PHYSICOCHEMICAL NATURE OF METALLIC INTERFACES

BY

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Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy.

1936

UMI Number: DP70315

UMI

Dissertation Publishing

UMI DP70315

ProQuest

Thanks are also due Dr. E. V. Potter of the
Bureau of Mines for a few of the measurements recorded
herein.

ACKNOWLEDGMENT

The writer wishes to express his appreciation to the director of this research, Dr. Malcolm M. Haring, for his counsel and guidance.

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STATEMENT OF PROBLEM AND METHOD OF APPROACH

It has long been recognized that the properties of poly-crystalline substances are not the same as those of single crystals. In the case of metallic substances these differences are especially marked and are of the greatest practical importance in metal work-ing. The property changes which are encountered in passing from a metal single crystal to a polycrystalline aggregate are the same ones which are produced by cold working a metal, or by the precipitation of a disperse phase. Hence, we may logically assume that the pro-perty changes are all due directly or indirectly to the formation of interfacial area or internal surface. Our problem then is to ascer-tain the physicochemical state of the metal atoms at such internal surface and show how this physicochemical condition accounts for the pronounced changes of mechanical, magnetic, and electrical properties which accompany increased internal surface. To do this we shall first consider the more definite and well established property changes brought about in metals by working, dispersion hardening, and anneal-ing, and interpret them in terms of the concept of internal surface. We shall then consider the several theories which have been offered to explain these property changes and see what physicochemical state they require either implicitly or explicitly at the internal surface. At the conclusion of this discussion, the pseudo-molecule theory of

metal surfaces, proposed by the writer in 1921, will be discussed
in detail and certain critical experiments to test this theory de-
vised.

The experimental part of this paper records the carrying
out of these critical experiments and their interpretation.

THE GENERAL CONCEPT OF INTERNAL SURFACE

In 1678 Huyghens attempted to explain the double refraction of calcite by postulating that crystals were built from a regular arrangement of ellipsoidal particles. Over a hundred years later, Abbe Hauy concluded from his studies of cleavage that crystals might be built from small units but that the units were of the same shape as the entire crystal. This idea which was prevalent in mineralogical thought before the advent of x-ray spectrometry was discarded when the great success of the Braggs made it appear that the chemical atoms were in reality the elements of structure. In the farther development of x-ray technique, however, C.G. Darwin in England and P.P. Ewald in Germany found it necessary to postulate crystal units containing many atoms. Ewald gave the name of mosaic crystals to those so constituted. The individual units are supposed to possess the ideal atomic arrangements revealed by the x-ray but are not ideally oriented with respect to one another.

It is obvious that if such units exist in crystals there must be regions of discontinuity between them which possess most, if not all, of the properties of a surface. The adsorption of gas on such an internal surface in apparently single crystals has been demonstrated by the writer in collaboration with Gross, Brighton, and St. Clair, (1) and also by Rideal. (2)

Smekal (3) has shown the effect of this internal surface on many properties and divides crystal properties into two types, those sensitive to such structure, which include elastic limit, breaking stress, thermal and electrical conductivity, magnetic properties, diffusion, etc., and those which are independent, such as thermal energy content, lattice constant, and coefficient of expansion. In the present paper, we are naturally concerned only with the so-called structure sensitive properties.

The entire subject of internal surface in minerals and metals was discussed in a recent paper by the writer and J. Koster. (4)

We shall now discuss in detail the various property changes which may be associated with the formation of such internal surface in metals by any of several means, including, especially, cold work, dispersion hardening, and aggregation of finely divided metallic particles. In this latter connection, the surface of a metallic solid formed by comminution must be considered as similar in many respects to that formed by gliding in a more ductile material.

PROPERTY CHANGES OF METALS INTRODUCED BY INCREASED INTERNAL SURFACE

A. Density and Lattice Parameter

The density of annealed metals is lowered by a moderate
amount of cold work. Wood (5) has shown that the lattice distortion
in copper which has been reduced in cross section 90 percent by cold
work is not uniform but is approximately six times as great in 1/16
of the mass of the metal as in the remaining 15/16. Maier (6) has
shown that the total density change is consistent with the overall
change in lattice parameter up to a reduction in cross section of
80 to 90 percent.

At any large reductions, copper and iron at least, and
probably other metals, increase in density. The change of lattice
parameter in this range has not been studied. Maier attributes
this density increase to the fact that lattice expansion has reached
its limit and a new more dense phase which has been formed from the
start of cold work continues to form in increasing amount.

An alternative explanation put forward by the writer (7)
is that the six percent of the mass which Wood finds to have the
markedly expanded parameter constitutes the new phase, which is ac-
cordingly less dense than the normal lattice, and the increase in
density is caused by a plastic flow in the new phase itself, which
becomes more dense on flow.

B. Energy Considerations

Taylor and Quinney (8) have measured the amount of energy stored in cold working copper, and the energy which can be stored as lattice distortion has been calculated from the density change by Maier. These calculations lead to the definite conclusion that the energy which can be so stored is entirely inadequate to account for the energy storage observed by Taylor and Quinney. The conclusion from this is that the internal surface must itself be an energy reservoir. The stored energy is a linear function of the density and thence presumably of the internal surface. Maier has calculated that the energy stored at this internal surface is 188 calories per gram-atom for fully cold worked copper. By assuming that the increase in energy of the atoms at the internal surface is equivalent to the heat of fusion, he obtains a figure of 5.8 percent for the percent of total atoms at the internal surface, compared with 6 percent estimated from Wood's results on lattice parameter. Using the 6 percent figure, we obtain an increase in energy of the surface copper atoms of 3,100 calories per gram-atom, which may be accepted as the proper order of magnitude.

C. Mechanical Properties

1. Strength

One of the most characteristic properties of metals is that of undergoing plastic deformation without rupture. A necessary corollary of plastic deformation is an increase in strength with deformation. Otherwise, any deforming force must of necessity produce fracture with a minimum of deformation. The quantitative relation of this increase of strength to degree of plastic deformation depends on the mode of producing the deformation as well as the individual metal or alloy. For ordinary rolling or wire drawing, Templin (9) has shown that the following relationship has general application:

$$y = ax + ce^{dx}$$

where y is the increase in tensile strength in percent, x is the reduction in cross-sectional area in percent, and a, c, and d are constants. The two terms of this equation represent presumably two processes which are going on in the metal. The process represented by the first term is dominant up to rather high values of x, but at reductions from 70 percent upward, depending on the metal, the process represented by the second term becomes important, and strength increases more rapidly with deformation. With aluminum, cold working in excess of 80 percent causes a marked increase in the rate of strain hardening.

Data on other metals indicate that strain hardening may reach a nearly constant value at reductions from 60 to 90 percent. Reported decreases of strain hardening (10) at high reductions without the introduction of actual defects have been checked in the writer's (11) laboratory and could not be substantiated. The Templin formula for the relation between increased strength and cold work may therefore be accepted as a sufficiently general one to require explanation by any acceptable theory of metallic interfaces.

Individual metals frequently show several changes of slope in the tensile strength reduction in area curve which must be smoothed out to bring them into agreement with the Templin formula. The inconsistency of the occurrence and position of these secondary deviations from a smooth curve relationship do not justify requiring any general theory of hardening to explain them individually. Their existence is, however, sufficiently well proven that an acceptable theory should indicate the possibility of such a stepwise increase in strength with continuous increase in reduction of area.

The work of Atkins (12) and of Johnson (13) has shown the existence of such irregularities in copper, and that of Comstock (14) has shown their existence in steel. Figure 1, which records unpublished work done in the writer's laboratory at the Western Electric Company some years ago, shows the very clearly stepwise increase of the tensile strength of copper wire with increasing reduction of area.
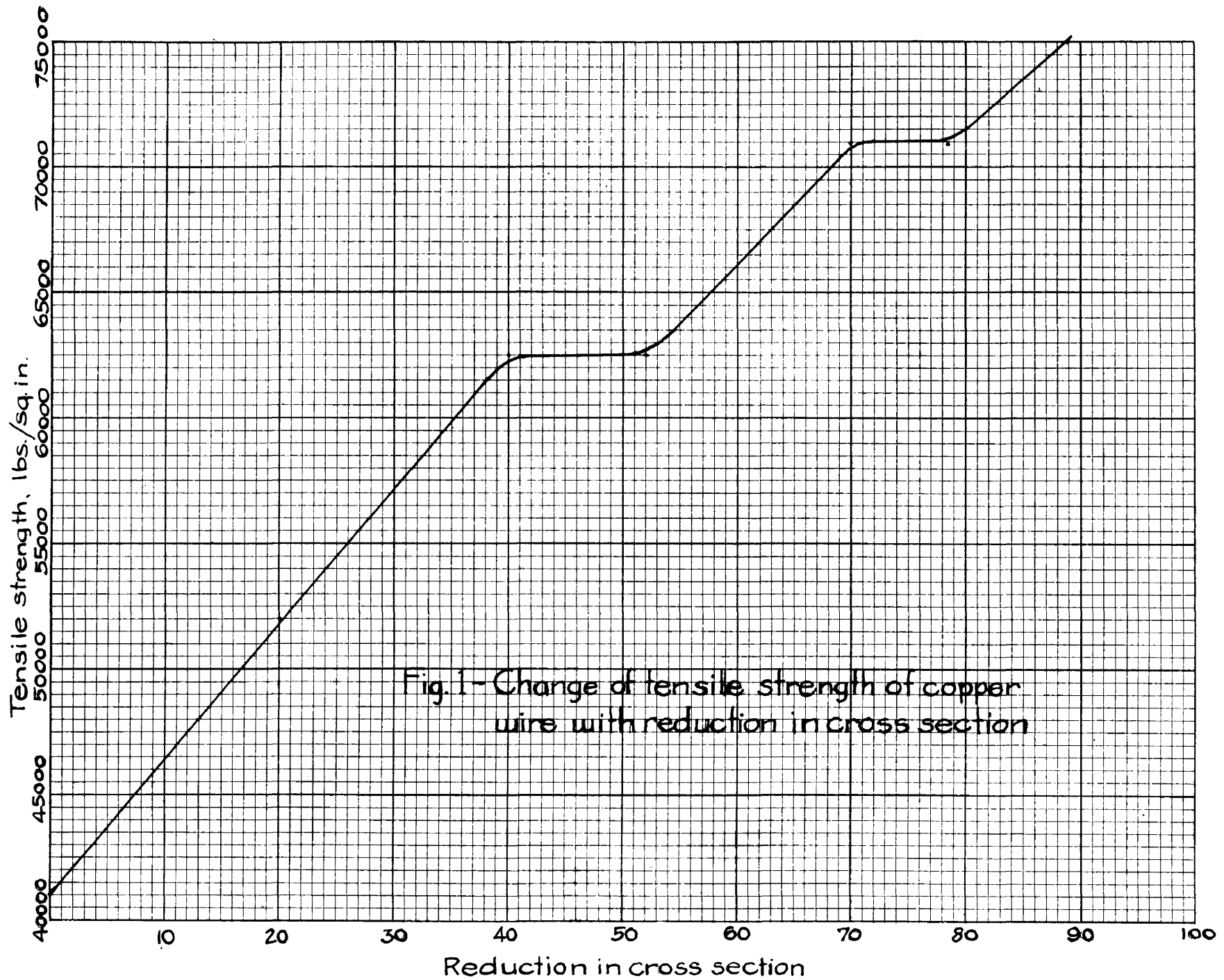
Fig. 1 - Change of tensile strength of copper wire with reduction in cross section

Tensile strength, lbs./sq. in.

Reduction in cross section

It has been pointed out by Jeffries and Archer (15) that
the ability of metals to withstand the amount of reduction found in
severe wire drawing proves that the gliding by which the metal is
deformed must take place more than once on a given plane. Hence,
any set of physicochemical conditions which is set up by the first
movement along a glide plane must not preclude further movement along
that plane without rupture.

