11}$$

Relation III-11 may be written

$$\frac{\delta T}{T} = \frac{1}{2}\frac{\delta m}{m}\left(\frac{-L_{\ell}}{L}\right) \qquad \text{III-12}$$

where

$L_{\ell} = {}_{\Gamma}E_{\ell} - {}_{\alpha}E_{\ell}$, Latent heat due to lattice vibrations only.

$L = L_{\ell} + ({}_{\Gamma}E_{r} - {}_{\alpha}E_{r})$, Total latent heat.

The quantity L_{ℓ} may be calculated from relation III-3, using experimentally determined estimates for the characteristic temperatures of the two phases.

$$\begin{aligned} {}_{\alpha}\theta &= 420^{\circ}\text{K} \\ {}_{\Gamma}\theta &\cong \frac{3}{4}\,{}_{\alpha}\theta \end{aligned} \qquad L_{\ell} \sim -20 \text{ cal./mole} \qquad \text{III-13}$$

The Debye temperatures, ${}_{\alpha}\theta$ and ${}_{\Gamma}\theta$, are estimated from specific heat measurements, directly on alpha iron in the case of ${}_{\alpha}\theta = 420^{\circ}$K, (43), and on a series of iron-manganese alloys with extrapolation to zero-manganese content in the case of ${}_{\Gamma}\theta \sim \frac{3}{4}\,{}_{\alpha}\theta$, (44,45). Thus lattice vibrations apparently make a small negative contribution to the latent heat.

Since E_r has an appreciable temperature dependence in iron, L cannot be calculated by any of the lattice vibration theories. Direct calorimetric measurement (46), however, indicates that L is approximately 218 calories/mole.

These estimated values of L_ℓ and L, substituted in relation III-12, suggest that the alpha-gamma transformation temperature of specimen "57" would exceed that of specimen "54" by about 2.5°C.

Measurement of allotropic transformation temperatures was accomplished in the present experiment by means of the well-known method of thermal analysis. In this method, which has been described in detail by Hume-Rothery et al. (47), the temperature of a specimen being slowly heated or cooled is recorded. The latent heat accompanying a change of phase produces an arrest in the temperature record, thus indicating the transformation temperature.

Figure 2 shows the radiation furnace used for the thermal analysis; the thermocouple wires that support the specimen inside the furnace may be seen. This assembly was operated in a chamber evacuated to a pressure of 10^{-5} mm. Hg. to prevent oxidation of the specimen. The thermocouple was formed of chromel and alumel wires, 0.012 in. in diameter, spot-welded to the specimen by the discharge of an electric capacitor. The same thermocouple was used for all the present thermal analyses.

Figure 3 shows the circuit used to record specimen temperatures. The bias potentiometer permitted suppression of the zero of the temperature scale and consequently increased amplification of this scale.

Figure 4 shows a thermal analysis record typical of those obtained in this experiment. The hysteresis associated with this transformation is evident in the figure. The arrests in the recordings could be located to within one degree centigrade in every case and to within one-half degree centigrade in a few favorable cases. The heating and cooling rates used varied from 3 to 10°C/minute and within this range of variation did not influence the transformation temperature more than one degree centigrade.

The results of the thermal analysis measurements are exhibited in Table 5. The conversion of thermocouple emf to degrees centigrade was made by means of the tables given by Roeser, Dahl, and Gowens (48).

The theoretical discussion of the alpha-gamma allotropic transformation presented earlier in this thesis referred to the equilibrium temperature for a change of phase. Examination of Table 5, however, indicates that appreciable hysteresis, and hence departure from equilibrium, characterized the transformations occurring in the experiment. The equilibrium temperature of transformation for each specimen must lie between the observed transformation temperatures for thermal analysis on heating and on cooling. The bounds placed on the equilibrium temperature by this consideration, however, leave such a large uncertainty in the equilibrium temperature that an isotopic effect of the order of 2.5°C could not be distinguished in such measurements. The averages of the observed transformation temperatures for thermal analysis on heating and on cooling are, therefore, indicated in Table 5 for the various specimens. These average temperatures of transformation form an arbitrary basis for comparison of the equilibrium temperatures of transformation of the various specimens. Examination of Table 5, however, indicates no relationship between the average temperatures of transformation and atomic mass. Thus the present results do not demonstrate an isotopic effect on the equilibrium temperature of the alpha-gamma allotropic transformation. An isotopic effect of the order of magnitude of that calculated earlier in this thesis cannot be excluded, however, in view of the hysteresis associated with the transformations occurring under experimental conditions.

A potentially more favorable case for the study of isotopic effects on allotropic transformations is the low temperature transformation reported for lithium by Barrett and Trautz (49). This transformation occurs near 70°K, which is about 20 per cent of the Debye temperature of the high temperature phase of solid lithium. The departure of the Debye theory from classical theory is considerably larger at such low temperatures than in the case treated in the present investigation. This fact suggests that the isotopic effects associated with the Debye theory may be more pronounced in the case of lithium than in the case presently investigated.

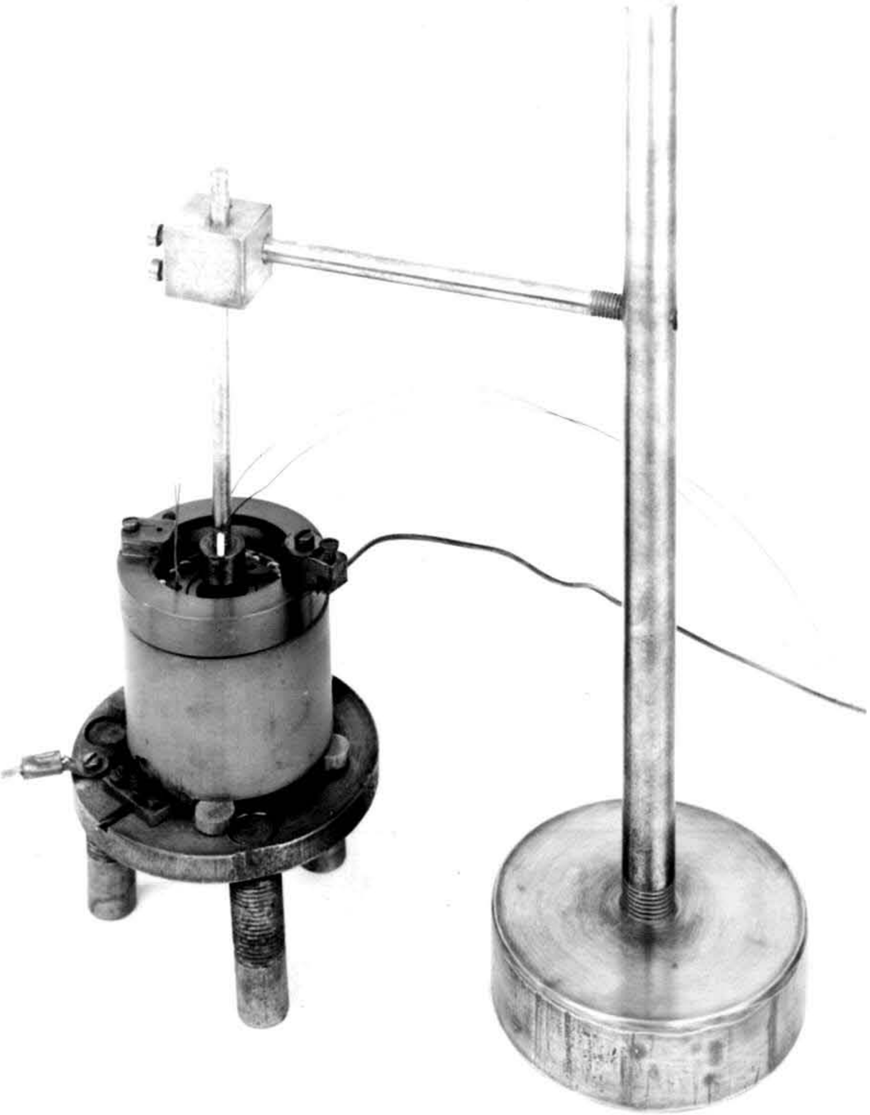
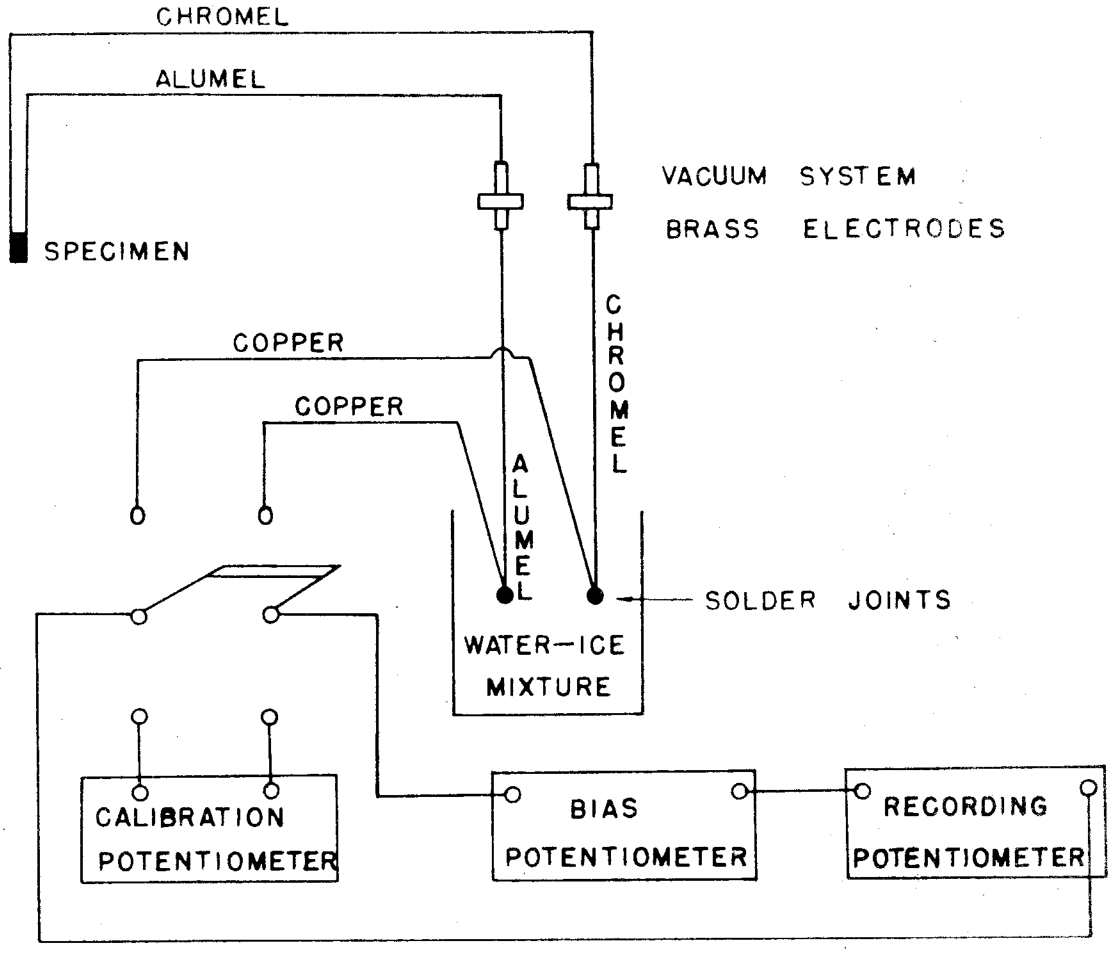


Figure 2. Furnace and Specimen Support used in Thermal Analysis.



NOTES

1. BOTH POTENTIOMETERS ARE LEEDS AND NORTHRUP TYPE NO. 8662.
2. THE RECORDING POTENTIOMETER IS A LEEDS AND NORTHRUP SPEEDOMAX TYPE G.

FIG. 3. DIAGRAM OF RECORDING CIRCUIT USED IN THERMAL ANALYSIS.

