FERROMAGNETIC COMPOUNDS
OF MANGANESE WITH GROUP V-A
ELEMENTS

by

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INTRODUCTION

OBJECTS.

We know that at room temperature iron, cobalt nickel and gadolinium are the only elements which show ferromagnetism. Manganese, occupying the position immediately preceding iron in the periodic table, though not ferromagnetic itself, can form some ferromagnetic compounds.

Manganese can be combined with any of the elements of group V-A of the periodic table to form ferromagnetic alloys (9,p 100). The discovery of these ferromagnetic alloys may date back as far as the first description of the Heusler alloys in 1898, though the first clear mention of ferromagnetic manganese phosphides was due to Wedekind (52,p 1268) in 1907. The ferromagnetism of manganese arsenides was noted in 1911 by Hilpert and Dieckmann (30,pp 2831-2) who noted ferromagnetic properties for the phosphides, antimonides and bismuthides as well. The ferromagnetism of manganese antimonides was reported in 1907 by R. S. Williams (56,pp 1-7); in the same year ferromagnetic nitrides were described by Wedekind (50,p 806).

Although these substances have been known for as long as 50 years, some of the measurements made on them have been superficial. As an example, in some of the earlier papers the intensity of ferromagnetic behavior was examined by comparing the distances a particle will jump to a magnet. Intensive studies of the relation of physical properties and magnetic behavior were not made until the period 1928 to 1935 when Bates, et. al. worked with the specific heat (3,54), resistivity (7), thermo-electric effect (5,6) and thermogalvanic action (4). All but one of these papers was concerned with the substance MnAs; the specific heat of MnP was studied by Whitmore (54). Therefore, the study of the specific heat of MnAs and of MnP represents the only attempt to find the effect of the change of group V-A element on the behavior of the ferromagnetic alloys, and the character of the experiments did not permit exact correlation in this case. Up to the time of the present investigation, however, no attempt has been made to find quantitatively the effect of changing the concentration of the group V-A element on its magnetic behaviour.

In conducting an investigation of the behaviour of the manganese group V-A alloys, the manganese-phosphorus and manganese-arsenic systems immediately suggest themselves

as being convenient systems for study. The magnetic transition for manganese phosphide is given as 18-25° C. by Stoner (49,p 335).

The objects of the researches of this paper can then be explained.

i. To investigate methods of preparation of the manganese-phosphorus and manganese-arsenic alloys and to prepare a series of these alloys of varying composition.

ii. To measure the magnetic behaviour of the alloys as a function of temperature and to correlate this with measured behaviour of the thermal expansion, thermoelectric potential and thermo-galvanic action of the alloys.

iii. To attempt to correlate the behaviour of the alloys as a function of composition in order to determine if the group V-A element is exhibiting an effect due to compound formation and dilution, or whether the alloying element is present in some other critical manner.

iv. To note the effect of the change of group V-A element from phosphorus to arsenic.

v. To correlate the data with existing magnetic theories.

Within the scope of the stated objects of this investigation are a number of additional questions which it is hoped can be answered in the light of additional research with these materials. As an example, Bates (5) noted a temperature hysteresis of MnAs while studying the thermoelectric effect that Whitmore (54) did not notice in working with specific heat properties of MnP. Guillaud (25) noted hysteresis effects that seem hard to explain. The temperature hysteresis noted by Bates (5) varied as the samples were reheated: repeated heatings of the sample lowered the temperature of the transition during the heating cycle. The question then presents itself: is the hysteresis real, or is the behaviour that of a slow equilibrium that has not been achieved in heating or cooling the sample?

FUNDAMENTAL RELATIONSHIPS OF FERROMAGNETIC THEORY

Ferromagnetism is characterized by a number of features which set it apart from diamagnetic or paramagnetic behavior. Ferromagnetism is defined simply as "magnetism similar to that of iron" (12,p.1). One of the main differences between ferromagnetism and paramagnetism is the dependence of susceptibility upon the field strength. In general ferromagnetism is characterized also by a susceptibility value of the order of a million times that observed with paramagnetic materials. In addition, ferromagnetic materials can be permanently magnetized.

Ewing's Contribution: The first attempt at explaining ferromagnetic behavior is credited to Ewing, in 1893 (8,pp.233-43;12,pp.126-64;13;57,pp.316-45). He suggested that ferromagnetic phenomena were due to forces between atoms; each atom is a small magnet.

Following the reasoning of Ewing, let us assume that we have a permanent magnet free to turn in any direction about its center. Then for the unmagnetized state, the atomic "magnets" will be oriented in a completely random manner and the resultant magnetic moment will be zero. As the field is gradually increased from zero, there will be at first a slow continuous rotation of the magnets followed by a sudden change in orientation.

Finally, a further continuous rotation takes place until all of the magnets lie parallel to the field. Ewing has used this model for the calculation of B,H curves and hysteresis loops and found the model satisfactory.

The only possible explanation for the magnetic transformation in ferromagnetic materials according to Ewing's theory is that the thermal agitation becomes great enough to break the orientation of the magnets. Since the ferromagnetic materials have a temperature above which they are paramagnetic behavior and below which they behave as ferromagnetic materials, we should be able to approximate the energy involved if thermal agitation could overcome the magnetic orientation forces at this temperature.