A similar increase in strength to that due to cold work is
produced by other methods of increasing internal surface. The ef-
fect of grain size on mechanical properties of annealed metals has
been studied by Bassett and Davis, (16) by Jeffires and Archer, (17)
and by Angus and Summers. (18) The latter investigators established
a linear relation between internal or grain surface and strength
(or Brinnel hardness) which may be taken as the most general rela-
tionship.

The production of increased internal surface by decom-
position of a solid solution is well known, having been first demon-
strated by Merica, Waltenberg, and Scott (19) for the case of
duralumin. A quantitative relation between internal surface and
increased strength has not been directly obtained due to practical
difficulties in measuring internal surface. The work of the present
writer and his associates on dispersion hardening of lead antimony
alloys (20) has shown however that when conditions are such that we
may reasonably assume the particle size to be constant, the in-

crease in strength is very nearly a linear function of the amount

of second phase precipitated. This would indicate, of course, a

linear relationship between increased internal surface and increased

strength. Similar results are found for other dispersion hardening

alloys.

2. Temperature Coefficient of Strength Below the
   Softening Temperature

The temperature coefficient of metals and alloys as a
function of cold work and precipitation hardening has been investigated
by the writer in association with Gregg. (21) According to these in-
vestigations, the Brinnel hardness is an approximately linear function
of absolute temperature for annealed cold worked and precipitation
hardened metals. The cold worked metals show an increased temperature
coefficient, and if extrapolated linearly would have a zero value very
much below the melting point. In the case of precipitation hardened
metals, the temperature coefficient is but slightly changed by in-
creased surface due to precipitation hardening.

D. Electrical Properties

The electrical resistance of metallic substances as a function of internal surface lends itself to more direct investigation than do the mechanical properties since the incidental effects of surface irregularities and structural inhomogeneities are less likely to mask fundamental relations.

It is a matter of common knowledge that electrical conductivity is decreased by cold work. Templin, in the study already referred to, has found that the decrease in electrical conductivity follows closely the formula given for increase in tensile strength, that is $y = ax + ce^{dx}$. Individual variations have been noted as with mechanical properties.

The temperature coefficient of electrical conductivity for cold worked metals has been found by Geiss and van Liempt (22) to follow Mathiessen's law, that is, the product of conductivity and temperature coefficient is a constant. Stated in another way, this means that the resistance of a cold worked metal at any temperature may be stated in an equation of two terms, the first of which is constant, not dependent on temperature, and the second having the same form and constants as does the unworked metal. This leads to the conclusion that the increase of resistance due to cold working does not change with temperature.

The effect of increased internal surface formed by dispersion hardening on electrical conductivity is greatly complicated by the simultaneous decrease in resistance due to decomposition of the solid solution. The writer has, however, presented data (23) to show that electrical resistance may under certain conditions actually increase in the first stages of dispersion hardening, indicating that in the process of dispersion hardening the formation of internal surface may precede the separation of the solute which would then precipitate at that surface.

The quantitative relation between internal surface and electrical conductivity may be studied to advantage in aggregates produced by other than cold working or dispersion hardening. In the case of extremely great extension of internal surface as in sputtered metals, the nature of electrical conductivity is fundamentally changed, since Kapitza (24) has shown the temperature coefficient of resistance to be negative instead of positive as in massive metals. The metallic minerals offer an especially attractive field for the investigation of this phenomenon since they have a low electrical conductivity and hence the effect of internal surface is emphasized. With this advantage in mind, the writer initiated a study of the properties of metallic mineral aggregates several years ago. As a part of this program, Koster (25) studied the electrical properties of crystallized lead sulphide. The relation between temperature and resistance for pastilles made from

powders of different sizes and hence possessing different internal
surfaces was measured. No quantitative relation between internal
surface and resistance was discernable. It was clear, however,
that with increased surface there was a continual increase in the
negative temperature coefficient. These temperature conductivity
curves have an exponential form, and Koster has shown that the
current-voltage relationships for the galena pastilles may be ac-
curately expressed by the equation

$$ R = IMe^{-\frac{Q}{T}} + BT + C. $$

The values of the constants M, Q, B, and C are given in the follow-
ing table.

Screen Size (mesh)	$\frac{100}{d}$ (microns)	M	Q	B	C
-200	----	0.122	2436	5.195	-1,511
-100 plus 200	.878	.0294	2636	3.10	- 915
- 80 plus 100	.521	.0164	2477	.76	- 229
- 60 plus 80	.415	.0110	2380	.73	- 221
- 40 plus 60	----	.0334	1839	.35	- 101
- 20 plus 40	----	.375	601	.20	- 60

It will be seen that as the particle size decreases a
constant value of Q is quickly reached and that for this condition
M is approximately a linear function of 1/d.

It therefore appears that the conduction process across
the interface in galena pastilles is one in which the electric
current is transported by some mechanism with an exponential work
function $e^{-\frac{Q}{T}}$ which is independent of the interfacial area. The
constant M merely serves to determine what part of the total po-

tential drop E takes place by means of this mechanism and what part by means of ordinary metallic conduction represented by BT + C in the formula. It is accordingly roughly proportional to the specific surface 1/d.

The similarity between these quantitative results of Koster and the qualitative results of the effect of interfaces which have been observed in silicon, zirconium, titanium, and graphite, and pressed powdered metals in general (26) justify the conclusion that the quantitative relations derived in the case of galena are general and must be explained by any complete theory of the physicochemical conditions at metallic interfaces.

E. Magnetic Properties

The change of magnetic susceptibility of metals with
cold work has been investigated by numerous investigators (27)
without, however, arriving at a generally accepted conclusion.
The change in any case is small and is indicated as a linear
function of the decrease of density caused by cold work and there-
fore probably a simple function of the internal surface. The
change of ferromagnetic properties with internal surface is much
more pronounced and in the case of coercive force is subject to
a simple and direct demonstration. Such a demonstration has been
arrived at for the first time as a part of the program of mineral
physics studies initiated by the writer in the Bureau of Mines.
In these studies by V.H. Gottschalk (28) it has been shown that
the coercive force of a magnetite powder is a linear function of
its specific surface and independent of packing density or size
distribution.

The writer has obtained a further confirmation of the
same relation (29) by an application of Rittinger's law of crushing,
that the energy input is proportional to the new surface produced.
By means of a falling weight device, known increments of energy are
put into a magnetite powder and its coercive force measured after each
increment. This test shows a definitely linear relation between
work input and coercive force and is therefore in a sense a confir-

mation of both Rittinger's law and the linear relation between co-
ercive force and surface.

The results of Kruesner (30) show that for the torsional
cold working of iron wires the increase in coercive force is a linear
function of the amount of deformation $\pi D/L$.

This linear relationship between internal surface and co-
ercive force has been confirmed by Maier (31) who measured the change
of density and coercive force over a considerable range and found
them to have a closely linear relation throughout the range of
torsional working and for a considerable portion of the range in wire
drawing.

The relation of coercive force to increased internal sur-
face produced by dispersion has been discussed at length by the
writer and his associates (32) and has been made the subject of a
patent. (33)

It is well demonstrated that increased internal surface
produced by dispersion hardening is accompanied by increased coercive
force qualitatively proportional to the amount of such increased
surface.

The relationship of other ferromagnetic properties to in-
ternal surface is not so simple as that of coercive force and no
quantitative relations have been derived.

Since coercive force has been shown to be so directly re-
lated to internal surface, its relation to temperature should be

considered. It has been found that coercive force falls rapidly as temperature increases and becomes zero at the Curie point. This means that magnetization curves become much more nearly rectangular at high temperatures, and the permeability at low fields increases greatly. (34)

Terry's results on relation of temperature to coercive force (35) are as follows:

T (degrees C.)	Hc (oersteds)
-190	5.16
-120	4.55
61	4.43
23	3.84
97	3.23
195	2.93
297	2.62
392	2.50
496	1.99
550	1.60
605	1.29
655	.90
704	.53
740	.29
762	.15

PROPERTY CHANGES ON ANNEALING COLD WORKED
AND DISPERSION HARDENED METALS

In general, the property changes which are brought about by cold working or dispersion hardening may be reversed at least to a large extent by annealing at a temperature below the melting point of the solid in question.

The internal surface due to grain boundaries may also be lessened by grain growth. The velocity of grain growth and ultimate grain size as a function of temperature and degree of deformation on lead-antimony alloys were studied by the writer and W.M. Hudson (36) and it was found that the ultimate grain volume at a given temperature was a linear function of the degree of deformation, that is, directly proportional to the internal surface produced in cold working. The ultimate grain volume for a given degree of deformation could be expressed as a function of temperature by the equation $V = Se^{\frac{-A}{T}}$. The ultimate grain volume could then be expressed by an equation $V = SCe^{\frac{-A}{T}}$, where S is the internal surface produced by cold work. The rate of crystal growth could be expressed by a velocity constant $K = \frac{1}{t} \log \frac{V}{V - x}$, where V is the ultimate grain volume and x the grain volume at time t.

The change of properties of cold worked metals on annealing does not take place suddenly but over a range of temperature which depends on previous history and degree of cold work. The importance of previous history was first clearly set forth by the writer and L. Ziekriek. (37) We found that the rate of change of elongation of

hard drawn copper wire with increments of temperature had the form of a probability curve whose maximum was displaced to higher temperatures by decreasing the temperature of annealing previous to cold working.

It is clear therefore that if part of the internal surface produced by cold working is not removed by the anneal, this part was not materially affected by the subsequent cold working which merely adds internal surface having a probability distribution of annealing temperatures. The net result of course is an increase in the temperature of the maximum of the curve.

If, instead of elongation, the change in tensile strength on annealing had been plotted, the maxima would have come at lower temperatures by 10-15 degrees. This phenomenon has been confirmed by Bradley. (38)

In Figure 2, the writer has replotted in the differential form some data on the annealing range of copper wire, after varying degrees of cold work which were obtained in his laboratories at the Western Electric Company in 1922 by T.C. Merriman but not heretofore published. These results show clearly that with moderate degrees of cold working the temperature of maximum increment of property change for a given temperature increment quickly reaches a constant temperature and is only displaced toward lower temperatures by severe cold work.

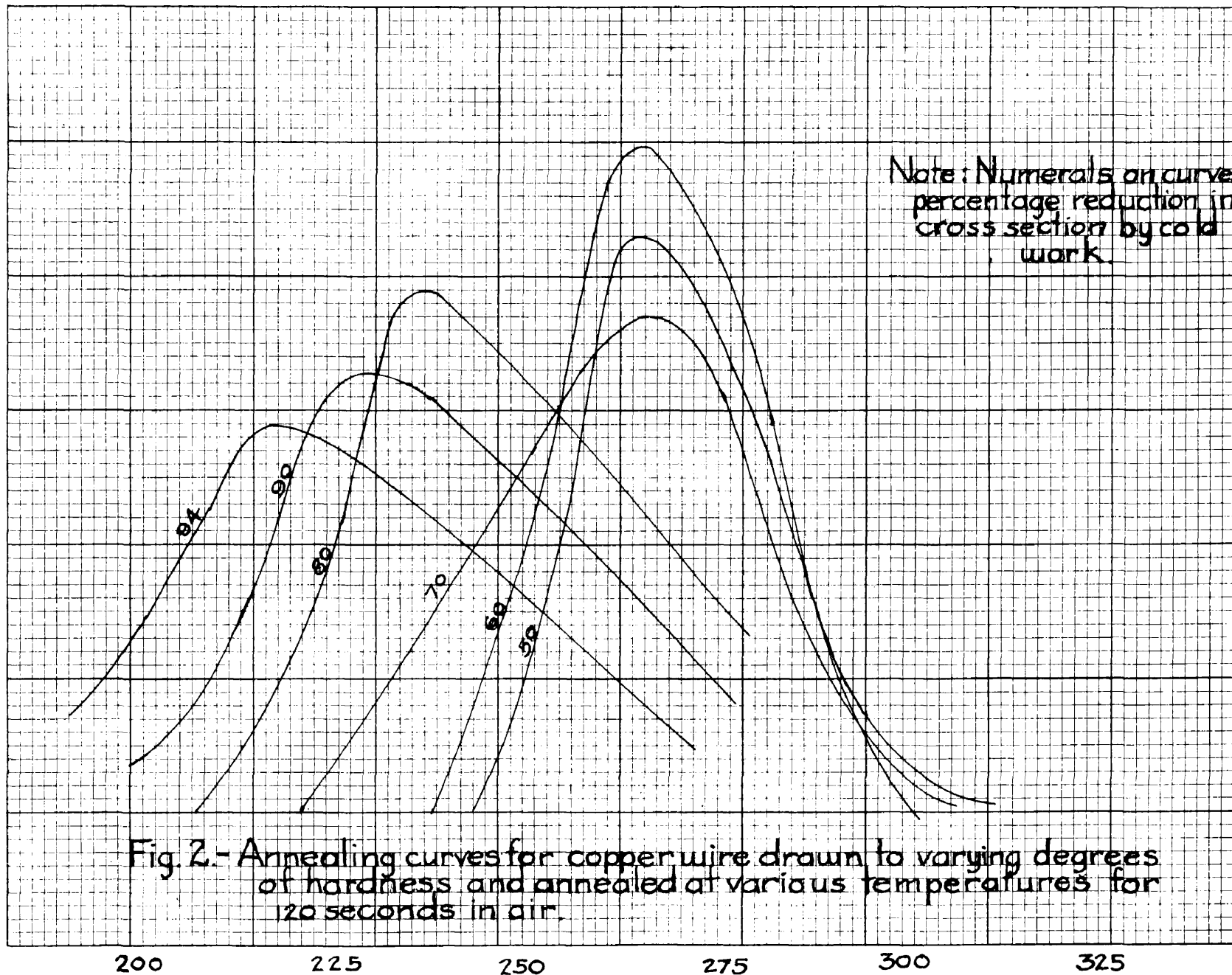Note: Numerals on curves percentage reduction in cross section by cold work.