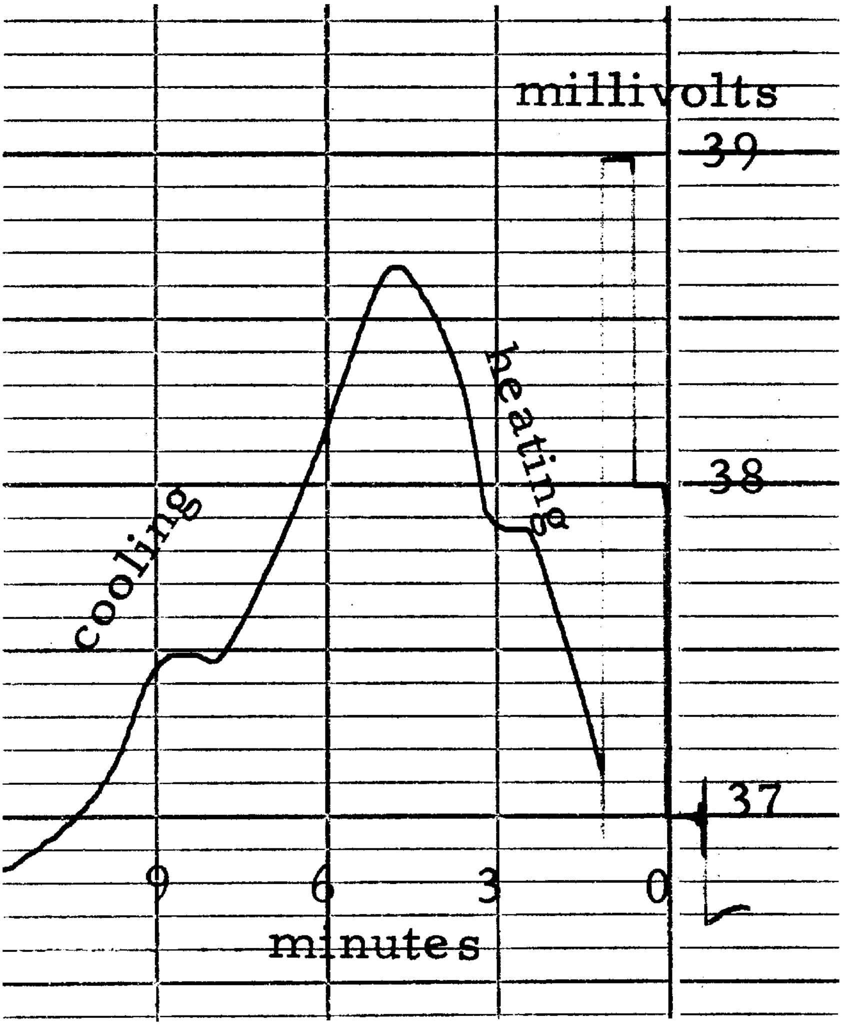


Figure 4. Typical Thermal Analysis Record. Temperature calibration marks are shown at right. One millivolt corresponds to a temperature difference of about 25°C.

TABLE 5.

Observed Transformation Temperatures.

Trial	Temp. Unit	Specimen "NR1"	"NR2"	"NR3"	"CP"	"54"	"57"
		Thermal Analysis on Heating					
1	mv.	37.92	37.88	37.84	38.3	38.18	38.46
2	mv.	37.88	37.87	37.88	38.32	38.16	38.48
3	mv.		- -	37.82	38.3	38.13	- -
Avg.	(mv.	37.9	37.88	37.85	38.31	38.16	38.47
	(°C.	914°	913°	912°	924°	920°	928°
		Thermal Analysis on Cooling					
1	mv.	37.43	37.57	37.50	37.22	37.38	37.14
2	mv.	37.41	37.59	37.49	37.2	37.39	37.05
3	mv.		37.53	37.54	37.2	37.4	37.13
4	mv.		- -	- -	- -	- -	37.09
Avg.	(mv.	37.42	37.56	37.51	37.21	37.39	37.10
	(°C.	902°	905°	904°	896°	901°	894°
		Hysteresis					
	mv.	0.48	0.32	0.34	1.10	0.77	1.37
	°C.	12°	8°	9°	28°	19°	34°
		Average of Results on Heating and Cooling					
	mv.	37.66	37.72	37.68	37.76	37.78	37.79
	°C.	908°	909°	908°	910°	911°	911°

IV. THE ELECTRIC RESISTANCE OF IRON ISOTOPES AT TEMPERATURES BETWEEN 67° and 270°K.

The electric resistivity of the heavier isotopes of a metallic element should be greater than that of the lighter isotopes, according to established theories of the resistivity. This prediction has not been confirmed in previous investigations. The problem is re-examined by the present investigator in an attempt to reconcile theory and experiment.

The resistivity, ρ, of high purity metals may be written (40,41)

$$\rho = \rho_{\ell} + \rho_{r} \qquad \text{IV-1}$$

where the subscripts have the same significance as previously. The residual resistivity, ρ_r, is due to the lattice imperfections and chemical impurities present in actual crystals and is distinctly less temperature dependent than ρ_{ℓ}, (40). This latter fact may be expressed by the relation

$$\frac{\partial \rho_r}{\partial T} = 0 \qquad \text{IV-2}$$

which is known as Mathiessen's rule and is a satisfactory approximation for impurity concentrations as great as one and two atomic per cent (40).

Several theories have been advanced to account for the resistivity, ρ_{ℓ}, due to lattice vibrations (40). The most successful of these is that due to Gruneisen (37), who gives the following formula

$$\frac{\rho_\ell}{T} = K\,G\left(\frac{\theta^G}{T}\right) \qquad \text{IV-3}$$

where

K is a constant

θ^G is a characteristic temperature*

$$G = \left(\frac{T}{\theta^G}\right)^4 \left[5\int_0^{\theta^G/T} \frac{y^4\,dy}{e^y - 1} - \frac{(\theta^G/T)^5}{e^{\theta^G/T} - 1}\right]$$

is known as the Gruneisen function.

This relation has been described as semi-empirical in view of the assumptions made in its derivation (42), but has given the most satisfactory agreement with experiment of any of the formulae for ρ_ℓ in the temperature range, $\sim 10^\circ K < T \leq \theta^G$, (42,50).

According to relation IV-3, the variation in resistivity due to a variation in characteristic temperature is

$$\delta\rho_\ell = -K\,\frac{\delta\theta^G}{\theta^G}\,T^2\,\frac{\partial G}{\partial T}\,. \qquad \text{IV-4}$$

According to the Gruneisen theory, the characteristic temperature, θ^G, varies inversely with the square root of atomic mass. Hence

$$\frac{\delta\theta^G}{\theta^G} = -\frac{1}{2}\,\frac{\delta m}{m} \qquad \text{IV-5}$$

for a small variation in atomic mass. Combining relations IV-4 and IV-5,

---

* The Debye and Gruneisen characteristic temperatures are, in general, not the same (51).

$$\delta\rho_{\ell} = K\left(\frac{1}{2}\frac{\delta m}{m}\right) T^2 \frac{\partial G}{\partial T} . \qquad \text{IV-6}$$

The isotopic effect indicated in this relation is not, in itself, necessarily small. For example, the percentage increase in resistivity associated with a one per cent increase in atomic mass, according to this relation, is two per cent at low temperatures, but decreases with increasing temperature. A hindrance to the detection of such an effect, however, arises from the difficulty of relating resistance measurements to resistivity.

The electric resistance of a metal specimen is related to its resistivity by a geometric factor. Since the resistances of small specimens, such as are used in the present investigations, can be measured with significantly more accuracy than can the geometries of the specimens, it is desirable to avoid the measurement of the latter. This latter measurement may be avoided by measuring the temperature dependence of the resistances of the specimens being compared.

The resistance, ${}_{i}R$, of specimen "i" may be written

$${}_{i}R = {}_{i}g({}_{i}\rho_{\ell} + {}_{i}\rho_{r}) \qquad \text{IV-7}$$

where ${}_{i}g$ is the geometric factor of specimen "i". The resistance ${}_{i}R$ is to be compared with the resistance of comparison specimen "Ph" over a range of temperatures.

$${}_{Ph}R = {}_{Ph}g({}_{Ph}\rho_{\ell} + {}_{Ph}\rho_{r}) \qquad \text{IV-8}$$

A plot of $({}_{i}R - {}_{Ph}R)$ versus ${}_{Ph}R$ is more useful for this comparison than a plot of ${}_{i}R$ versus ${}_{Ph}R$, however. Since ${}_{i}\rho_{\ell} = {}_{Ph}\rho_{\ell} + \delta\rho_{\ell}$, where $\delta\rho_{\ell}$ is the mass dependence of the resistivity,

$$ {}_{i}R - {}_{Ph}R = \left(\frac{{}_{i}g}{{}_{Ph}g} - 1 \right) {}_{Ph}R + {}_{i}g({}_{i}\rho_{r} - {}_{Ph}\rho_{r}) \qquad \text{IV-9} $$

$$ + {}_{i}g(\delta\rho_{\ell}) $$

where ${}_{i}g(\delta\rho_{\ell}) = \delta_{i}R$.

The first term on the right of relation IV-9 is a linear function of ${}_{Ph}R$. The second term, which depends on the differences in residual resistance of the specimens, is temperature independent according to Mathiessen's Rule, relation IV-2, and hence is a constant. The last term exhibits the dependence of resistivity on atomic mass.

If $\delta\rho_{\ell}$ were a linear function of ${}_{Ph}R(T)$, its contribution to $({}_{i}R - {}_{Ph}R)$ would be indistinguishable from that of the geometric factors and residual resistances, since the latter are not measured in the present experiment*. Furthermore the slope associated with the linear contribution of the term

$$ \left(\frac{{}_{i}g}{{}_{Ph}g} - 1 \right) {}_{Ph}R $$

is not known. Thus the linear components of both of these terms may be removed in such a way as to keep the ordinates of the points

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* Residual resistances can be measured at temperatures near 0°K, since $\rho_{\ell} \rightarrow 0$ as $T \rightarrow 0$. Estimates of differences in residual resistance can be obtained by extrapolation in plots of relation IV-9 (see Fig. 13).

of extreme values of the abscissae $_{Ph}R$ equal in plots of relation IV-9. This procedure is undertaken for convenience in plotting. The primed notations, e.g., $_{i}R'$ and $\delta' \, _{i}R$ indicate that this operation has been performed. A comparison of δR and $\delta' R$ is given in Figures 11 and 12.

Temperature is an implicit variable of relation IV-9, whereas resistance appears explicitly. Hence, efforts to achieve precision in the present experiment were devoted to the measurement of resistance rather than of temperature. Furthermore, precise determinations of comparative resistance values instead of absolute values was emphasized, since the former are more important for relation IV-9.

The circuit used for the comparison of resistances is indicated in Fig. 5. A current of about one-half ampere was drawn from the six volt storage cell. Potentials across the specimens and the standard resistance were measured, and the specimen resistances were calculated from these measurements.

Resistance measurements were made at several temperatures between 67° and 270°K. These temperatures were obtained by immersion of the specimens in liquid nitrogen for temperatures between 67° and 79°K and a mixture of carbon dioxide and petroleum ether for temperatures between 200° and 270°K. The arrangement of the specimens and associated apparatus in the fluid bath is indicated in Figures 6 and 7. Three specimens are shown clamped in electrodes in Fig. 6.

This assembly fitted in the copper enclosure shown in Fig. 7, which in turn was placed in a Dewar flask. The whole assembly was placed in a vacuum chamber so that a range of temperatures could be obtained with liquid nitrogen*.

The specimen potential leads, which are shown attached to the specimens in Fig. 6, were of 0.010 in. iron thermocouple wire. These wires were spot welded to the specimens by capacitor discharge.

Temperature was measured by means of the copper/constantan thermocouple indicated in Fig. 6. The measuring junction of this couple was located in the center of the copper enclosure, Fig. 7, and was about one-half in. from each specimen. The insulated thermocouple wires were led out of the Dewar flask in paraffin-filled copper tubing.

The procedure used in this experiment was as follows. The assembly of specimens shown in Fig. 6 was placed in a chamber which was evacuated to 10^{-5} mm. Hg. The specimens were annealed at about 1000°C for one minute by passing an electric current through them. The specimen assembly was lowered into the copper enclosure in the Dewar flask, which was then filled with liquid nitrogen. The pressure on the system was reduced, thus lowering its temperature about 12°C. Measurements were made over the period of about two hours required for the system to return to atmospheric pressure.

One resistance at a time could be measured by simultaneous readings of the two potentiometers shown in Fig. 5. Simultaneous

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* Explosive boiling of the nitrogen was avoided by placing crushed brick in the bottom of the Dewar flask.

resistance values for all three specimens were desired, however. Hence the interpolation method illustrated in Fig. 8 was adopted. Each resistance value used in the interpolation against time was the mean of a pair of values obtained for the two possible current polarities. Thus the effect of parasitic potentials was minimized.

Temperature readings were taken immediately before and after the series of resistance readings necessary for interpolation. The rate of temperature increase indicated by these readings was less than 0.25°C/min. in every case and less than 0.1°C/min. in most cases.

The tests in the liquid nitrogen temperature range were followed by tests in the range, 200° to 270°K. The latter tests were conducted at atmospheric pressure. This sequence of tests was first performed on the three specimens: "Ph", "BS", and "NR1". Then the same tests were repeated for the three specimens: "Ph", "54", and "57".

Meissner (50) gives the value 519°K for the Gruneisen characteristic temperature of iron. The temperature dependence of the resistance of iron according to the Gruneisen formula, relation IV-3, with $\theta^G = 519^\circ K$ is compared with results obtained in the present experiment in Fig. 10. A Gruneisen curve with $\theta^G = 570^\circ K$ is also included in the comparison. The experimental results agree more closely with $\theta^G = 570^\circ K$ than with $\theta^G = 519^\circ K$ for temperatures between 200° and 270°K, and vice versa for temperatures between 67° and 79°K. The comparison in the latter temperature range suggests that specimen "Ph" has a residual resistance of about 600 micro-ohms. In any case, Meissner's results are probably preferable to the present ones, since temperature was not measured accurately in the present experiment.

The increase in resistance, δR, due to a one per cent increase in atomic mass, as predicted from the Gruneisen formula with $\theta^G = 519^\circ K$, is plotted in Fig. 11 against the resistance ${}_{Ph}R_{\ell}$ ($= {}_{Ph}R - 600 \mu\Omega$). The corresponding variation, $\delta' R$, which would be detectable in a plot of relation IV-9, is shown in Fig. 12 for $\theta^G = 519^\circ K$ and $\theta^G = 570^\circ K$. Evidently $\delta' R$ is not affected by more than about 12 per cent by the possible uncertainty in θ^G.

The resistance data obtained in the present experiment are presented in Figures 13, 14, 15, and 16. Figure 13 shows the general range of data secured. The complete data are presented in the expanded plots, Figures 14, 15, and 16. The scale factors by which the measured values of ${}_iR$ were multiplied to obtain ${}_iR'$ were as follows:

Specimen		Scale Factor
"NR1"	. . . . . .	0.92854
"BS"	. . . . . .	0.9013
"54"	. . . . . .	1.0104
"57"	. . . . . .	1.0426

The predicted values shown in Figures 13, 14, 15, and 16 are derived from relation IV-6 with $\theta^G = 519^\circ K$.

The differences in residual resistance, ${}_{i}R_{r} - {}_{Ph}R_{r}$, may be estimated by extrapolation in Fig. 13, with the following results:

Specimen	${}_{i}R_{r} - {}_{Ph}R_{r}$
"BS"	~ - 100 $\mu\Omega$
"54"	~ + 200 $\mu\Omega$
"57"	~ + 500 $\mu\Omega$
"NR1"	~ +1000 $\mu\Omega$

The resistance cross-plots for natural iron in Figures 13, 14, 15, and 16 should exhibit no curvature, according to Mathiessen's Rule, relation IV-2. Examination of the expanded plots, Figures 14, 15, and 16, indicates that this prediction was more closely confirmed in the case of specimen "BS" than of specimen "NR1", as could be expected from their residual resistances. The curvature exhibited by these plots for either of the isotopically enriched specimens, however, is significantly larger than that for either of the natural iron specimens. This latter result can be explained approximately by the theoretical discussion given previously. Examination of predicted values and experimental values in Figures 13, 14, 15, and 16 indicates approximate agreement.

The isotopic effect on resistance observed in the present experiment was generally less than that predicted by relation IV-6. Such a discrepancy is hardly surprising, however, in view of the likelihood that the Gruneisen theory does not agree perfectly with the actual resistance of iron. The present experimental method is particularly sensitive to the temperature coefficient of resistivity predicted by theory, since curvature, and hence higher order derivatives, are involved in this method. The present results do indicate, however, an isotopic effect in approximate agreement with that predicted from the Gruneisen theory.

This problem has been investigated previously by Jaeger and Steinwehr (35), Onnes and Tuyn (14), Tuyn and Onnes (33), Tuyn (34), and Justi (15), as was indicated in the Introduction to this thesis. Except for the work of Justi, these investigations preceded the Gruneisen theory and were not interpreted as indicating an isotopic effect on electric resistance. In view of the magnitude of the isotopic effect implied by the Gruneisen theory, as indicated in relation IV-6, the negative results obtained by most of these early investigators may be ascribed to the unfavorable temperatures at which the investigations were made and to the low degree of isotopic enrichment of the materials available to them. In the case of the investigation of Tuyn, however, some evidence for an isotopic effect may be adduced if his results are analyzed in a suitable way. Furthermore, Justi has presented results which indicate an isotopic effect opposite in sign to that anticipated by the Gruneisen theory. Therefore, the investigations of Tuyn (34) and of Justi (15) must be considered further.

Both Tuyn and Justi studied the electric resistances of uranium-lead and normal lead at several temperatures between 7°K, the transition temperature for superconductivity in lead, and 273°K. The results obtained by these investigators are presented in Fig. 17, which employs the present plotting method*. Examination of Fig. 17 indicates that the results of the two investigators are contradictory, so that it is difficult to decide whether an isotopic effect is indicated or not. The effect suggested by the measurements of Justi depends upon a more limited number of measurements than does that of Tuyn, however. Furthermore, the results of Tuyn are in better agreement with the results of the present investigation, insofar as the Gruneisen theory is concerned. Therefore, the measurements of Tuyn appear preferable to those of Justi. The results obtained by Tuyn were published in tabular form and without analysis as to evidence of an isotopic effect. Examination of Fig. 17, however, indicates that the agreement of the results of Tuyn with the predictions of the Gruneisen theory is somewhat better than could be accounted for by random scatter of the data obtained by him. Thus the investigation of Tuyn apparently constitutes the first evidence for an isotopic effect on electric resistance, provided the disagreement of his results with those of Justi is resolved as indicated here.

The technique employed by Tuyn, Justi, and the present investigator to avoid the measurements of the geometries of small specimens results in one major disadvantage. Since this technique

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* Most previous investigators tabulate their results in terms of relative resistance, r, instead of resistance in ohms. Either coordinate may be used in relation IV-9 and plots derived therefrom.

permits the verification of theoretical predictions only with regard to the curvature present in certain plots, the absolute magnitude of the change in resistivity due to a change in atomic mass remains uncertain. The determination of this absolute magnitude may become feasible if isotopically enriched materials continue to become available in larger amounts.

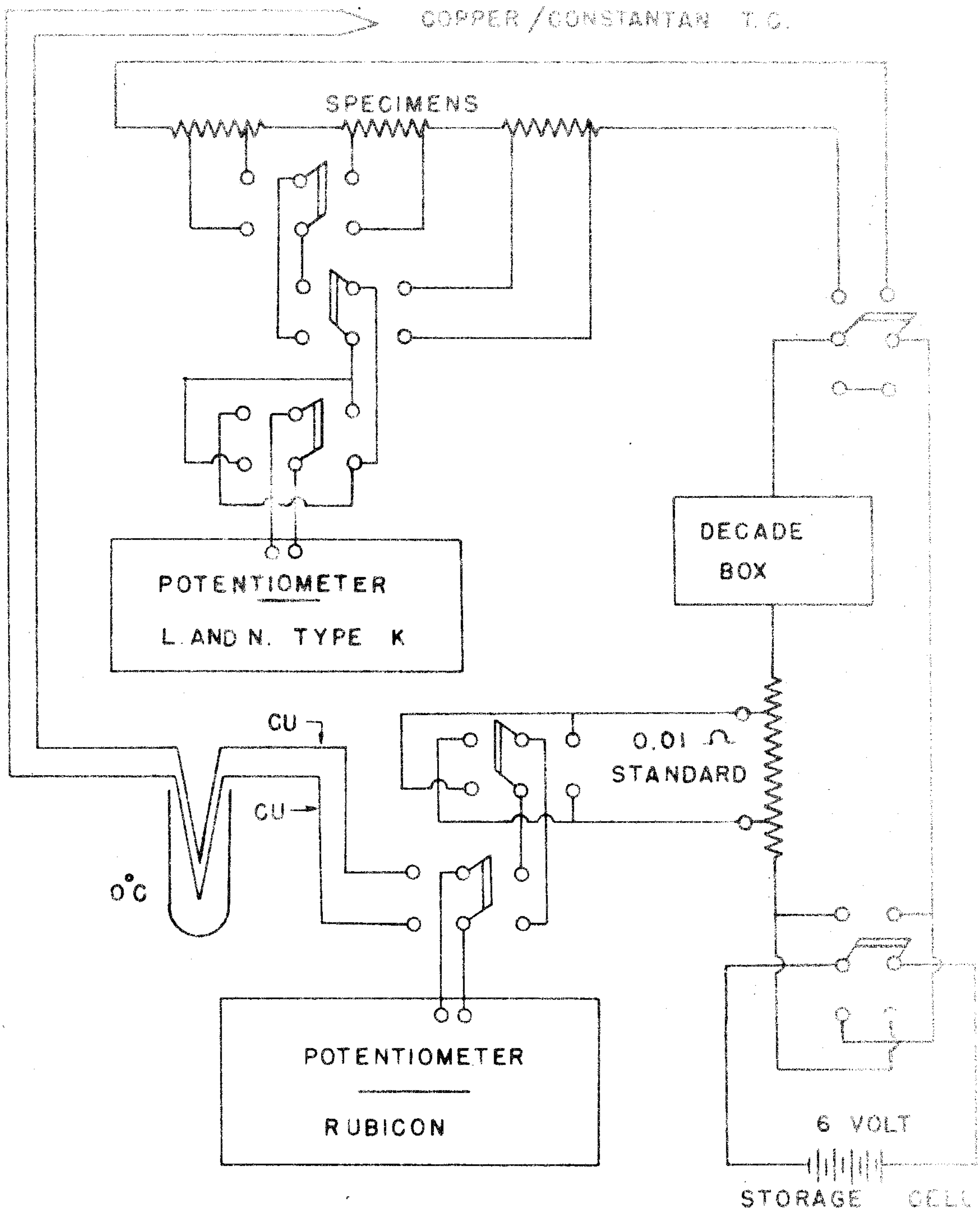

FIG. 5. DIAGRAM OF CIRCUIT USED IN COMPARATIVE RESISTANCE STUDY.

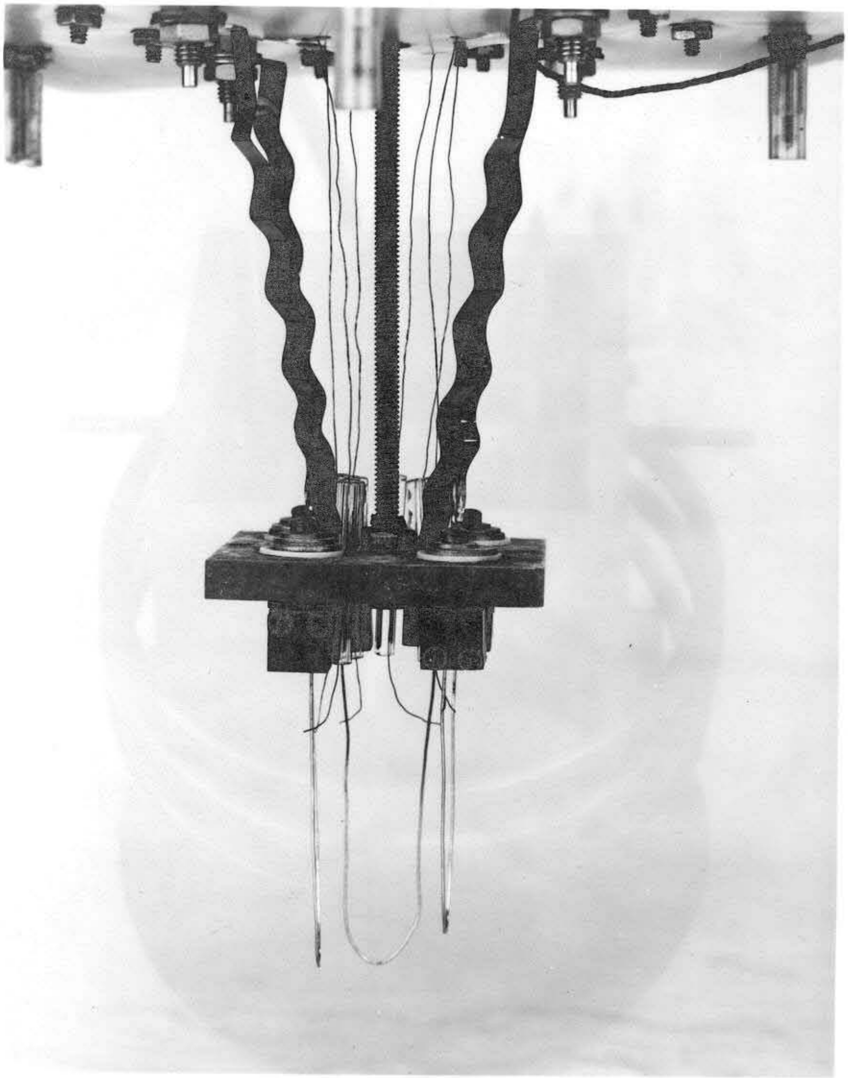

Figure 6. Arrangement of Specimens in the Resistance Study.