Fig. 2.- Annealing curves for copper wire drawn to varying degrees of hardness and annealed at various temperatures for 120 seconds in air.

Change in tensile strength per arbitrary unit of temperature increase

Temperature of annealing, degrees Centigrade

We have noted that tensile strength and ductility are not affected uniformly by annealing temperature. The same is true of other properties. Unfortunately, quantitative studies of these effects have not been made.

The change of properties on heating metastable solid solutions to produce dispersion hardening has been carefully studied and some important generalities found. A study of the dispersion hardenable carbon-free magnet alloys of iron, cobalt, and molybdenum, invented by the writer, (39) showed that the temperature for the production of maximum coercive force was very much higher than that for the production of maximum hardness. It would appear that in the deposition of the solid solution, internal surfaces were formed at an increasing rate over a considerable temperature range but that in the simultaneous annealing process the hardness decreased before the coercive force was affected.

This confirms a mechanism of dispersion hardening suggested by the results of conductivity and strength changes in quenched lead-antimony alloys; namely, that the first process in the decomposition of solid solution is to form internal surface by breaking up the mass into blocks before any actual phase separation takes place.

This mechanism of dispersion hardening is in line with the recent results of Gloeker, Pfister, and Wuest, (40) who found that in the aluminum-nickel-cobalt magnet steels there was no hardening of of lines in the x-ray diffraction pattern or change of lattice con-

stants when the coercive force was a maximum. Only at much higher temperatures did the lattice constant undergo a change.

Clayton (41) has recently obtained results on the change of coercive force of ordinary carbon steels during hardening and tempering. These results show that the increased coercive force produced by quenching falls rapidly on tempering and has greatly decreased before any perceptible decrease of hardness occurs. This is explained on the internal surface theory by formation of internal surface by quenching through the transition point of iron. Some of this internal surface is stabilized by actual precipitation and is responsible for hardening; the unstabilized internal surface is rapidly destroyed by annealing with a decrease of coercive force.

THEORIES OF METALLIC INTERFACES

The theories which have been proposed to account for the
change in properties of metals by the increase of internal surface
may be conveniently divided into four groups.

1. Theories which postulate the formation of new Gibbsian
phase at the interface.

2. Theories which postulate nothing definite concerning
the physicochemical nature of the interface and attribute all pro-
perty changes to distortion of the lattice which is incidental to
the presence of increased internal surface.

3. Theories which attribute the property changes to dis-
registry of the lattice across the internal surface.

4. Theories postulating a non-Gibbsian phase at the inter-
face.

A. Theories Postulating a New Gibbsian Phase

The earliest complete theory of metallic interfaces is the amorphous metal hypothesis of Sir George Beilby. (42) The amorphous theory postulated that at metal interfaces, whether formed at the boundaries of crystals grown from a melt or by cold work, a layer of amorphous metal was formed. This amorphous metal, according to Beilby, had the structure and properties of a super-cooled liquid, and the properties of the resulting aggregate were those of a mixture of the super-cooled liquid and solid phases of metal. Beilby developed interesting experimental evidence of such an amorphous film on polished surfaces and recent work with electron diffraction has confirmed Beilby's work. (43)

The properties which must be assigned to a super-cooled liquid do not enable its presence to account for the property changes brought about by internal surfaces. The writer pointed out this discrepancy many years ago. (44)

It is now generally accepted that if an amorphous layer does exist at metallic interfaces, it is not a super-cooled liquid and must be assigned properties which are not consistent with the ordinary or Gibbsian definition of a phase.

B. Theories Postulating Lattice Distortion

The theory that the hardening produced by cold work was due to elastic strain was perhaps first proposed by Heyn. (45) It has been further developed by Sachs. (46)

The inability of lattice distortion to account for electrical property changes on cold working has been shown by Geiss and van Liempt. (47) The discrepancy between energy storage in cold worked metals and that possible due to lattice distortion has already been pointed out.

Fink and Van Horn have studied lattice distortion as a factor in hardening of metals (48) and concluded that lattice distortion approximating the elastic limit did not alter hardness.

It may therefore be reasonably concluded that lattice distortion per se is not adequate to account for the effect of internal surface on property changes in metals.

C. Theories which Postulate Disregistry of the Lattice

These theories have been very successful in the hands of Jeffries and Archer (49) and, more recently, of Taylor (50) in accounting for certain mechanical properties of cold worked metals. Their inadequacy to account for changes of electrical or magnetic properties without some additional hypothesis concerning the physicochemical nature of the metallic interface has been thoroughly discussed by the writer (51) and more recently by Maier. (52)

D. Theories Postulating Non-Gibbsian Phases at the Internal Surface

The simplicity of the Beilby theory has prompted many investigators to suggest that the amorphous phase was not a super-cooled liquid or a second crystalline modification but some state of aggregation not definable as a phase from a phase rule standpoint.

Honda (53) and Polanyi (54) have suggested that the new phase is in reality merely an aggregate of fine crystals.

Oatao and van Liempt (55) have suggested that the atoms forming the new phase have deformed outer shells which give rise to the changes in properties. Van Liempt has followed the idea further (56) and has postulated this atomic deformation to result in higher energies for the deformed atoms which may be calculated from the usual quantum formula, $E = .75 Q_v = nh\nu$, where Q_v is the heat of vaporization. From these considerations, about 50-250 quanta are added to the energy of the atom by deformation.

Mater (57) has been less definite in the nature of the new phase, postulating merely an accumulation of atoms having a higher heat content than the normal lattice and stating "convenience and expediency require a concise term for the designation of the total content of atoms not having lattice spacings either normal or distorted". He suggests that such nondescript atoms are in fact adsorbed on the lattice.

The pseudomolecule theory of hardening which was first proposed by the writer in 1922 (58) had much in common with these more recent proposals. It suggested that the amorphous layer, if it existed, would not be a stable or Gibbsian phase but would resemble a monotropic form. It went further and postulated the exact structure of such a monotropic form. This postulate recognised that the metallic lattice was built of ions, not atoms, and that in addition to those ions the lattice contained electrons either in a random distribution or a lattice of their own. It was then postulated that if the ions were displaced from their equilibrium positions they would tend to take on electrons and become atoms, and in view of the competition for electrons in such a process the ions might in some cases share electrons, thus forming dipoles which were called pseudo-molecules. They might have more properly been called merely molecules. Since the ions which would form such a molecule might come from opposite sides of a glide plane, their strengthening effect was at once apparent. Their effect on electrical properties was also patent, since free electrons were bound and hence conductivity reduced.

This theory was further elaborated and its advantages discussed by the writer and Gregg in 1927. (59) We shall now attempt to give it a highly explicit statement and show how it satisfactorily explains the change of properties of metals due to internal surface.

EXPLICIT STATEMENT OF PRESENT CONCEPT OF PSEUDO-MOLECULE THEORY

1st Postulate. The ions in a metallic lattice are displaced from their equilibrium position at a surface.

2nd Postulate. This displacement results in the formation of electrical dipoles in which the ions share electrons.

3rd Postulate. Energy of thermal vibration of these dipoles (heat content) is greater than that of ions in the lattice, and such energy is distributed according to a Boltzmann or probability relation.

A. Effect of Internal Surface on Density and Lattice Parameter in the Light of Pseudo-Molecule Theory

The distance between ions in the pseudo-molecule may be either more or less than the normal lattice distance. Accordingly, internal surface may increase or decrease density and apparent lattice parameter. On this basis, it appears that the ions of the pseudo-molecules formed under usual cold working conditions are farther apart than those in the normal lattice, but by extreme compressional cold work, such as severe wire drawing, the ions in the pseudo-molecules may be brought back to the normal lattice distance (corresponding to what Maier has called mechanical recrystallization) and compressed so that they are closer than in the normal lattice. Such a concept accounts for the density minima frequently observed and is as we shall see also consistent with annealing phenomena.

B. Theory Considerations

The increased energy at the surface is accounted for by the greater kinetic energy of vibration at a given temperature of the pseudo-molecules over the atoms in the lattice. From density and energy absorption data, Euler gives a figure of 2,800 calories per gram-atom for the high energy atoms. The pseudo-molecule theory permits an estimate of this energy for a plane surface from Euler's measurements of the temperature coefficient of electrical conductivity. If we assume that the electrical energy was transformed in Euler's experiments by the thermal vibration of the pseudo-molecules, the value of Q in his term $e^{-\frac{Q}{kT}}$ becomes the maximum energy which a pseudo-molecule can have before breaking down. Multiplying this by the Boltzmann constant to give the value per gram-molecule, we obtain a value of 6,000 calories per gram-atom which is of the right magnitude, being somewhat less than the latent heat of fusion.

C. Mechanical Properties

In its means of dealing with the simpler phases of change of mechanical properties with increased internal surface, the pseudo-molecule theory does not differ essentially from other theories. Any phenomenon which makes gliding more difficult on a plane once it has undergone gliding will account for the substantially linear relation between strength and degree of cold work which is found up to high percentages of deformation.

The change of slope of the deformation-strength curve at high deformations may be accounted for by a variety of assumptions without recourse to a change in the structure of the internal surface. We may, for example, assume that preferred orientation becomes an increasing factor and the glide planes are thereby rotated into less and less favourable angles with the direction of force. Such assumptions, however, fail to account for the frequent occurrence of several changes of slope in the strength-reduction in area curves of drawn wire.

The pseudo-molecule theory postulates that during the linear part of the curve the dipoles which are formed are normal or surface dipoles in which the distance between the ions is a little greater than that of the normal lattice. As the available gliding surface is used up, however, the pseudo-molecules undergo compression and flow takes place by breaking down the original pseudo-molecules and the formation of more dense dipoles with higher energy level.

A considerable number of such energy levels are stable, so that
the curve relating strength to reduction in area will undergo a
change in slope as the pseudo-molecules change from one energy
level to the next. It will be seen later that such a hypothesis
is consistent with the annealing data which can not otherwise be
satisfactorily accounted for.

For internal surface formed by other than cold work, the
pseudo-molecule theory is competent to explain the observed facts
but not unique in being able to do so.

In its treatment of the temperature coefficient of cold
worked metals, the pseudo-molecule theory is rather more satisfac-
tory than other theories.