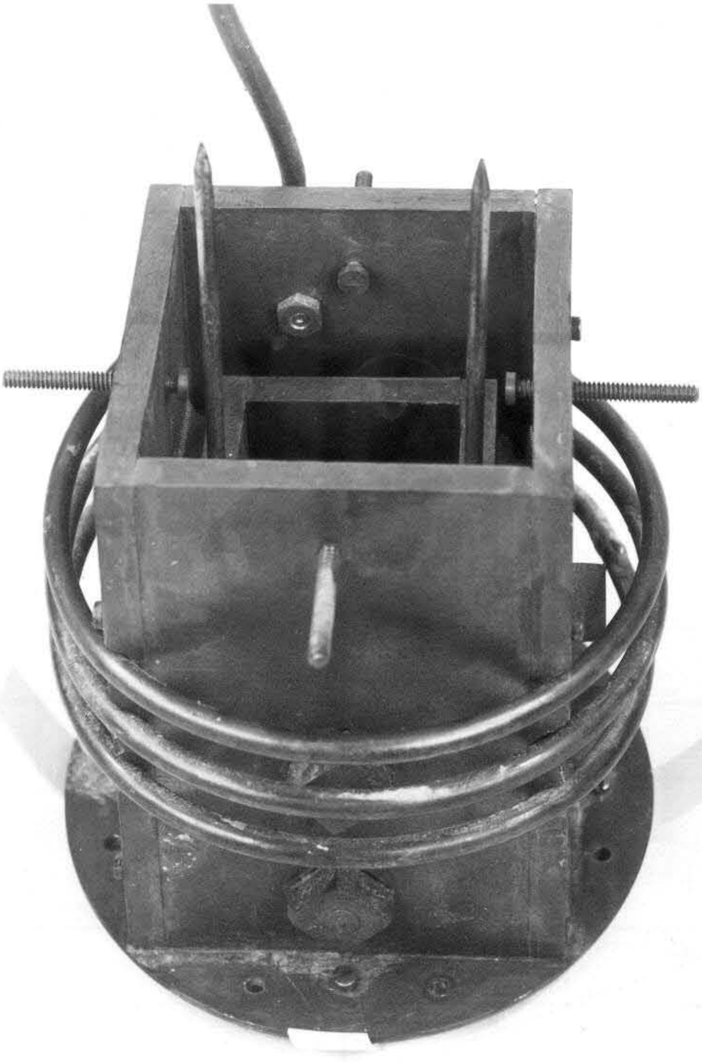

Figure 7. Copper Enclosure for Specimens in the Resistance Study.

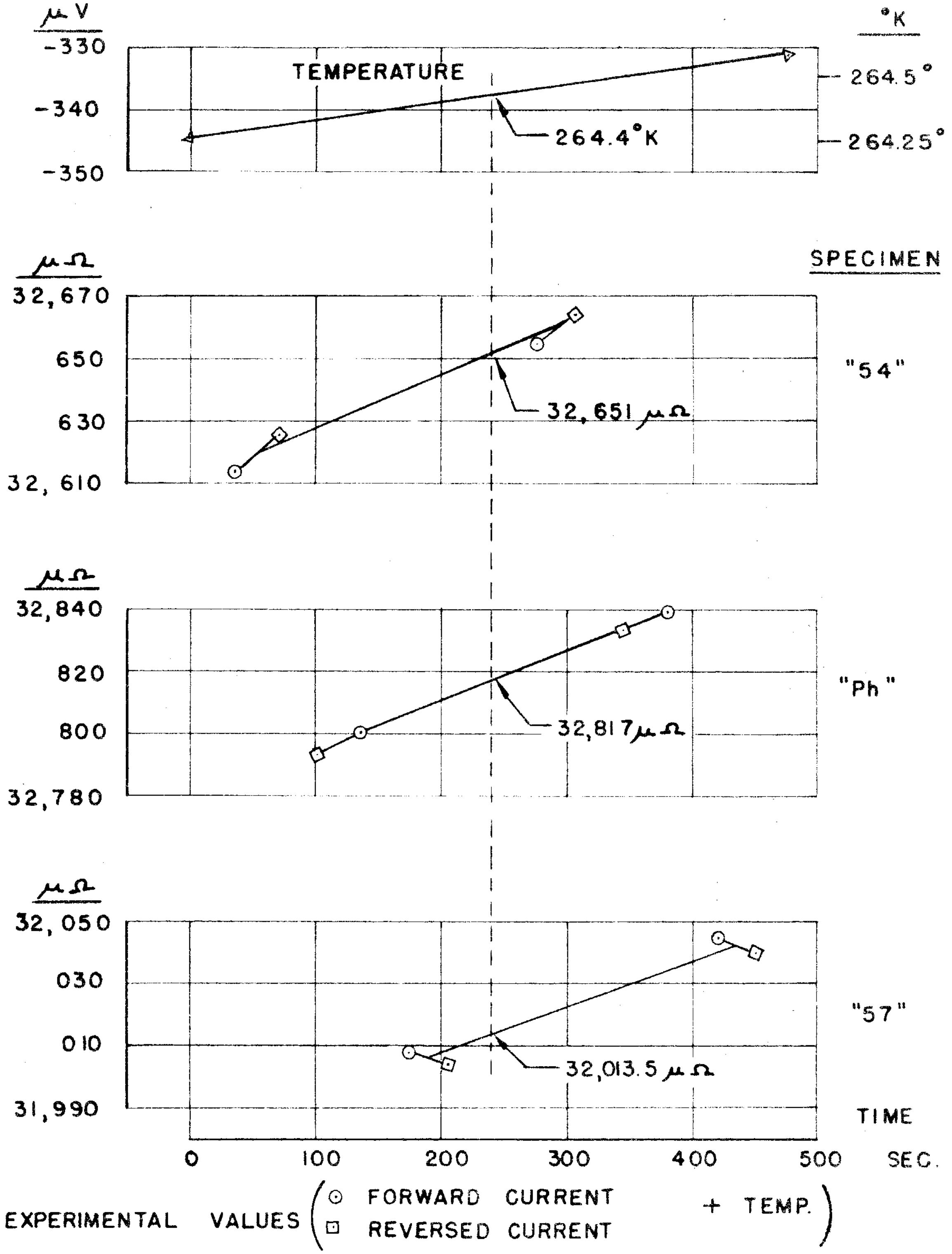

FIG. 8. ILLUSTRATION OF INTERPOLATION METHOD USED TO OBTAIN SIMULTANEOUS VALUES OF THE RESISTANCES AND TEMPERATURE.

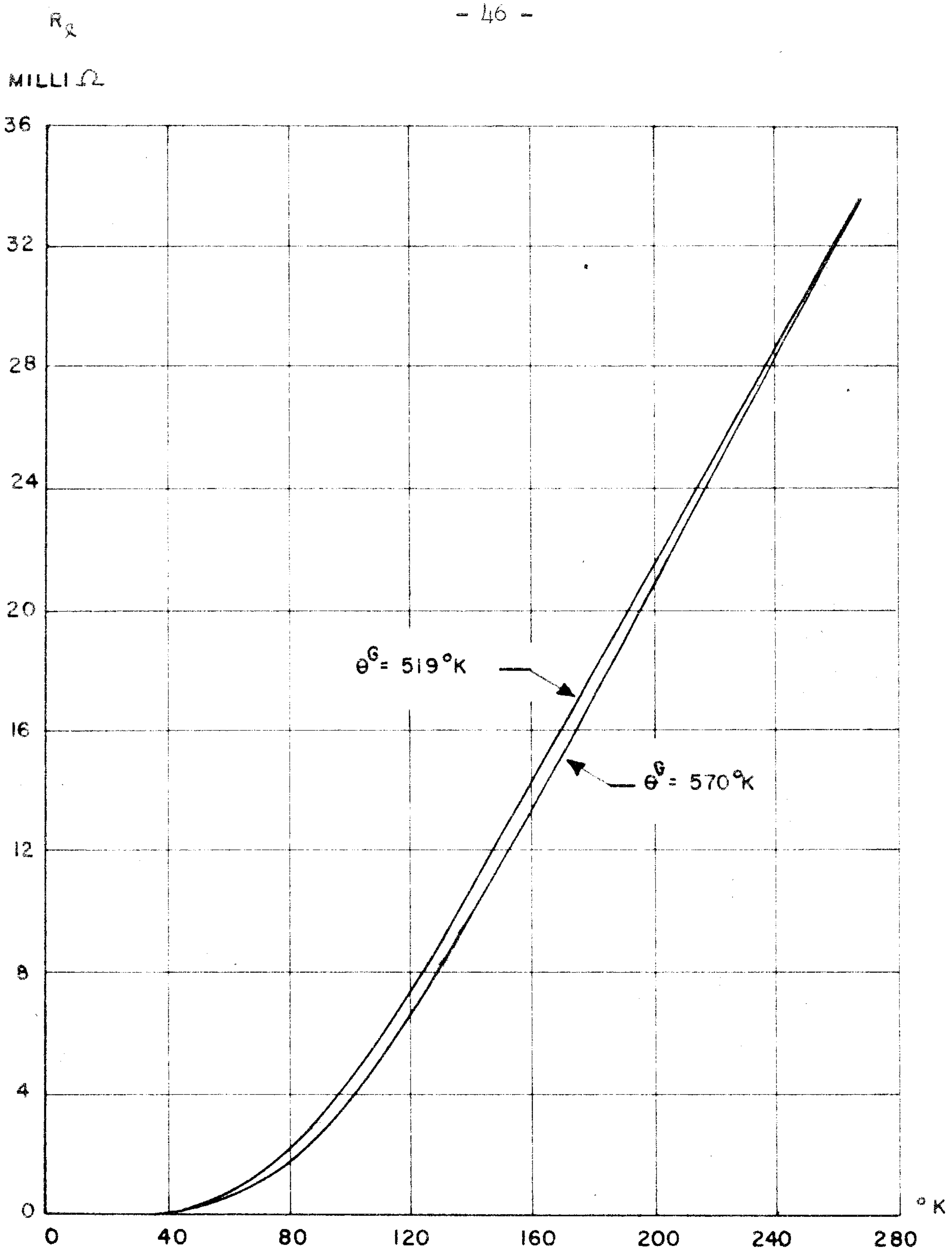

FIG. 9. THE TEMPERATURE DEPENDENCE OF ELECTRIC RESISTANCE ACCORDING TO THE GRUNEISEN FORMULA. THE PROPORTIONALITY CONSTANT, K, IS CHOSEN TO FIT THE EXPERIMENTAL VALUE ${}_{Ph}R$ AT 270 °K

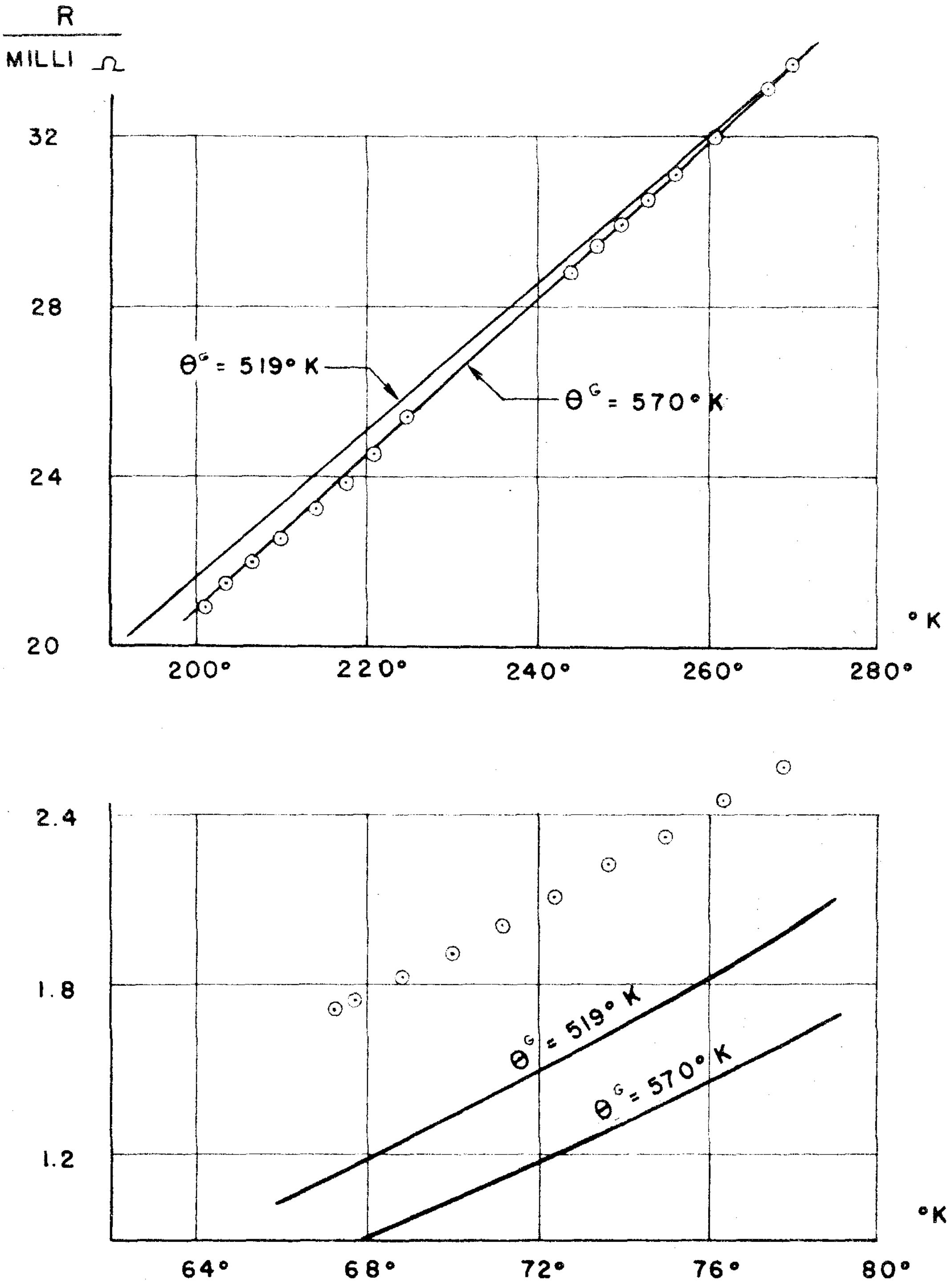

FIG. 10. COMPARISON OF THE EXPERIMENTAL VALUES $_{ph}R$ (INDICATED BY THE SYMBOL ⊙) AND THE GRUNEISEN FORMULA, RELATION IV-3