It is difficult indeed to see how a theory based on
orientation of slip planes or length of individual slips can ac-
count for the marked change in temperature coefficient of hardness
which takes place with increased internal surface and the closely
linear relation of the hardness to temperature in both annealed and
worked metals. According to the pseudo-molecule theory, the resis-
tance to deformation (by which hardness is measured) is decreased
by the thermal vibration of the dipoles. This decrease is propor-
tional to the increased tendency to vibrate or inversely to the
mean moment in the direction of the faces. The hardness at any tem-
perature t will be given by $H_t = H_o (1 - \frac{c}{\overline{m}_t})$ where H_o is the hard-
ness at absolute zero, $\overline{m}_t$ is the mean moment of the dipoles in the
direction of the deforming force at temperature t, and c is a con-
stant.

Now it is well established from kinetic theory that

$$\bar{m} = \frac{\mu}{3kt}$$

where μ is the dipole moment, k the Boltzmann constant, and t the temperature. We find accordingly that

$$H_t = H_o \left[1 - \left(\frac{3ck}{\mu^2} \right) t \right].$$

By putting H_t equal to zero, we find that

$$\frac{\mu^2}{3ck} = t.$$

Hence for $\frac{\mu^2}{3ck}$ we may write T_o, the temperature at which the mean moment in the direction of the deforming force becomes equal to 1/e and the hardness zero. The formula then becomes

$$H_t = H_o - \left(\frac{H_o}{T_o} \right) t$$

which is in agreement with the observations of the writer and Gregg. (59)

The value of T_o may be approximated by the application of the Clausius-Clapeyron formula to the change from normal lattice to the high energy state and assuming that the change in T_o is produced by the volume expansion alone. Proceeding in this way, we obtain

$$dT_o = \frac{(v_2 - v_1) T dp}{\lambda f}$$

For copper, we obtain

$$V_2 - V_1 = .05 \text{ c.c. per c.c.}$$
$$\lambda f = 5,000 \text{ cal. gram atoms} = 5,260 \text{ atm. c.c. per gm.}$$
$$T = 1,500$$
$$dp = 5,500 \text{ atm.}$$

(Compressibility $\beta = 1.5 \times 10^{-6}$ at 1000° Abs.)

$$dT_o = \frac{.05 \times 1500 \times 36,000}{5260} = 670.$$

T_c for copper   1300 - 670 = 630

Actual value = 700.

The relations between volume and energy of the atoms in the dipoles and in solid solution are not known, so that similar calculations can not be made for the case of dispersion hardening.

D. Electrical Properties

The pseudo-molecule theory offers a simple explanation of the effect of internal surface on change of electrical properties, namely, the reduction in the number of free electrons. In the case of good conductors and a small specific surface, the contribution of the pseudo-molecules themselves may be neglected, so that the effect is a simple function of amount of cold work, the same as is strength increase. For such good conductors, the increase in resistance is independent of the temperature, since it arises from the simple decrease in number of electrons. This accounts for the application of Mathiessen's rule to cold worked metals.

When the conductors are poor and internal surface greatly extended, the contribution of the pseudo-molecules themselves must be considered and may in fact become dominant.

To derive an expression for this contribution of the pseudo-molecules to conductivity, we must postulate a mechanism of conduction. The simplest possibility is that the pseudo-molecules only contribute to conduction when they are dissociated by the combined action of their thermal agitation and the applied field. Under these conditions, the number which will dissociate with a given applied field can be calculated from a Boltzmann distribution of the energies of the dipoles.

$$n = N e^{-\frac{\varphi}{T}}$$

where n is the number having a kinetic energy above a certain

minimum Q, N is the total number, and T is the absolute temperature.

This would give a current $I = EAe^{\frac{-Q}{T}}$ for the pseudo-

molecules.

$$\frac{E}{R'} = EAe^{\frac{-Q}{T}} \qquad \frac{1}{R'} = Ae^{\frac{-Q}{T}}$$

Now the total resistance of the piece if the pseudo-molecules are

in parallel with the electronic conduction is given by

$$\frac{1}{R} = \frac{1}{R'} + \frac{1}{R''}$$
$$\frac{1}{R} = Ae^{\frac{-Q}{T}} + \frac{1}{R''}$$

Multiplying by $R^2 I$, we obtain

$$E = R^2 I Ae^{\frac{-Q}{T}} + \frac{R^2}{R''}$$

Since most of the conduction is due to the dipoles, $R'' = R$ and we

may write

$$E = IMe^{\frac{-Q}{T}} + bt + C$$

in conformity with Koster's results.

Now the quantity -Q is the energy of dissociation of the

pseudo-molecules. To obtain this in terms of calories per gram atom.

Koster's value of Q must be multiplied by 2R which gives a value of

5,000 calories. This value is in excellent agreement with Maier's

value for the energy of transition of his omega phase in copper.

It will be remembered that in deriving this equation, we

assumed that a certain field, independent of the resistance, caused

conduction by the pseudo-molecules. Hence, when I becomes zero, the

remaining field gives rise to a certain potential E. This is in

accord with Koster's observations which show that the voltage-
current relations for any temperature can be expressed by an equation
of the form E = IR + A, the value A representing the applied field
necessary to start conduction by pseudo-molecules. The field neces-
sary would be that at absolute zero less the reciprocal mean moment
of the dipoles in the direction of the field, that is

$$E_t = E_o - \frac{c}{\overline{m}}$$

and since $\quad \overline{m} = \frac{\mu^2}{3kt}$

$$E_t = E_o - ct$$

which is in agreement with Koster's equation A = Bt + C.

E. Magnetic Properties

We have seen that increased internal surface exerts a
profound effect on magnetic properties causing the normal magnetiza-
tion curve to approach saturation more gradually and giving an in-
crease of coercive force which is a linear function of the increased
internal surface. In order to discuss the explanation of these
changes on the basis of the pseudo-molecule theory, it will be neces-
sary to outline briefly the modern theory of ferromagnetism.

As a model for a ferromagnetic substance, we shall take
an array of elementary permanent magnets of atomic dimensions having
a marked tendency to be parallel to their neighbors. The exact
nature of these elementary magnets need not concern us. At the
moment, physicists prefer to think of them as spinning electrons
somewhere near the outer surface of the atoms. In the absence of
restraining forces, these elementary magnets will point in the
direction of any applied field. The I - H curve of such a model
will be a straight line parallel to the H axis. This is not in
accord with the I - H curve for the materials with which we are used
to dealing. However, it is found that single ferromagnetic crystals
when magnetized in certain crystallographic directions do behave
like the model. Akulov (60) has shown that for the (100) direction,
that is along the edge of the cube for pure iron, saturation is
reached at about 100 oersteds, and thereafter the magnetization fol-

lows the theoretical line closely. Since magnetization proceeds
to saturation in very small fields only if applied parallel to the
(100) direction, it may be assumed that the elementary magnets are
constrained to point along these axes. For the other axes, the re-
sultant magnetization in the direction of H must be given by

$$I_{(110)} = I_s \frac{1}{\sqrt{2}}$$
$$I_{(111)} = I_s \frac{1}{\sqrt{3}}$$

Now Akulov found I_s for a cubic iron crystal to be 1710 from which
we calculate $I_{(110)} = 1210$ and $I_{(111)} = 990$. These figures are
within the experimental error of those found by extrapolation to
zero H of the I - H curves of Akulov.

The fact that the I - H curves of even the purest iron
crystals do not conform to the theory at fields below 100 oersteds
has been accounted for by lack of perfection in the crystals. Thus
Becker (61) has accounted for the rounded I - H curves by the as-
sumption of random distortions in the iron crystals.

The variation of I_s with temperature is satisfactorily
accounted for by the Weiss extension of the Langevin Theory.
Langevin postulated that the tendency to magnetic orientation in
paramagnetic substances was opposed by thermal agitation. Weiss
extended this conception to ferromagnetics by adding an intrinsic
field proportional to the intensity of magnetization. This in-
ternal field acted in the same direction as the external force.

These considerations lead to the well known Weiss equation

$$\frac{I_s}{I_o} = \tan h \; A \; \frac{I_s}{T}$$

where I_o is the saturation value at absolute zero, T the absolute temperature, and A a constant.

So far, nothing has been said concerning hysteresis effects, and there is nothing in the theory of magnetism of perfect crystals to account for the existence of such effects. As a matter of fact, there is good reason to believe that hysteresis would be absent in ideal crystals.

At an internal surface, the pseudo-molecule theory postulates the existence of electrical dipoles in thermal vibration. These dipoles will restrain the motion of the elementary magnets so that saturation is reached at higher field strengths. Further, the reversal of the field will not reverse the restrained magnets at once, and the unrestrained magnets will require further rotation to produce statistical demagnetization at the coercive force. For this condition of statistical demagnetization,

$$I H c = \frac{I_d N}{I_s - I_d N}$$

where IHc is the magnetization coercive force, $I_d N$ is the intensity of magnetization produced by the restrained magnets, and I_s the saturation intensity.

Since $I_d N$ is usually small in comparison with I_d, it follows that

$$I H c = \frac{I_d N}{I_s}$$

and since the number of restrained magnets may be taken as proportional to the specific surface,

$$IHc = \frac{S}{I_s}$$

This explains the surface-coercive force relationship which has been found for both internal and external surface.

The temperature relationships of magnetic properties of internal surface are all accounted for by the application of the conception that the magnetizing force is opposed by the thermal motion of the dipoles, the mean moment of the dipoles in the direction of the field being given by

$$\bar{m} = \frac{\mu^2}{kt}$$

Accordingly, the coercive force at any temperature is given by

$$IHc(t) = IHc(o) - \frac{c}{m}$$

$$IHc(t) = IHc(o) - \frac{3ck}{\mu^2}T$$

where

$$\frac{3ck}{\mu^2} = \frac{THc(o)}{Tc}$$

where T_c is the Curie temperature.

F. The Property Changes on Annealing Cold Worked and Dispersion Hardened Metals

The pseudo-molecule theory differs essentially from new phase theories in that the high energy atoms are not limited to any particular energy level or range of energy levels, but are postulated to be formed by cold work with a probability distribution of energy levels. Further, there is no partition of energy among them, so that on annealing at a given temperature the dipoles with higher energy are decomposed with the formation of normal lattice while those having energies below a certain minimum corresponding to the temperature will remain unaffected.

The number of atoms having an energy high enough to decompose at a given temperature T will be given by the usual probability equation

$$n = Ne^{\frac{-Q}{RT}}$$

where N is the total number of dipoles, Q is the heat of decomposition per gram-atom, R is the Boltzmann constant, and T is the absolute temperature.

This distribution is a satisfactory explanation of the observed rate of grain growth in cold worked metals. It also explains the effect of previous history on the annealing range of cold worked metals. Since a true probability distribution would be found only for the cold working of a single crystal. Other metals will possess a deficiency of high energy dipoles due to their decomposition in previous annealing.

Since the properties of metals depend not only on the total number of pseudo-molecules but also on the energy distribution, all properties change together on cold work where the energy distribution is a probability one, but on annealing the properties do not change together. Some properties, as coercive force, appear to be affected by dipoles of an extremely wide energy range and hence serve as a measure of the total number of dipoles. Others as density and strength are affected by only the higher energy dipoles and hence decrease sharply before coercive force is affected.

PROPOSED EXPERIMENT TO DIRECTLY DEMONSTRATE THE EXISTENCE
OF DIPOLES AT METALLIC SURFACES

The evidence for the existence of dipoles at metal surfaces which we have presented so far is all of an indirect nature. It should be possible to directly demonstrate the existence of such dipoles by a dipole loss in an electrical field of appropriate frequency.

From the assumptions which have been made, it is possible to calculate approximately the natural frequency of such dipoles, and hence the frequency of the field in which the transference of energy by the dipoles would reach a maximum.

We have assumed that the dipoles are formed by the sharing of electrons between metal ions and that the parameter change necessary to bring this about was small; hence, the length of the vibrating element may be taken as roughly one-half the inter-atomic distance or 10^{-7} cm. If the restoring force is gravity, we obtain a frequency which will be of the order $\left(\frac{l}{g}\right)^{-\frac{1}{2}}$ or 50,000 cycles.