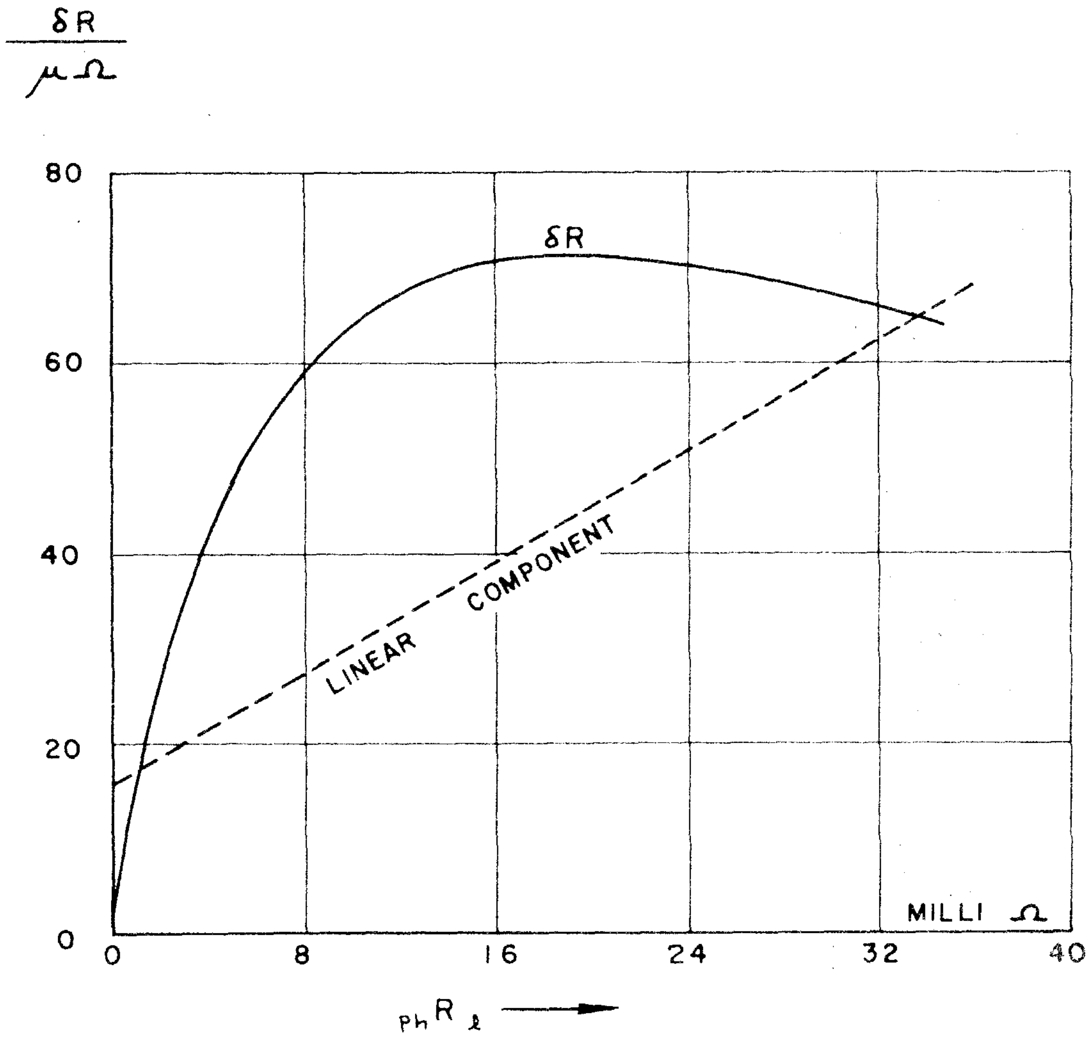

FIG. 11 THE INCREASE IN RESISTANCE, δR, DUE TO A ONE PERCENT INCREASE IN ATOMIC MASS, AS CALCULATED FROM THE GRUNEISEN FORMULA WITH $\Theta^G = 519°K$. THE LINEAR TERM IN δR WHICH IS SUBTRACTED TO OBTAIN $\delta' R$ IS ALSO SHOWN.

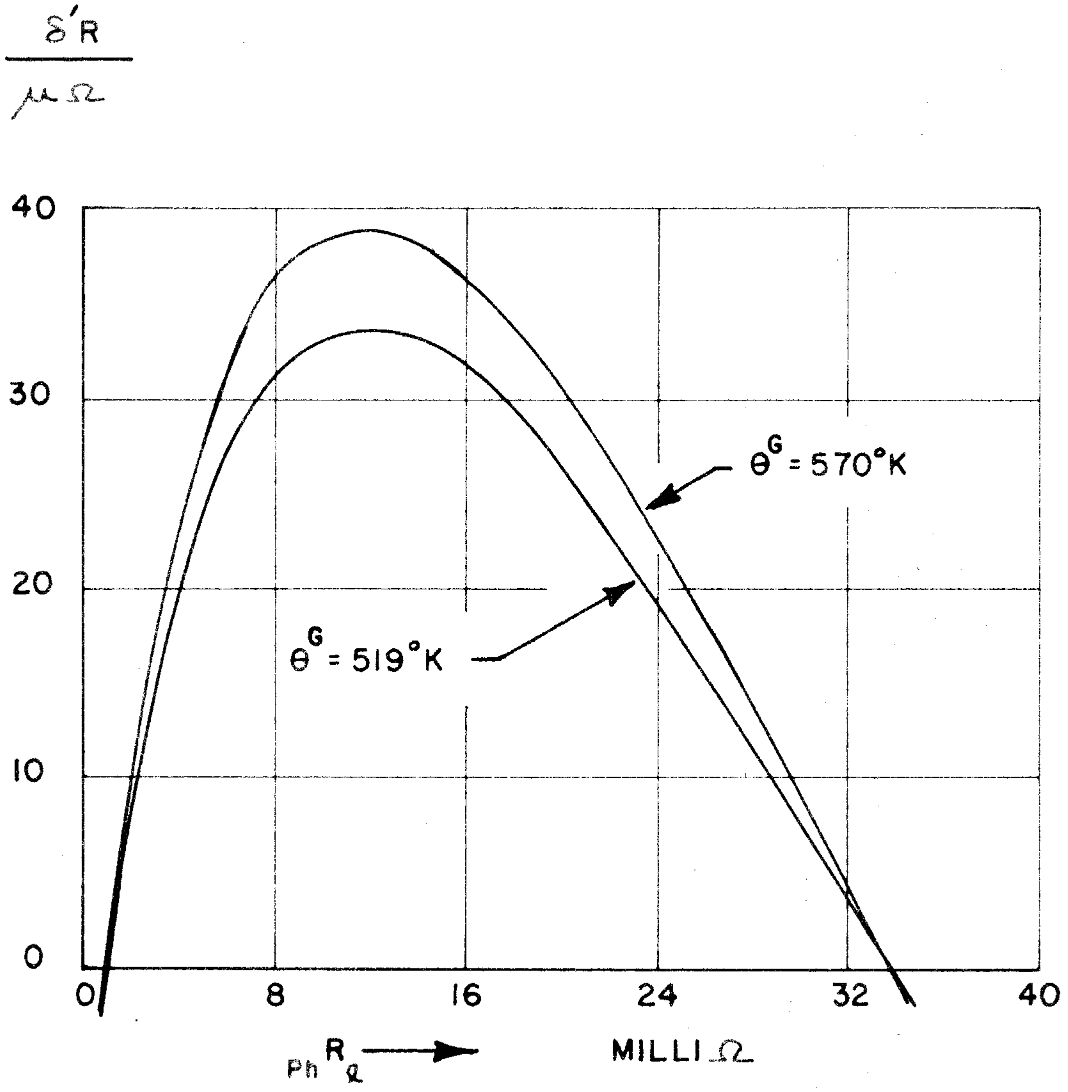

FIG. 12. THE INCREASE IN RESISTANCE, $\delta' R$, DUE TO A ONE PER CENT INCREASE IN ATOMIC MASS AS CALCULATED FROM THE GRUNEISEN FORMULA.

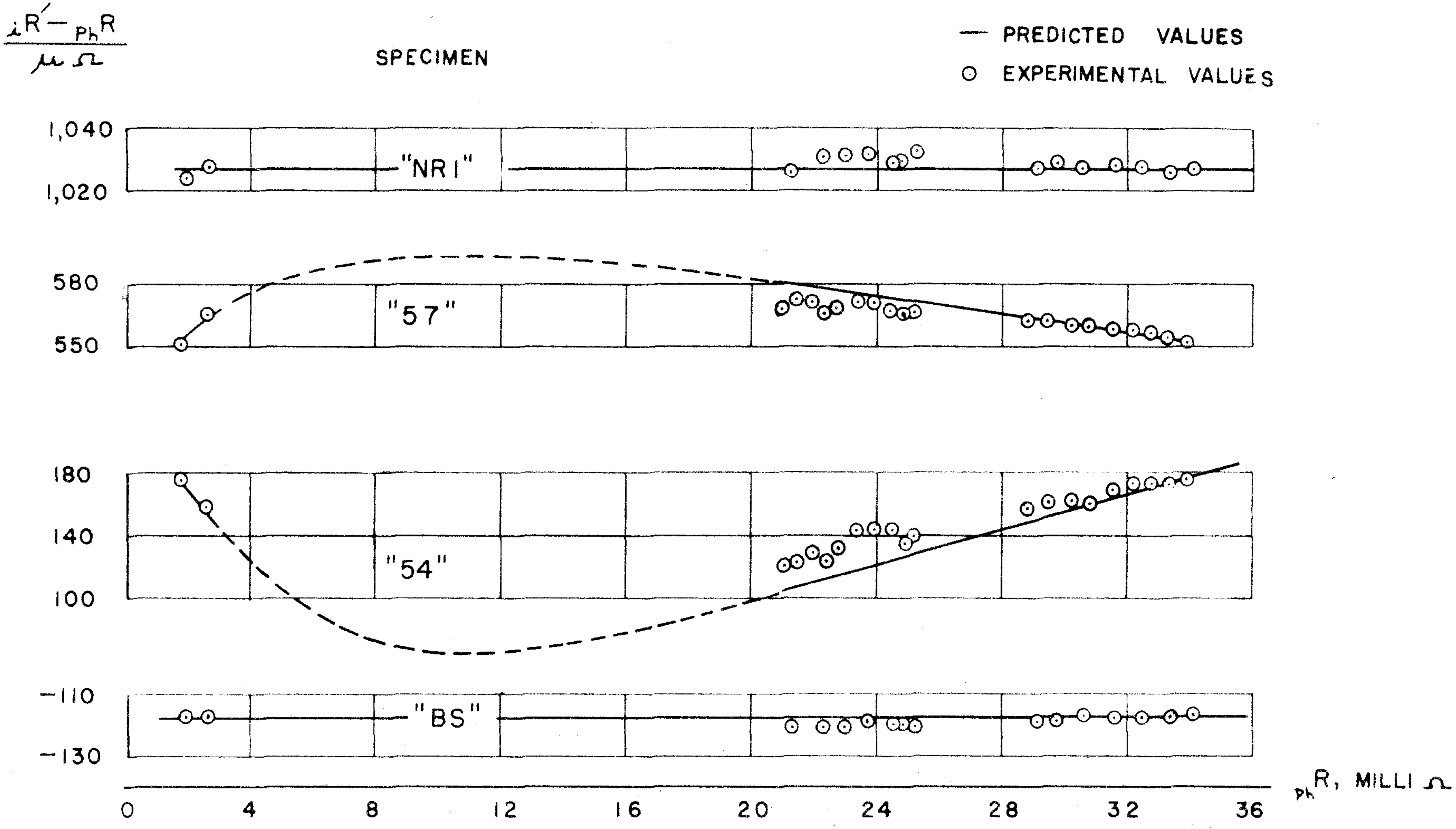

FIG. 13 RESISTANCE CROSS – PLOT OF PRESENT MEASUREMENTS.