EXPERIMENTAL

A. Measurement of Core Losses as a Function of Frequency

1. General Plan

If electrical dipoles exist at the surface of metallic substances, then metallic powders should absorb energy in an alternating field having a frequency of the same order as their natural frequency. Our calculations have shown that such frequency should be between zero and 100 kilocycles. Hence measurements were undertaken over this range.

The method employed was an application of the well known method for analyzing core losses in telephone loading coils. This method has been described by Speed and Elmen.(62) In this method, the inductance and effective resistance of a coil are measured at different frequencies and the losses due to hysteresis and eddy currents separated by a graphical analysis in which $\frac{\Delta R}{Lf}$ is plotted against f, ΔR being the increase in effective resistance, L the inductance, and f the frequency. Such a plot gives a straight line, the slope of which is a measure of the eddy current loss, and the intercept on the $\frac{\Delta R}{Lf}$ axis is a measure of hysteresis loss. At the frequencies which we shall employ, hysteresis becomes negligible and $\frac{\Delta R}{Lf} = 8\pi^2 \nu \mu f$ where ν is the eddy current coefficient and μ the permeability. Any loss due to dipoles should result in a deviation from the linear relation of $\frac{\Delta R}{Lf}$ and f by a sharply increased slope as the resonant frequency is approached.

2. Apparatus

For the measurements, an Owens bridge was selected. This bridge was constructed with the usual precautions regarding shielding, etc. The circuit is shown in Figure B-1. The inductance L consisted of a coil having 530 turns of number 36 wire wound on a bakelite spool. The coil was 21 cm. long and had a radius of 0.957 cm. The calculated inductance was L = 0.464 millihenry. The inductance measured at 200 kc. was L = 0.467 millihenry.

The powder to be measured was tamped lightly into the bakelite spool and $\triangle R$ and L measured for frequencies from 18 to 65 kilocycles.
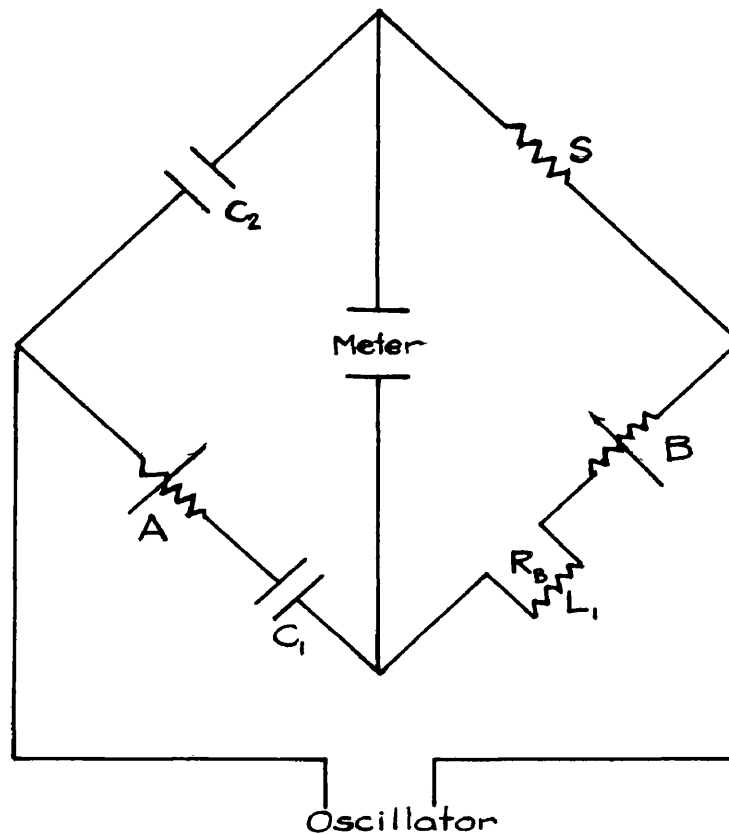
Balance equations -

Real $\quad \dfrac{L}{C^2} = SA$

Imaginary $\quad \dfrac{B}{C^2} = \dfrac{S}{C_1}$; i.e., $\quad \dfrac{B + R_B}{C_2} = \dfrac{S}{C_1}$

Fig. E-1. - Owens bridge used in
core loss measurements.

3. Results

Preliminary experiments showed that with magnetite powder a straight line relation was obtained for $\frac{\Delta R}{L f}$ vs. f. This indicated that with this material the loss was due to eddy currents within the accuracy of measurement. Further, the loss was substantially independent of particle size, being nearly the same for reduced hematite having a coercive force of several hundred. It was therefore apparent that no internal surface exists in magnetic powders at which the dipoles if present might be expected to oscillate. This is presumably due to some sort of magnetic chaining. The results for magnetite, hematite, and powdered iron are shown in Table 3-1 and plotted in Figure 3-2. The practical identity of $8\pi\nu$ for magnetite and reduced hematite will be noted.

TABLE 3-1

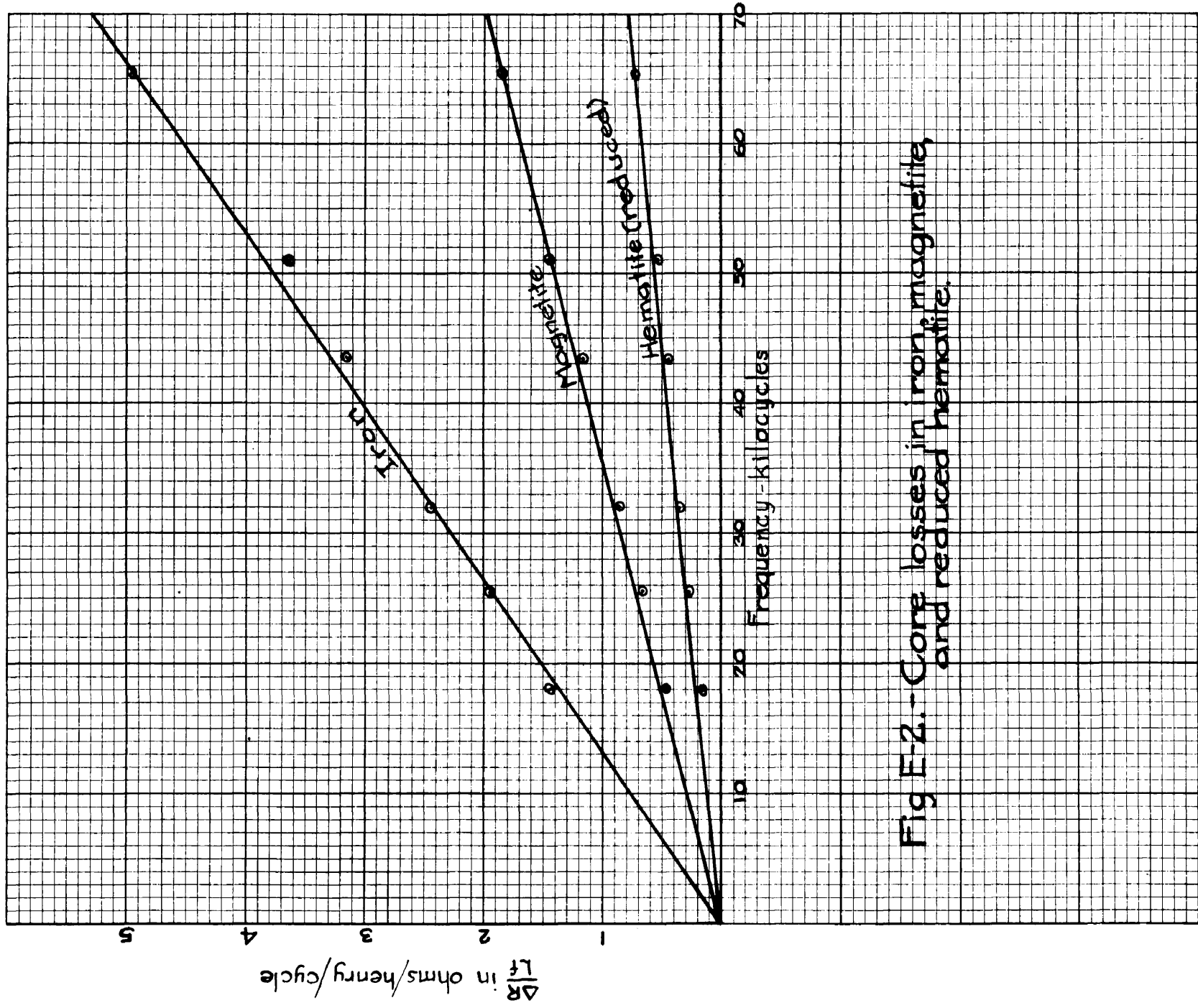| Frequency Kilocycles	$\frac{\Delta R}{L f}$ (Ohms/Henry per Cycle)		
	Magnetite	Reduced Hematite	Powdered Iron
65.5	.162	.071	.495
61.0	.142	.068	.368
45.5	.119	.042	.324
32.0	.086	.034	.244
25.4	.067	.027	.196
18.1	.048	.018	.142
$\frac{\mu}{8\pi\nu}$	3.16 $.847 \times 10^{-6}$	1.45 $.818 \times 10^{-6}$	2.53 3.37×10^{-6}

Fig E-2.- Core losses in iron, magnetite, and reduced hematite.

In order to furnish surface at which the dipoles, if

present, might oscillate, the magnetite was mixed with fifty percent

of its weight of sand. The results are shown in Table E-2 and

Figure E-3.

TABLE E-2

| Frequency Kilocycles | $\frac{\Delta R}{LF}$ (Ohms/Henry/Cycle) | |
	Magnetite	Magnetite and Sand
66.6	.185	.115
51.0	.140	.082
43.5	.118	.065
32.0	.087	.045
25.4	.066	.035
18.1	.049	.025
		too small to measure
λ	3.13	1.62

It is evident from this result that with the introduc-

tion of definite internal surface into a magnetite powder a new

loss appears at a frequency between 50 and 65 kilocycles. We can

not, of course, positively identify this loss with the existence

of dipoles, but it occurs at the right frequency.

Attempts have been made to use non-magnetic materials,

but the losses become either too small to measure with fine powders

or are vitiated by eddy current shielding with large particles.

The results on 10-mesh aluminum powder were reproducible

and are worth recording. They are given in Table E-3 and Figure

E-4.