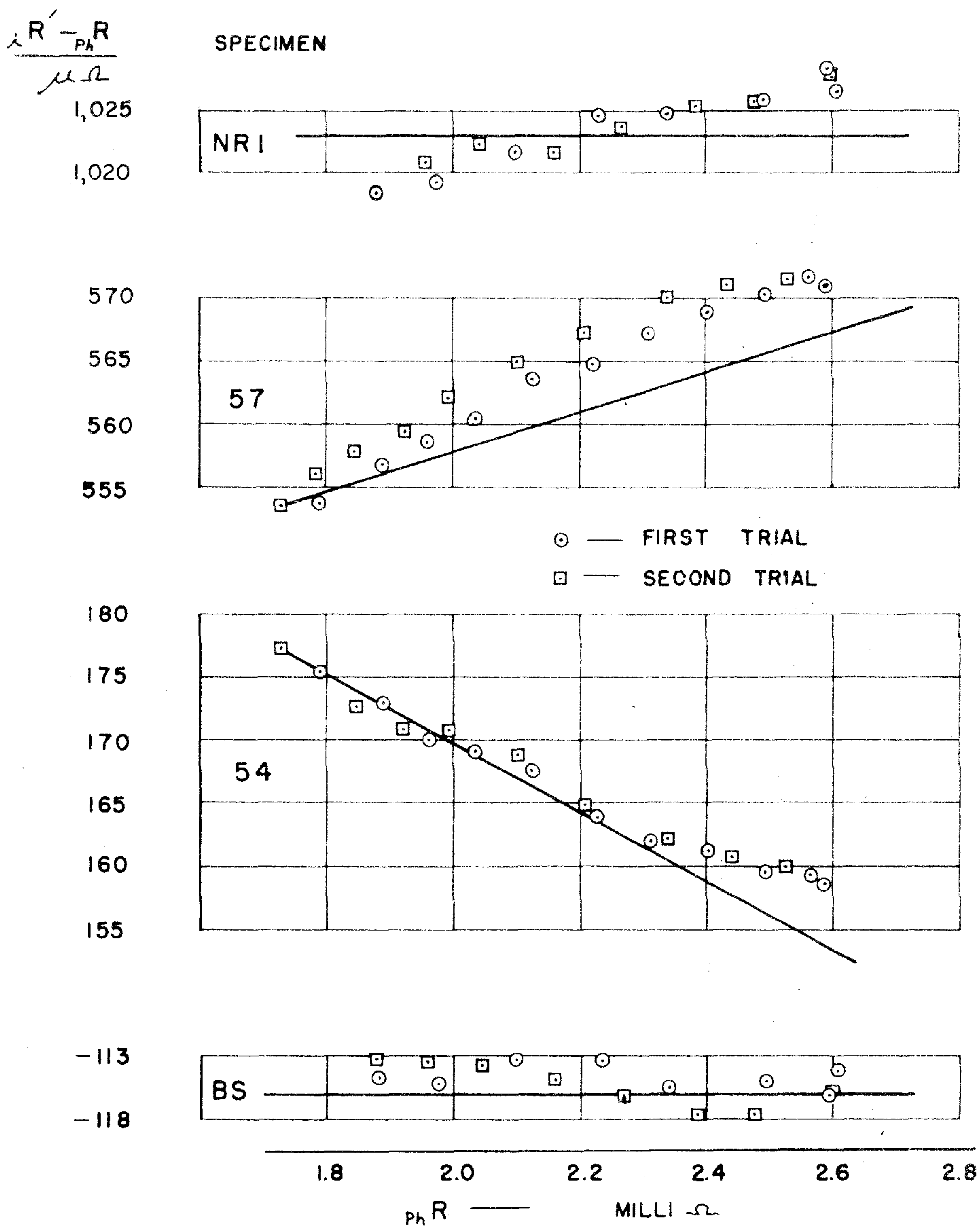

FIG. 14 EXPANDED PLOT OF FIG. 13 FOR LOW TEMPERATURES.

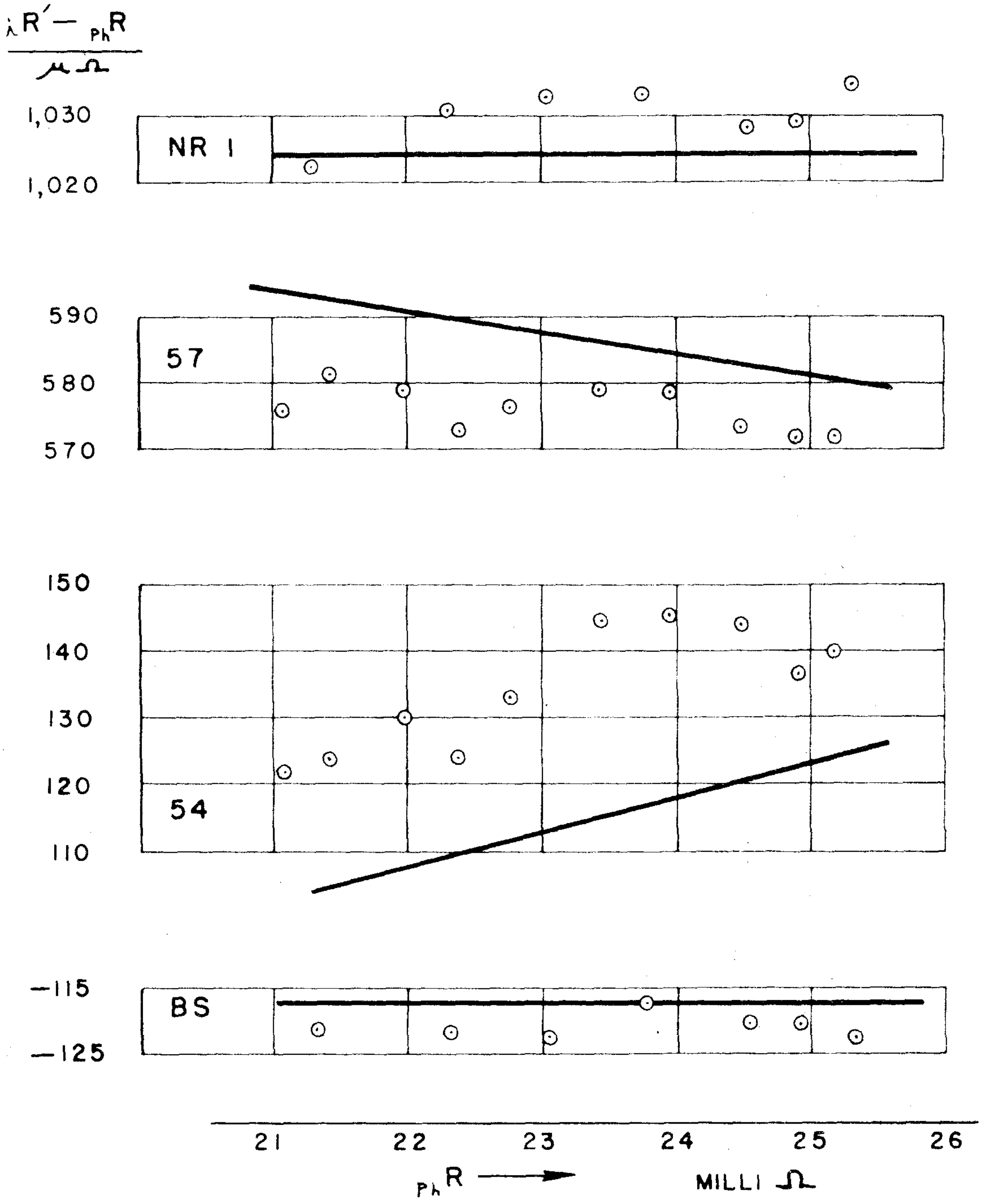

FIG. 15 EXPANDED PLOT OF FIG. 13 FOR INTERMEDIATE TEMPERATURES.

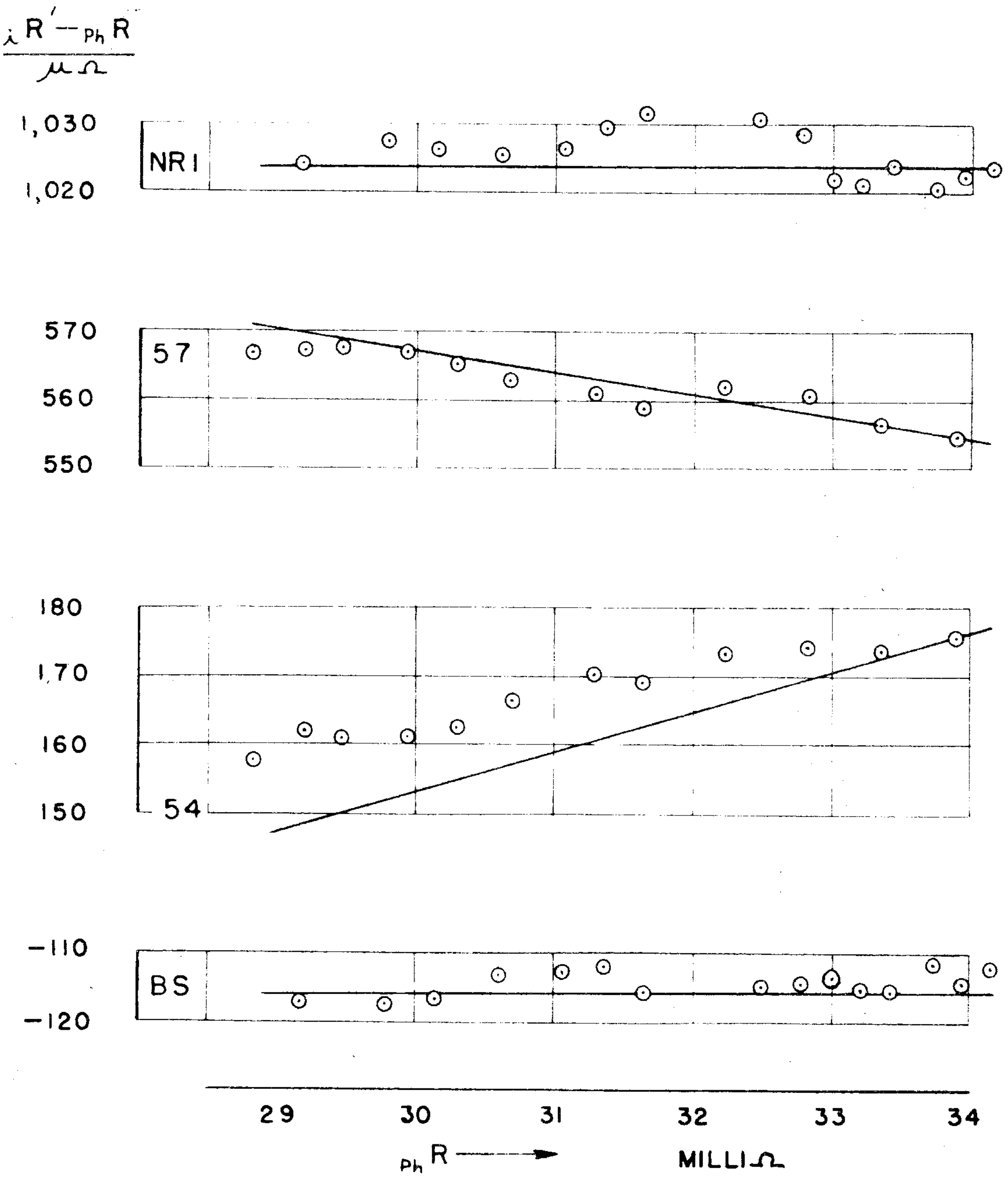

FIG. 16 EXPANDED PLOT OF FIG. 13 FOR TEMPERATURES NEAR 260° K.