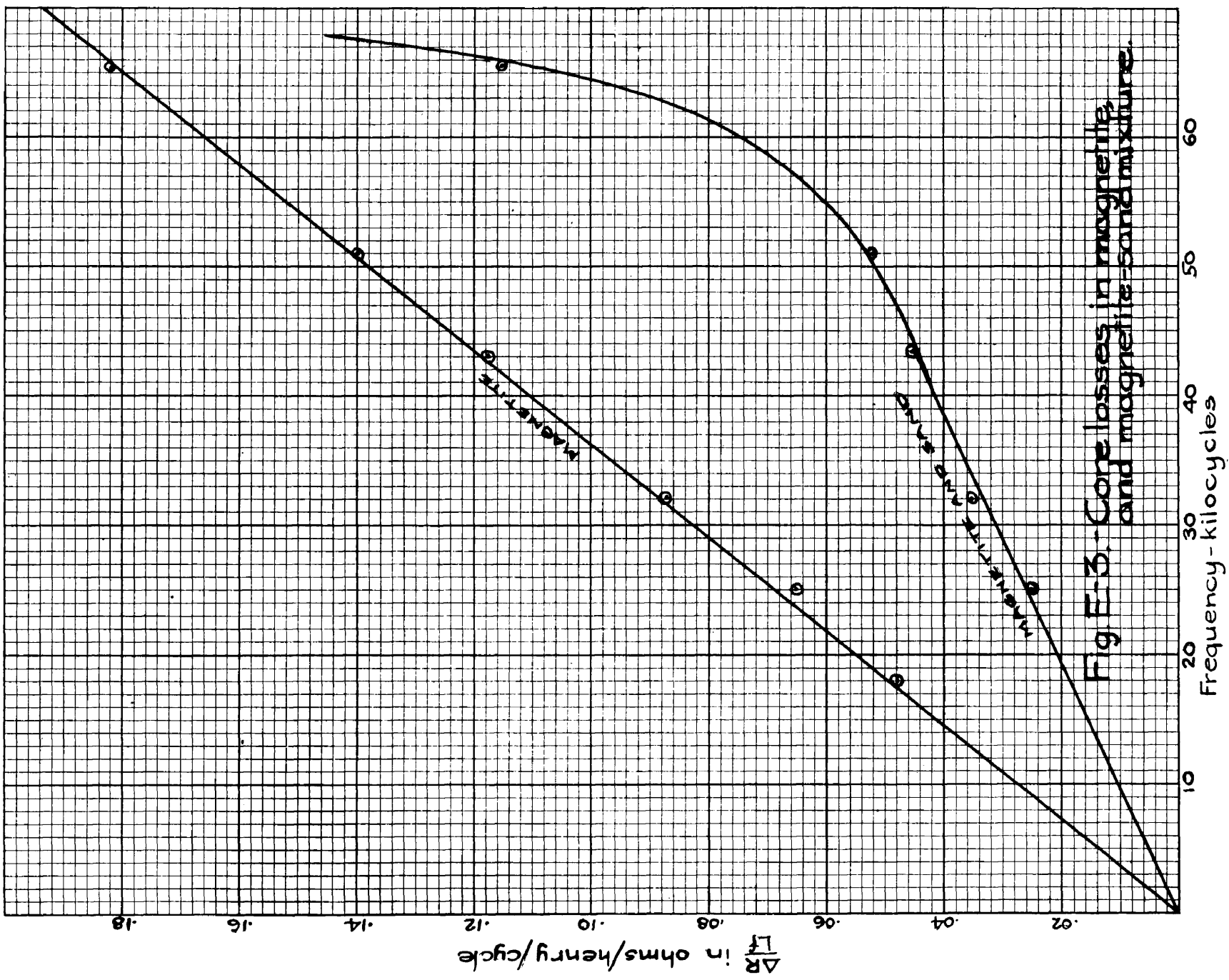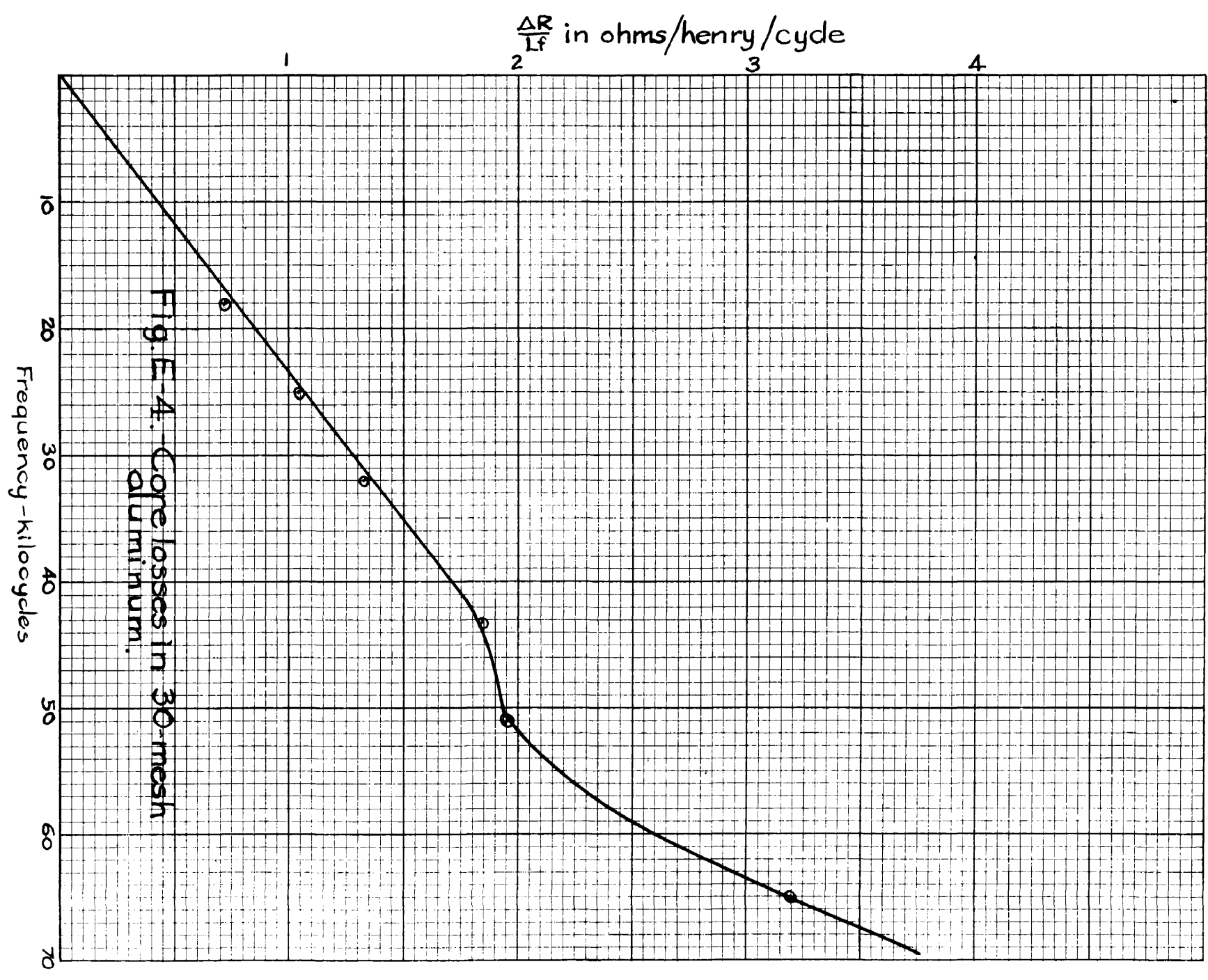Fig E-3.- Core losses in magnetite and magnetite-sand mixture.

Frequency - kilocycles

$\frac{\Delta R}{Lf}$ in ohms/henry/cycle

MAGNETITE

MAGNETITE AND SAND

.18 .16 .14 .12 .10 .08 .06 .04 .02

10   20   30   40   50   60

Fig. E-4. Core losses in 30-mesh aluminum.

TABLE E-3

Frequency Kilocycles	$\frac{\triangle R}{L f}$ Ohms/Henry/Cycle
65.5	.321
51.0	.195
43.5	.187
52.0	.132
25.4	.104
18.1	.073

A sharp increase in losses around 50 kilocycles is also indicated in this case.

While the results of these tests are qualitatively in accord with the theory, the method is not capable of sufficient refinement. It was therefore decided to make direct measurements of electrical conductivity of slightly compressed powders. For this purpose, the oscillator and bridge set set up were somewhat changed and improved.

B. The Measurement of Electrical Resistance as a Function
of Frequency

1. General Plan

The conduction of electricity in a metallic powder has
been indicated by Koster's work to take place largely by thermal
vibration of conducting elements under the influence of a definite
potential which is set up across the internal surface. If these
conducting elements be identified with the pseudo-molecules or
dipoles, then the action of the initial potential may be conceived
as causing orientation toward the negative surface. As this
negative biasing potential is changed to zero by the alternation
of the field, the oriented dipole will fall away from its position
under an acceleration due to gravity and a very small electrical
repulsion. Figure B-5 represents a highly idealized picture of
the postulated mechanism. When the time of fall to equilibrium is
equal to that between the times of zero or slightly positive po-
tential, the energy of vibration would reach a maximum and, hence,
the resistance would pass through a minimum.

The time of descent of a mass along any chord passing
through the highest point of a vertical circle is given by
$t = 2\sqrt{\frac{r}{g}}$ (Hastings and Beach, General Physics, p. 67) where r is
the radius of the circle and g the acceleration of gravity. For
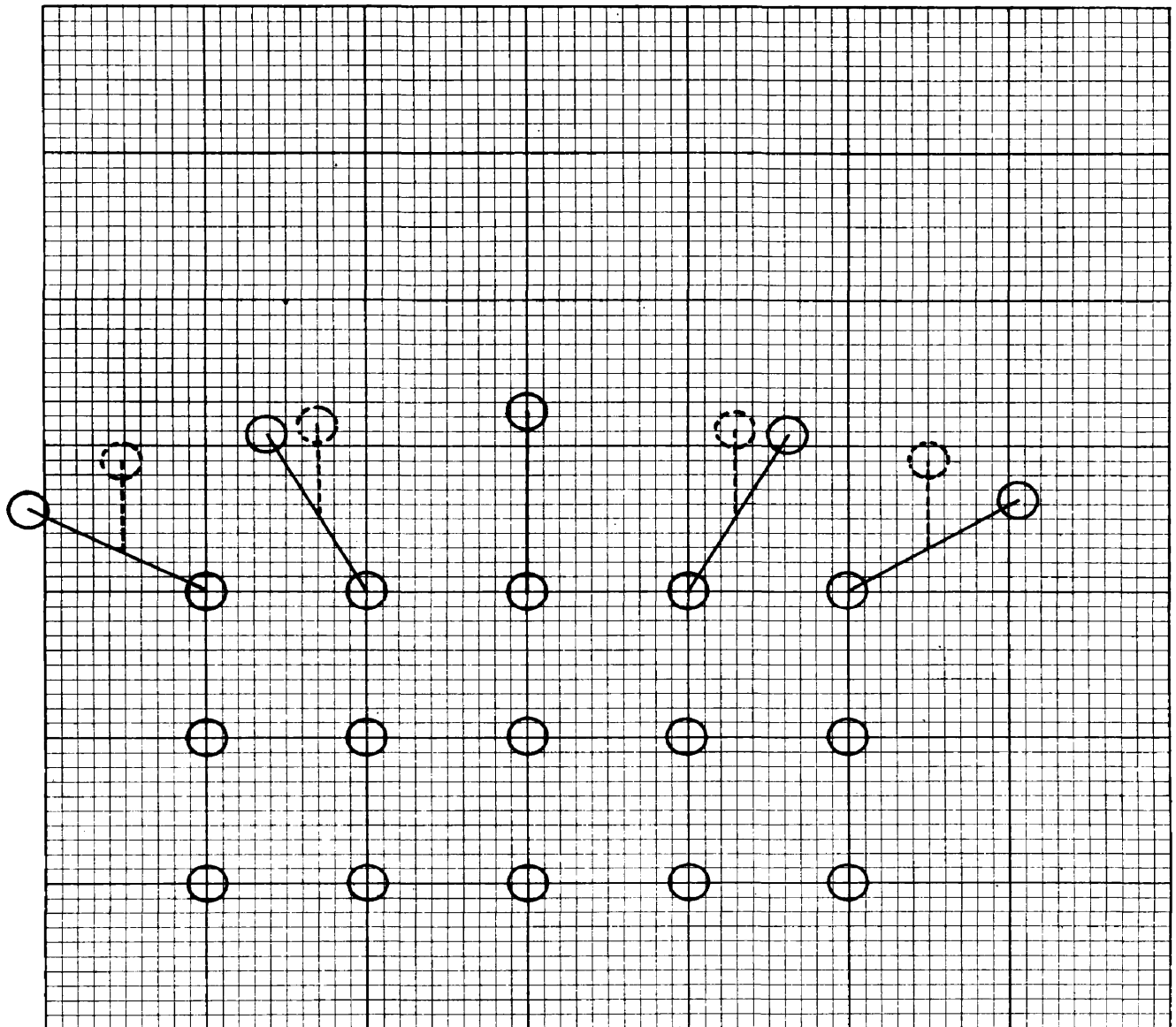purposes of approximation, r may be taken as approximately 1/2

Fig. E-5.- Model of metallic surface
showing oscillation of dipoles

of the inter-atomic distance or 1×10^{-7} cm.; g is 900 cm./sec.^{2}; hence, as an approximation

$$t = 2 \sqrt{\frac{1 \times 10^{-7}}{1 \times 10^{-3}}} = 2 \times 10^{-5}$$

The frequency of minimum resistance is therefore given as 50,000 cycles.

2. Apparatus

The bridge which was employed is shown in Figure E-6.

The powder to be measured was placed in the conductivity cell described by Koster. (63) In this cell the powder is lightly compressed between silver electrodes to a pastille 1/4-inch diameter and 1/2-inch long. The compressed powder was allowed to stand overnight to insure constancy of resistance.

The procedure in an individual measurement was as follows:

1. Throw switch "a" to position (2) and switch "b" to position (2).

2. Put switch "c" on (2). Adjust B and C_B for balance.

3. Put switch "c" on (1) and adjust Wagner ground for balance.

4. Repeat 2 and 3 until both hold simultaneously.

5. Then: $R_1 S = R_a B$ and $WC_B R_1 = WC_B R_a$ or

$$WC_B B = WC_S S.$$

6. Throw switch "a" to position (1) and switch "b" to position (1).

7. Put switch "c" on (2) and adjust A and C_S for balance.

8. Put switch "c" on (1) and adjust Wagner ground for balance.

9. Repeat 7 and 8 until both hold simultaneously.

10. Then: C_S^1 = new setting of C_S

$$R_x = \frac{AS}{B} \frac{(1 + W^2 C_B^2 S^2)}{(1 + W^2 C_S C_S^1 S^2)} = \frac{AS}{B} \quad \text{within } 1\%$$

$$C_x = \frac{B}{A} \frac{(C_S^1 - C)}{(1 + W^2 C_S^2 S^2)} = \frac{B}{A} (C_S^1 - C_S) \quad \text{within } 1\%$$
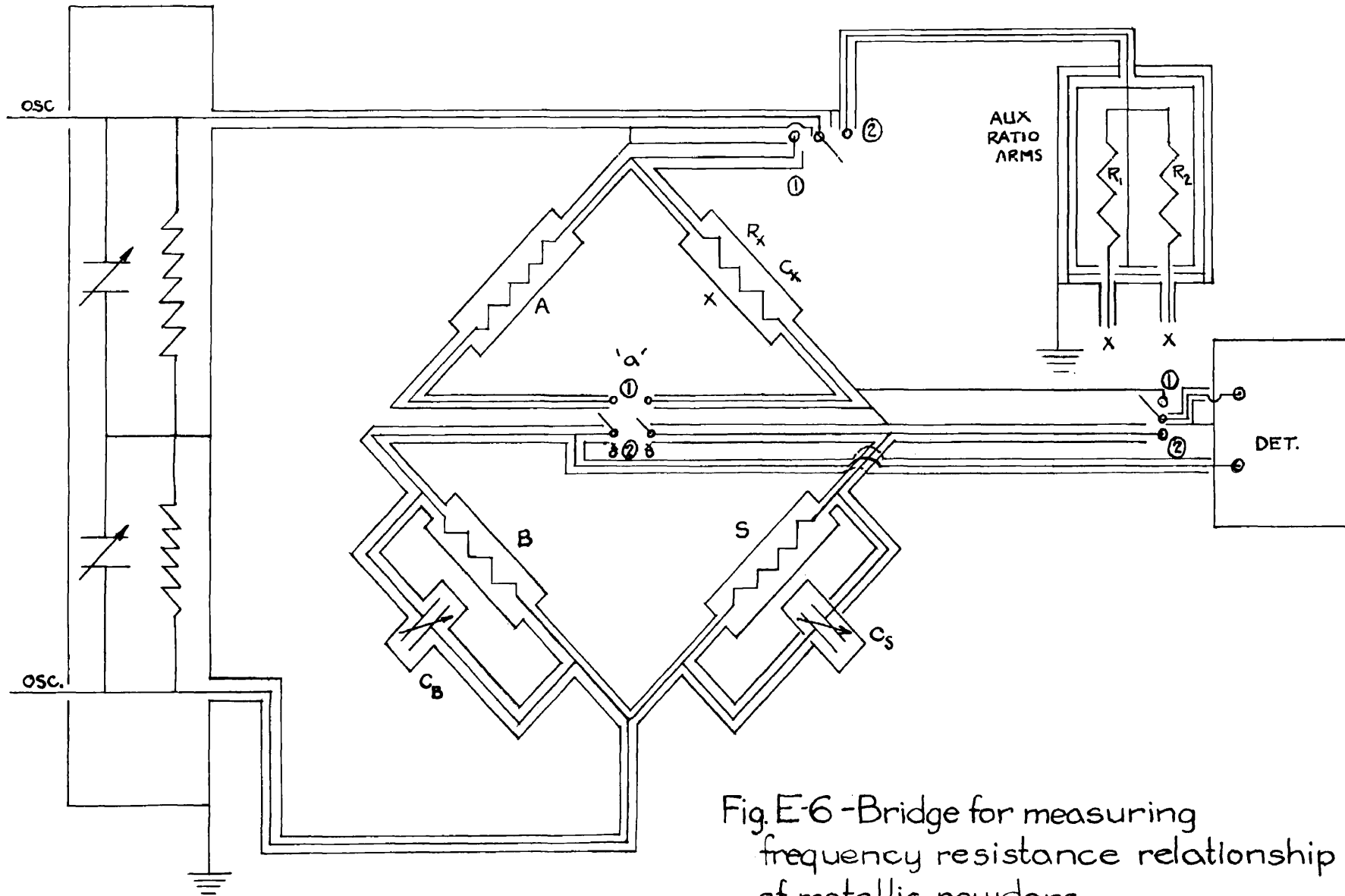
Fig. E-6 – Bridge for measuring
frequency resistance relationship
of metallic powders.

3. Results

I. Measurements on Powdered Antimony

Antimony was selected as a suitable material because it could be easily reduced to powdered form and sized. The numerical value of the resistance is determined by the degree of compacting of the powder as well as by the size. The compacting was adjusted in every case to give a value which was easily measured on the bridge.

Table E-4 gives a number of the results obtained.

These results when plotted give curves of the same general shape, all having a minimum at approximately 50 kilocycles. Figure E-7 shows the results for specimen number 2 of the 250-270 mesh powder.

The minimum at 50 kilocycles is in surprisingly close agreement with the theory. The resistance of a wire resistor of similar resistance as a function of frequency is given for comparison and to test the possibility of the minimum of resistance being due to skin effect or some unsuspected peculiarity of the bridge. It will be seen that the change in resistance is small and is a steady increase for increased frequency, doubtless due to skin effect.
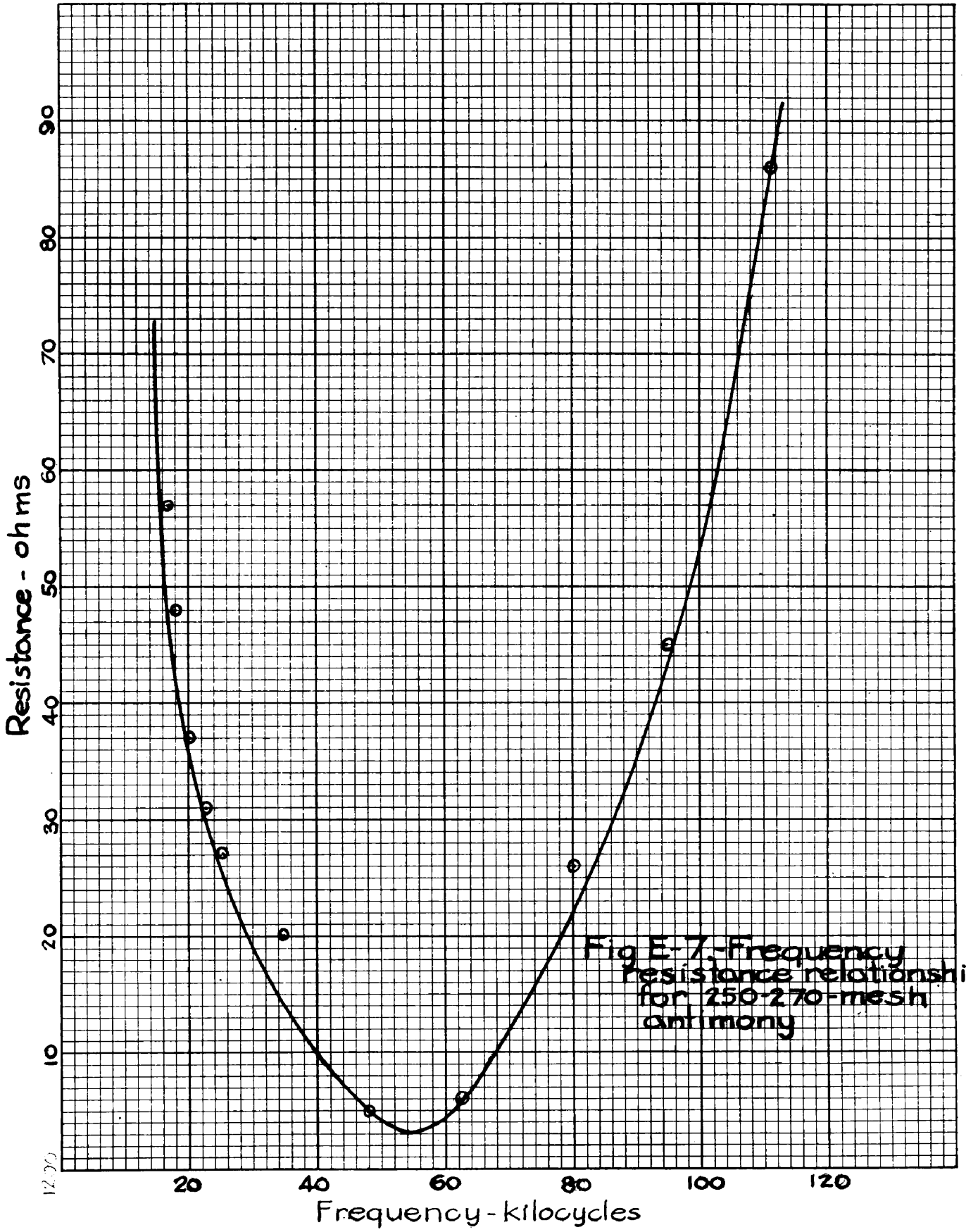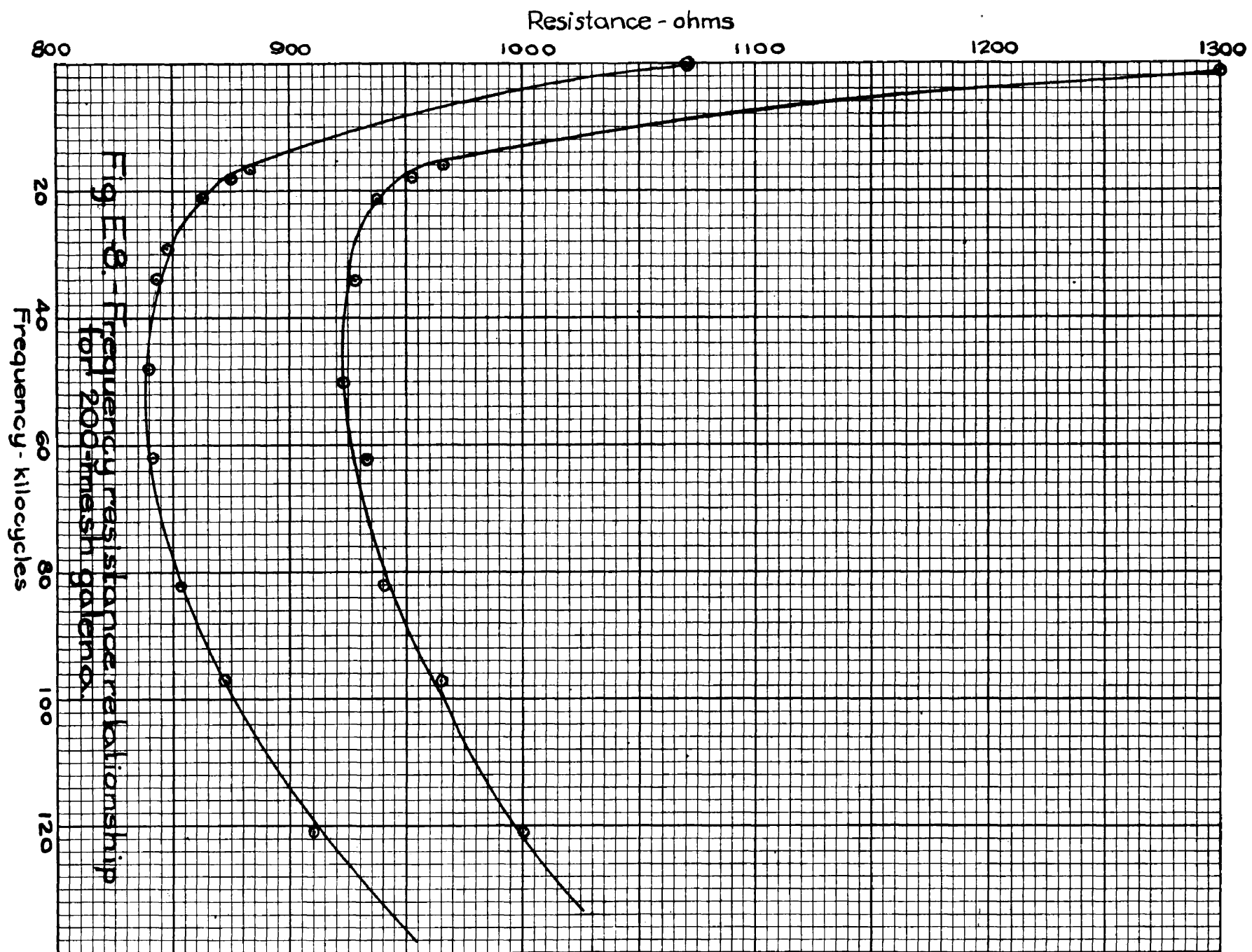
Fig E-7 - Frequency resistance relationship for 250-270-mesh antimony