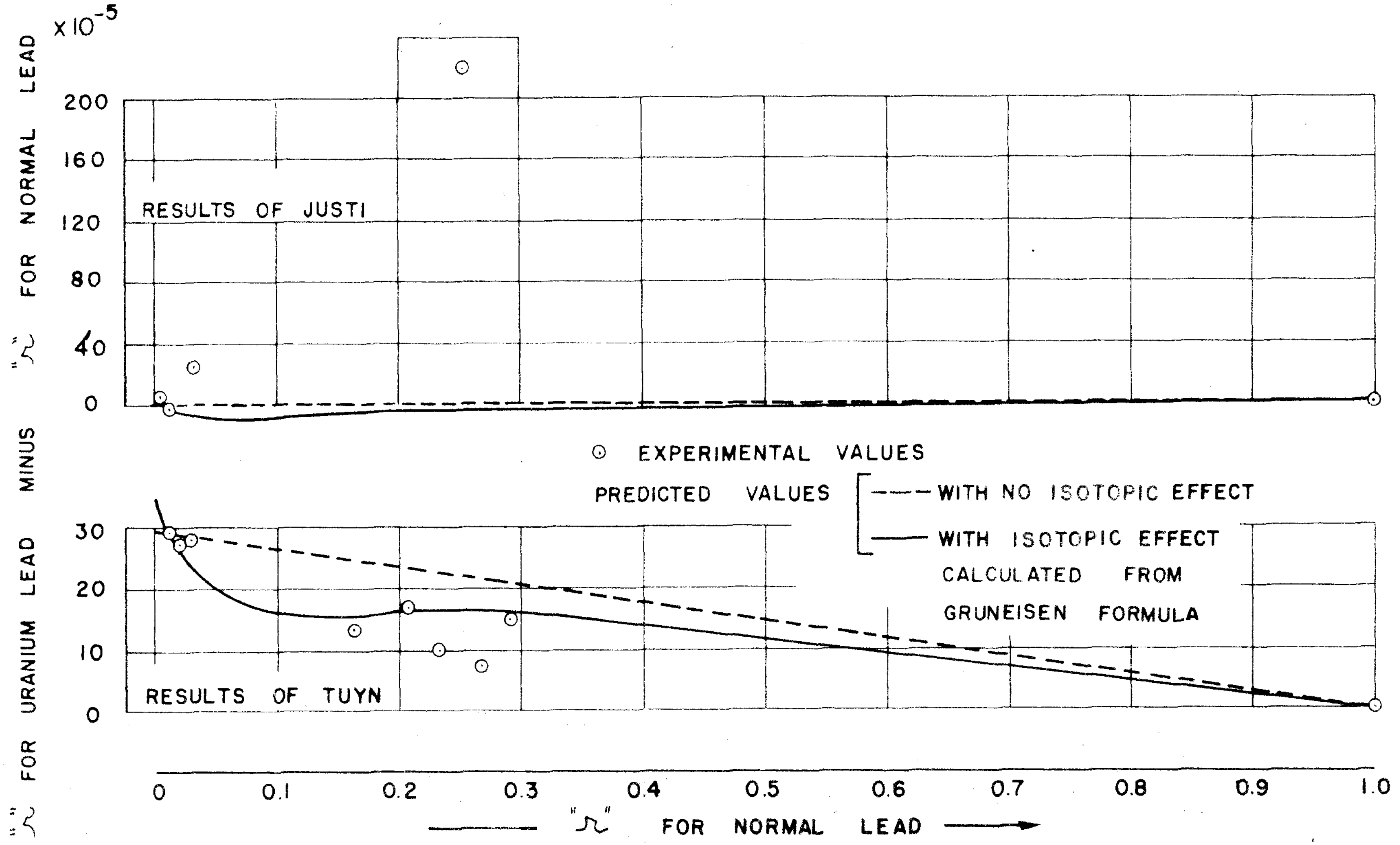

FIG. 17 RESISTANCE CROSS-PLOT OF THE OF TUYN AND JUSTI FOR URANIUM LEAD AND NORMAL LEAD.

V. THE THERMOELECTRIC POWERS OF IRON ISOTOPES AT TEMPERATURES BETWEEN 80° and 270°K.

The thermoelectric powers of metals are known from experiments in which the influences of chemical composition and lattice imperfections are studied. Both of these influences change the structure of the metal in complicated ways, however, so that their study has not been very useful in the theoretical sense. According to Crussard (52), "....there is a general lack of information on the physical meaning of the observed effects..... thermoelectric properties are very complicated from the physical point of view...". The only electronic parameter likely to be affected by a change in atomic mass, however, is the electronic mean free path, which is directly related to the electric resistance. In view of the previously discussed dependence of electric resistance on atomic mass, an isotopic effect in thermoelectricity can be anticipated. If such an effect can be detected, it may contribute to an understanding of thermoelectric properties.

The thermoelectric circuits employed in the present experiment are indicated in Fig. 18. The specimen circuits were comprised of the following elements: copper lead wires, junction blocks of high purity iron*, specimens, and potentiometer. One junction block was common to the three specimens and could be varied in temperature from 80° to 270°K; the other blocks were partially submerged in oil, which

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* These blocks were machined from the National Research Corporation ingot described in Part II of this thesis.

was at ambient temperature. A copper/constantan thermocouple indicated the temperature of the common junction block; mercury thermometers, which could be read to 0.05°F, were placed in each of the oil-bath junction blocks.

The physical arrangement of much of this equipment is indicated in Fig. 19. The specimens were clamped at each junction and a drop of light oil placed between the two clamping surfaces to improve the thermal conductivity at the joint. The measuring junction of the copper/constantan thermocouple was joined in similar fashion to the common junction block, which was clamped to a receptacle for liquid nitrogen. Nickel foil was placed between the nitrogen receptacle and the oil-bath to reduce radiative heat transfer. The whole assembly was placed in a vacuum chamber so that heat transfer through the surrounding atmosphere could be reduced.

The assembled equipment shown in Fig. 19 was placed in the vacuum chamber, which was then evacuated to a pressure of about 10^{-4} mm. Hg. The specimens were annealed at about 1000°C for one minute. The vacuum chamber was opened and liquid nitrogen poured into the receptacle therefore, until a temperature of about 80°K was obtained at the common junction block. The vacuum chamber was then closed and re-evacuated. Measurements of thermal emf and temperature were made during the period of about three hours required for the temperature of the common junction block to increase to 270°K. The temperature of the oil-bath decreased about 3°C during this time, but the temperatures of the oil-bath junction blocks were observed to differ by no more than 0.15°C, their mean temperature being 23°C. The maximum rate of temperature increase at the common junction block was about 3°C/min.

The thermal emf's exhibited by specimens "BS", "54", "57", "NR1", and "NR4" in comparison with the reference specimen "Ph" were measured. Two trials were made in the cases of some of these specimens in order to obtain an estimate of the reproducibility of these measurements. The results which were obtained are presented in Figures 20 and 21. Thermal emf is considered positive when current flows away from the reference specimen at the common junction block.

The uncertainty in the reproducibility of the present measurements appears from Figures 20 and 21 to be about 10 μV at temperatures near 80°K and tends to decrease at higher temperatures. Thus the uncertainty in the mean thermoelectric powers of the specimens for the temperature range, 80° to 270°K, is about $\pm$ 0.03 μV/°K. This estimate is necessarily only a rough approximation due to the limited number of measurements which were made. The principal factor causing this lack of reproducibility is thought to be the conditions obtaining at the ends of the specimens. Clamping of the ends of the specimens was necessary to obtain good thermal conductivity between specimens and junctions blocks, but introduced stresses into the specimens which may cause spurious thermal emf's, as is well-known (52).

The present data indicate an almost linear dependence of thermal emf on temperature. This result is somewhat surprising in view of the tendency of the thermoelectric powers of most metals to approach zero at low temperatures (53). According to the Nernst heat theorem, thermoelectric power should vanish at 0°K, (53), and thus curves such as those plotted in Figures 20 and 21 should approach horizontal asymptotes at sufficiently low temperatures. Evidently the specimens examined in the present investigation would not exhibit the expected decrease in thermoelectric power until temperatures below 80°K were obtained.

As a result of the nearly linear relationship just discussed, a mean thermoelectric power in the temperature range, 80° to 270°K, may be estimated for each specimen. The mean thermoelectric powers listed below were obtained from Figures 20 and 21 by measuring the slope between the leftmost and rightmost points obtained in each trial. Where two trials were made on any one specimen, an average slope is listed. The residual resistances estimated earlier in this thesis for some of these specimens are listed for comparison.

Annealed Specimen	Mean Thermoelectric Power	Residual Resistance
	$\mu V/^\circ K$	$\mu\Omega$
BS	-0.02 ± 0.03	-100
54	$+0.13 \pm 0.03$	$+200$
57	$+0.28 \pm 0.03$	$+500$
NR1	$+0.26 \pm 0.03$	$+1000$
NR4	$+1.78 \pm 0.03$	(not measured)

Evidently the mean thermoelectric powers of these specimens are more closely related to their residual resistances than to their atomic masses. Since the values tabulated above are for annealed specimens, the observed residual resistances and mean thermoelectric powers are probably associated with chemical impurities. Even if no allowance is made for the effects of chemical impurities, however, the mean thermoelectric power of an Fe^{54}/Fe^{57} thermocouple for the temperature range of 80^{o} to $270^{o}K$ would only be of the order of $0.15\ \mu V/^{o}K$, which is about 0.5 per cent of the mean thermoelectric power of a copper/constantan thermocouple for the same temperature range.

In principle, the present results could be analyzed for deviations from linearity in the relation of thermal emf to temperature. Some curvature is evident in the plots of Figures 20 and 21, particularly for the isotopically enriched specimens. These variations from linearity are small compared to the uncertainty in the reproducibility of the present data, however, and hence will not be considered further.

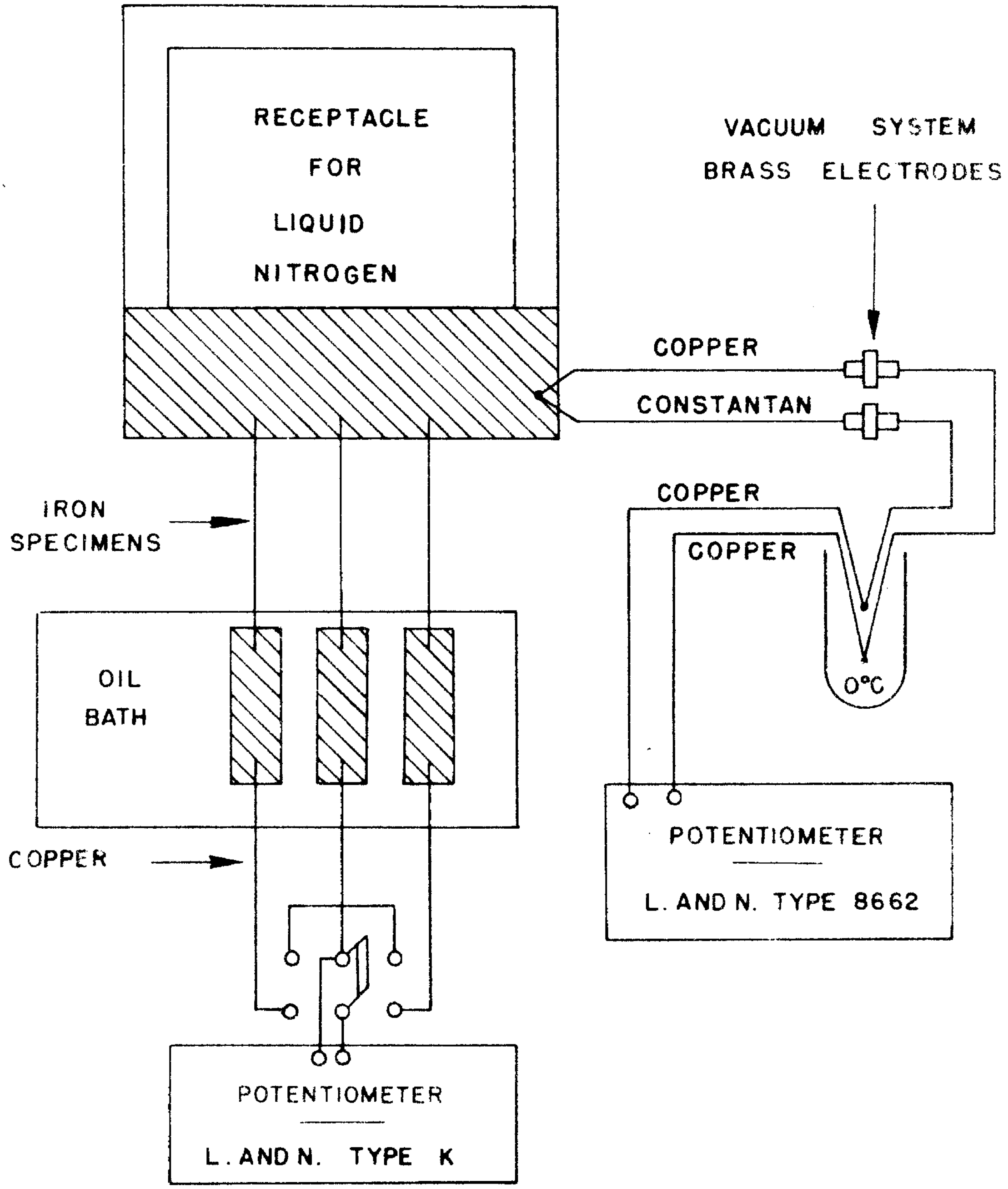

FIG. 18. DIAGRAM OF ELECTRIC CIRCUITS USED IN THE THERMOELECTRIC EXPERIMENT. PARTS MADE OF HIGH PURITY IRON ARE INDICATED BY SECTIONING ▨.