TABLE E-4

Frequency Kilocycles	150-200 Mesh (1) Ohms	150-200 Mesh (2) Ohms	200-250 Mesh (1) Ohms	200-250 Mesh (2) Ohms	250-270 Mesh (1) Ohms	250-270 Mesh (2) Ohms	270-325 Mesh (1) Ohms	270-325 Mesh (2) Ohms	-325 Mesh Ohms	Wire Resistor Ohms
111	1067.45	767.5	1429	885	1363	1285	812.5	1204	852	987
95	1062.4	757.61	1396	872.5	1353	1245	804.5	1196	872.5	987
80	1062.35	751.58	1377	865.5	1320	1226	800.5	1191	859	987
62	1060.08	747.95	1364	864	1307	1206	794	1186	864.2	987
48	1060.60	747.51	1366	863	1304	1205	794	1186	853	986
35	1060.50	749.17	1373	863.5	1310	1210	794	1186.9	854	985
29	1061.50	750.50	1377	865.5	1315	1220	794	1186.2	854	985
25.5	1062.10	751.80	1381	867.2	1319	1227	795.5	1187.7	856	984.5
22.9	1062.60	753.00	1389	870.2	1323	1232	797	1189	859	984.5
20.8	1063.10	755.77	1395	871.2	1333	1237	799	1190	860	984
18.1	1064.80	759.44	1404	873.2	1336	1248	802	1192	864	984
16.3	1066.47	762.11	1409	873.2	1345	1257	804.5	1194	867.5	984

II. Measurements on Powdered Galena

The work of Koster has given us more detailed information on the direct current conductivity of galena than we have on any other metallic powder; hence measurements were made on ~200 mesh galena as representative of a conducting mineral. The technique was exactly the same as for powdered antimony. The direct current resistance was, however, measured for the galena samples so that the curve could be extended to zero frequency. The results for two samples of ~200 mesh galena are given in Table E-5 and plotted in Figure E-8.

TABLE E-5

Frequency Kilocycles	Sample 1 Ohms	Sample 2 Ohms
121.8	1000.	910.
97.68	965.1	878.75
82.00	940.5	851.50
62.73	926.75	842.62
48.61	924.50	840.12
34.85	927.75	844.62
29.22	923.75	846.37
25.53	933.60	851.62
20.99	938.25	851.6
18.16	953.25	875.4
16.33	966.25	884.6
0	1304	1070

Fig. E-8.—Frequency-resistance relationship for 200-mesh galena.

It will be seen that the minimum in resistance occurs in the same frequency range as for antimony, that is, about 50 kilocycles. This is in accord with the theory of essentially similar dipoles at all metallic surfaces.

III. Measurements on Powdered Copper

In order to obtain measurements on a definitely metallic conductor, powdered copper was used in the final set of measurements.

The copper used was -325 mesh material furnished by the U.S. Metals Refining Company and was said to be electrolytically produced.

The results are given in Table E-6 and plotted in Figure E-9. With copper as with antimony and galena, there is a distinct minimum of resistance near 50 kilocycles. It may, therefore, be concluded that this behaviour is a general one for powdered conductors.

TABLE E-6

Frequency Kilocycles	Ohms
121.8	662.0
97.68	661.8
82.00	661.2
62.73	660.45
48.61	660.0
34.85	660.4
29.22	660.6
25.53	660.65
20.99	660.8
18.16	661.15
16.33	661.75
0	1073

Fig. E-9- Frequency resistance relationship for -325-mesh copper.
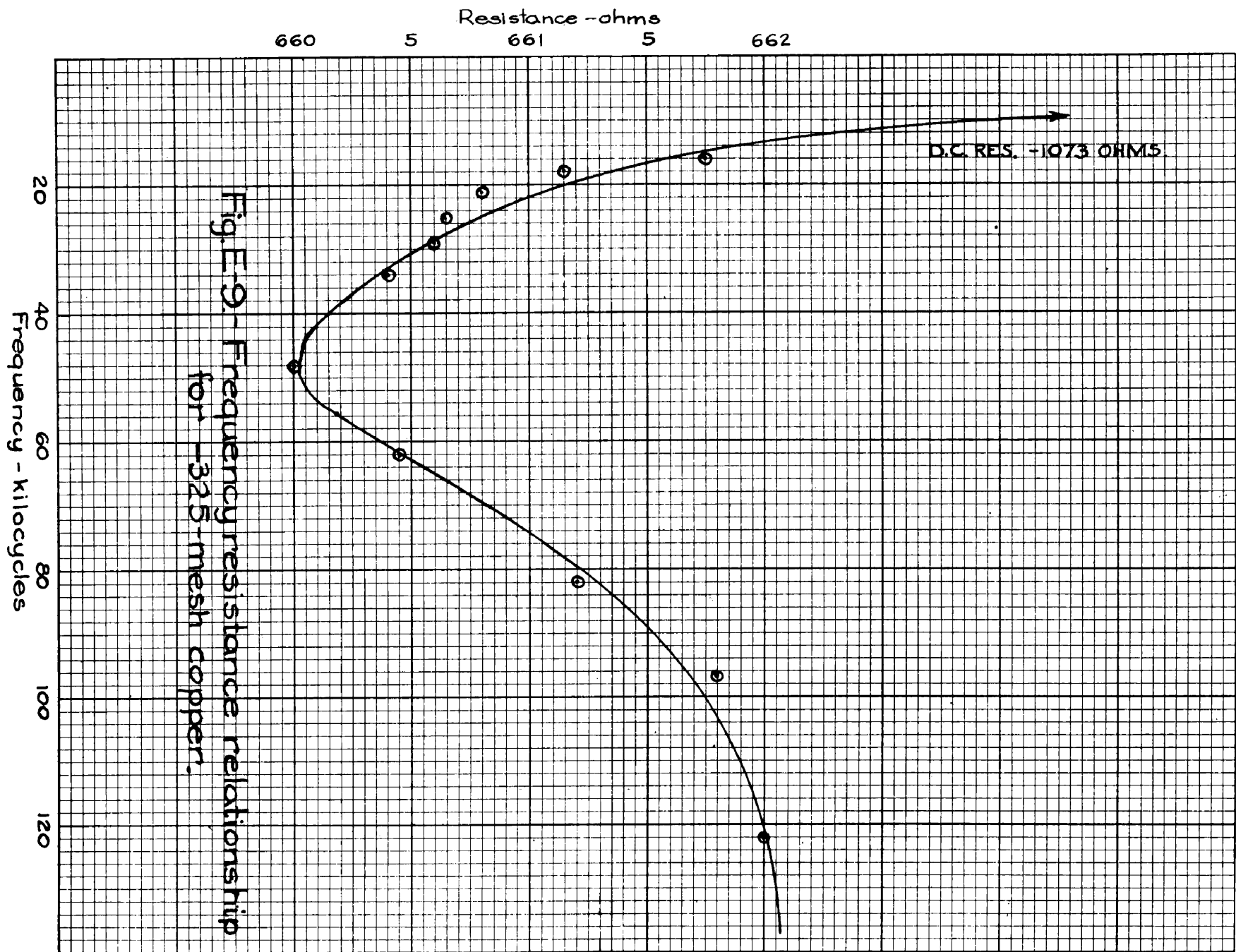
CONCLUSIONS

The concept of internal surface in metals has been developed in detail, and it has been shown that the properties which must be assigned to it are the same whether formed by (a) movement of the parts of a metallic solid with respect to each other by plastic deformation, (b) comminution and reaggregation of a brittle metallic solid, or (c) production of a two-phase system by the spontaneous break-down of a solid solution.

The extent to which the various properties of metals are influenced by internal surface is, however, found to depend on its method of formation and subsequent history. This leads to the necessity of postulating a physicochemical condition at the internal surface which varies in its energy content and hence in its temperature stability.

The pseudo-molecule theory of metallic hardening which was first proposed by the writer in 1922 is given more explicit statement, and it is shown that this theory provides for the variation of temperature stability of internal surface in metals and likewise satisfactorily explains the properties of internal surface, no matter how formed.

This theory postulates the formation of electrical dipoles at metallic surfaces which may under certain conditions form a bond at an interface, hence increasing strength. In metallic

powders, however, they may be thought of as standing on the surface
of particles and vibrating under the influence of thermal agitation
and gravity like a field of grain in a breeze. This highly
mechanized concept leads to a satisfactory explanation of the elec-
trical properties of metallic powders and, in particular, to a
minimum of resistance with an electric current having a frequency
of 50 kilocycles. Such a minimum has been found for antimony,
galena, and copper powders, and is the first direct evidence of the
actual existence of electrical dipoles at metallic surfaces, which
were postulated from indirect evidence by the writer in 1922.

In studying the application of the pseudo-molecule theory
to problems of metallic hardening, a new concept of the dispersion
hardening phenomenon has been brought forth. The development of
this concept has been made possible by the fact that coercive force
measures total internal surface. It is proposed that dispersion
hardening takes place in two steps. In the first step, the solid
solution breaks up into a block structure, thus forming internal
surface; in the second step, a new phase is precipitated at this
internal surface. The first step is practically without effect on
hardness or x-ray pattern, since the blocks remain in practically
perfect registry; the second step greatly increases hardness.
The steps may take place practically simultaneously or in a definite
sequence. In the quenching of ordinary carbon steel, the first step
takes place completely, the second step only partially. Hence, on

tempering, the total internal surface as indicated by coercive force decreases rapidly. The internal surface due to the presence of the second phase, however, actually increases, and hence the hardness rises a little.

In the case of iron-cobalt-molybdenum alloys, the internal surface forms very slowly, while the precipitated phase, once formed, quickly grows to a size having little effect on hardness; hence, maximum coercive force is reached in this instance at a much higher temperature than maximum hardness. This is indicative of the great stability of the iron-cobalt-molybdenum solid solution.

The more explicit form of the pseudo-molecule theory of metallic interfaces which it has been possible to give thus makes possible the satisfactory explanation of obscure metallurgical phenomena, and the direct evidence presented for the existence of the pseudo-molecules themselves gives greater confidence in the application of the theory to practical metal working.

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