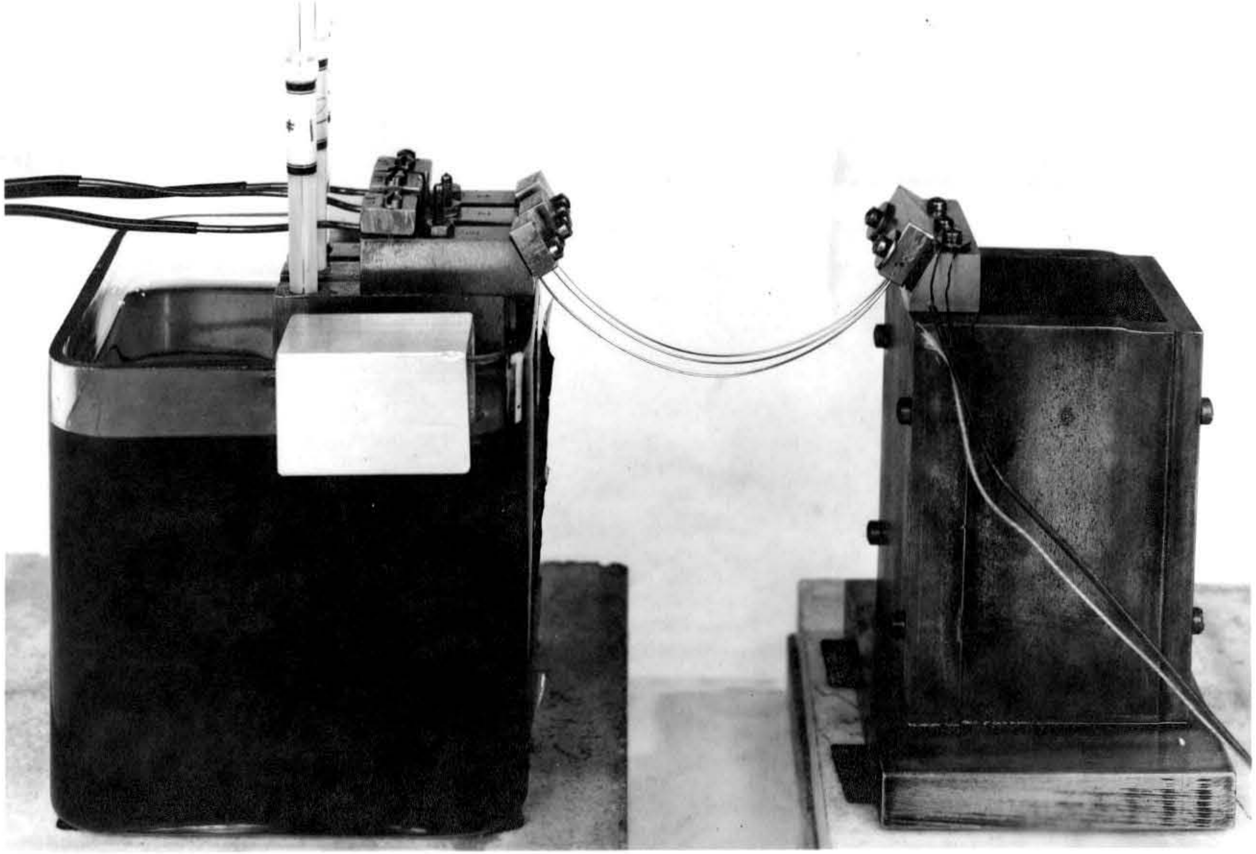

Figure 19. Physical Arrangement of Specimens and associated Equipment in the Thermoelectric Experiment. The span of the catenary shape in which the specimens are suspended is about three inches.

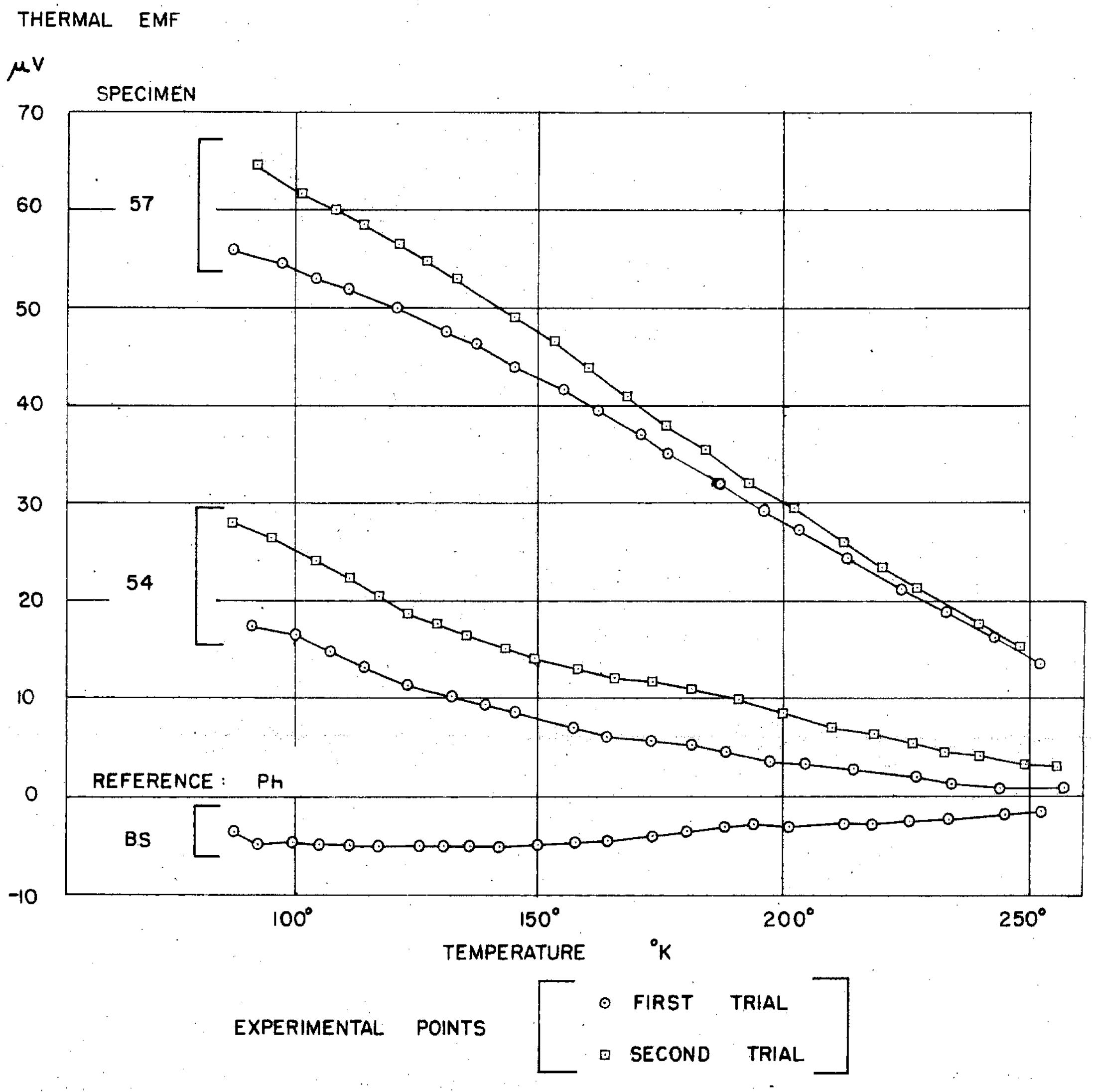

FIG. 20. MEASURED THERMAL EMF'S OF SPECIMENS "54", "57", AND "BS".

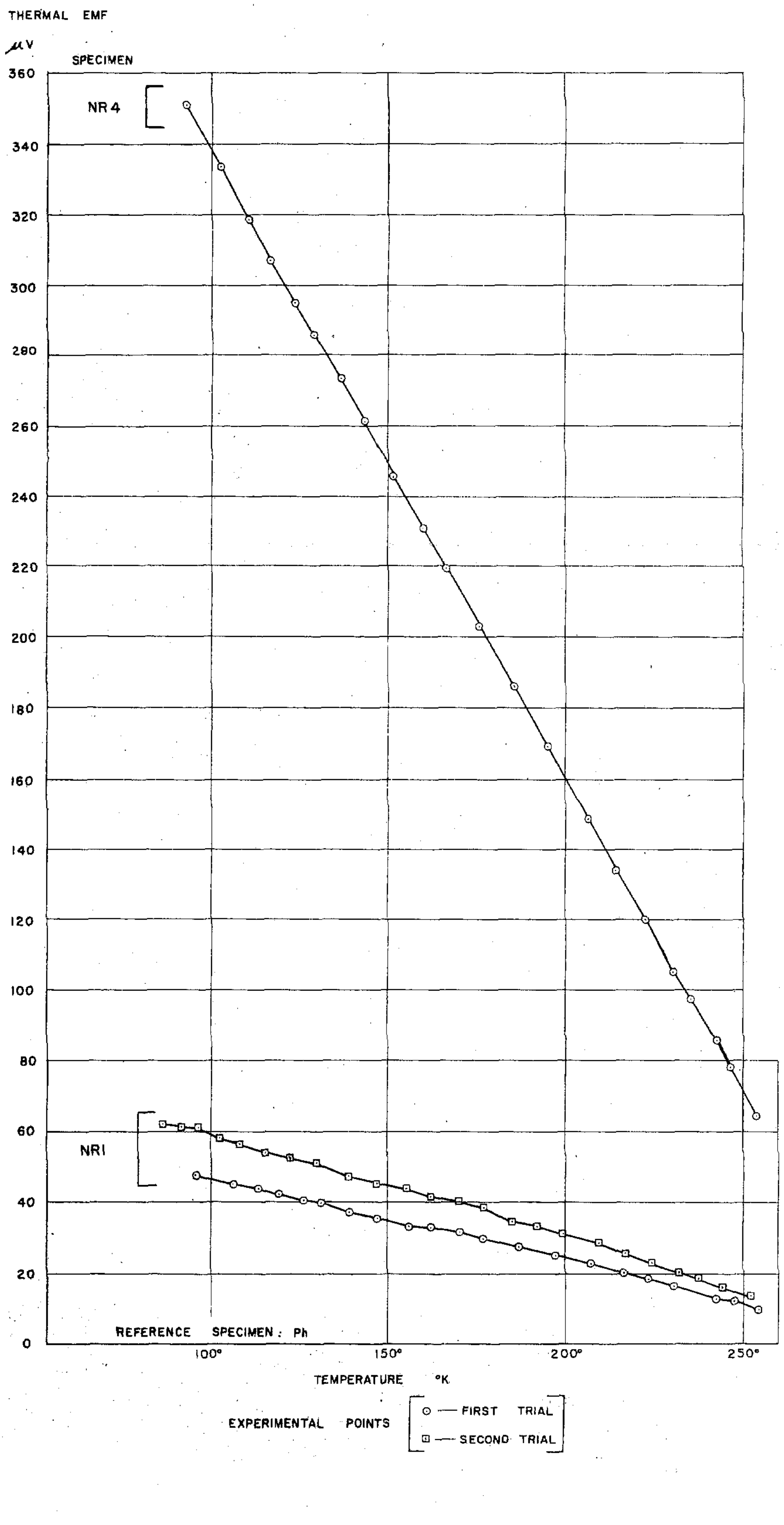

FIG. 21. MEASURED THERMAL EMF'S OF SPECIMENS "NR1" AND "NR 4".

VI. SUMMARY AND CONCLUSIONS

Three physical properties of iron were selected for an investigation of isotopic effects in solid metals. One of these properties, the electric resistance, was chosen because a review of previous work in this field had suggested that further study of this property was needed. The two other properties chosen for this investigation, thermoelectric power and a temperature of allotropic transformation, had not been studied previously with respect to isotopic effects, but were considered to be of potential interest in this respect.

The results of this investigation show that the temperature dependence of the resistance of iron at temperatures between 67° and 270°K is influenced by atomic mass in approximate agreement with predictions from the Gruneisen theory. The previous investigations of Tuyn (34) and of Justi (15) also indicate an isotopic effect on the temperature coefficient of resistance of metals, but the results of these two investigators are contradictory. The present study offers an interpretation of the results of Tuyn and suggests that his results are preferable to those of Justi. The investigation of Tuyn constitutes the first evidence for the isotopic effect implied by the Gruneisen theory, and the present results serve to strengthen the evidence for such an effect.

An investigation of the absolute magnitude of the change in resistivity due to a change in atomic mass is suggested for future studies in this field when larger amounts of isotopically enriched materials may become available than is the case at present. This absolute magnitude is not indicated in studies of the temperature coefficient of resistance.

An influence of atomic mass on thermoelectric power is not demonstrated in the present study. If such an influence does exist, however, the present results indicate that it probably does not exceed 0.15 $\mu V/^{\circ}K$ at temperatures between 80° and 270°K for a thermocouple made of Fe^{54} and Fe^{57}.

The present results do not demonstrate an isotopic effect on the equilibrium temperature of the alpha-gamma allotropic transformation of iron. A difference of about 2.5° C indicated from theoretical considerations for the transformation temperatures of Fe^{54} and Fe^{57} cannot be excluded on the basis of the present measurements, however, because of the hysteresis associated with the transformation occurring under the present experimental conditions. It is suggested that the allotropic transformation in lithium may be a more favorable case for the study of such problems.

NOMENCLATURE

C	specific heat
E	internal energy
F	free energy
G	the Gruneisen function (see relation IV-3)
g	a geometric factor relating electric resistance to electric resistivity
K	a constant in the Gruneisen formula (see relation IV-3)
L	latent heat
m	atomic mass
R	the gas constant electric resistance
r	electric resistance relative to the resistance at 0°C
S	entropy
T	temperature
θ	Debye characteristic temperature
θ^G	Gruneisen characteristic temperature
ρ	electric resistivity

Preceding subscripts, e.g., α, used in connection with the allotropic transformation study denote a phase. Preceding subscripts, e.g., "Ph", used in connection with the electric resistance study indicate a specimen.

The succeeding subscript ℓ denotes contributions to the property considered which arise from lattice vibrations. The succeeding subscript r denotes all other contributions to the property.

The prime notation, used in connection with electric resistance, denotes that a linear component of the property considered has been subtracted for convenience in plotting.

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