The magnetic energy of a permanent magnet of moment μ in a field of strength H is

$$E = - \mu H \qquad (1)$$

when μ and H are directed parallel.

Considering that the magnets are held parallel by a fictitious internal field H_1, then when the substance is heated to the magnetic transformation or Curie temperature T, thermal energy will overcome the internal field and destroy the alignment of the atomic magnets.

The energy of thermal radiation $\approx kT$, so

$$kT \approx \mu H_1 \qquad (2)$$

considering iron, with $T = 1043^\circ K$. and $\mu = 2.04 \times 10^{-20}$ ergs/gauss,

$$kT = 1.4 \times 10^{-13} \text{ erg} = 0.09 \text{ electron-volts}$$

and $H_1 = 7,000,000$ oersteds, indeed a tremendous field.

These approximate calculations indicate that the magnetic energy is quite small compared with the ionization potentials of the atoms, but is large enough to require a tremendous field in order to align the Ewing magnets.

The Ewing model would be more useful if it were applied to the space geometry of atoms in a ferromagnetic crystal; Bozorth (13, pp.12-3) reports that this has been successful in explaining the anisotropy of crystals.

The theory of Ewing tells of the forces necessary to give rise to ferromagnetism but does not explain the origin of these fields.

The Weiss Theory: The next step in the development of the ferromagnetic theory was that due to Weiss (8, pp.233-8).

Langevin proposed for materials that can be treated as paramagnetic gases, each particle behaves as if it possessed an average magnetic moment $\bar{m}$ given by

$$\frac{\overline{m}}{\mu} = \coth a - \frac{1}{a} \tag{3}$$

where each gram of substance contains Z elementary magnetic particles each of moment μ. The symbol a is defined by the expression

$$a = \frac{\mu H_T}{kT} \tag{3a}$$

where the total field is of intensity H_T

The right hand expression of (3) can be expanded, giving as a result

$$\frac{\overline{m}}{\mu} = \frac{a}{3} - \frac{a^3}{45} + \frac{2a^5}{945} --- \tag{4}$$

Weiss extended the theory to ferromagnetic materials by proposing that the field experienced by the particles was more than an external field. He said that the total field was the sum of the applied field H and an internal field H_1 given by $CZ\rho\overline{m}$, where ρ is the density of the substance and C is a constant;

$$H_T = H + C \rho Z \overline{m}. \tag{5}$$

Solving (5) for $\overline{m}$ and (3a) for H_T, and substituting the expression for H_T in (5), we have

$$\frac{\overline{m}}{\mu} = \frac{kT}{C\rho Z\mu^2} a - \frac{H}{C\rho Z\mu}. \tag{6}$$

For high values of T, where $a \to 0$, (4) becomes

$$\frac{\overline{m}}{\mu} = \frac{a}{3} \tag{7}$$

Eliminating a between (6) and (7), and rearranging.

$$\frac{\overline{m}}{\mu} = \frac{\mu H}{3k} \; \frac{1}{T-\left(\frac{C\rho Z\mu^2}{3k}\right)} \tag{8}$$

which is simply an expression of the type

$$\frac{\overline{m}}{\mu} = \frac{\mu H}{3k} \; \frac{1}{T-\theta} \;. \tag{9}$$

Since molar susceptibility $\chi_M = \frac{N\overline{m}}{H}$, then (9) becomes

$$\chi_M = \frac{N^2\mu^2}{3R} \; \frac{1}{T-\theta} = \frac{1}{T-\theta}C \tag{10}$$

Equation (10) represents the well known Curie-Weiss law which explains the paramagnetic behavior of ferromagnetic substances above the magnetic transformation temperature; this relationship has been experimentally proven. The temperature θ is the Curie temperature, or magnetic transformation point.

We can then calculate the magnitude of the internal field of Weiss, since the Curie temperature can be experimentally determined. Some values (12,p.38) are given in Table 1 of estimates of the internal field, as calculated from equation (8).

Table 1

Substance	Θ, $^{\circ}$K.	Internal Field, Oersteds
iron	1060	3.4×10^7
cobalt	1385	5.6×10^7
nickel	700	2.5×10^7

These fields are tremendous indeed, though of the order of the field calculated to oppose thermal agitation, as noted previously.

When T is low, the equation may be solved for I_0, the saturation intensity of magnetization (intensity of magnetization if all Ewing magnets were parallel). The intensity of magnetization is μN, and given the symbol I. By calculating I as a function of temperature, Weiss calculated the spontaneous magnetization curve. Applying a field H = 0 and solving the equation, the result is given

$$\frac{I}{I_0} = \tanh \frac{I/I_0}{T/\Theta} \qquad (11)$$

where I/I_0 is the relative magnetization. This equation is significant in showing that at all temperatures below the Curie temperature Θ, the intensity of magnetization has a definite value even though no field is applied.

This curve has been experimentally verified (13,p.16) and agrees quite well with the experimental value for iron, cobalt and nickel.

The explanation given by Weiss for the apparent unmagnetized state of a ferromagnetic material below the Curie point follows the concept of domains as now known. At ordinary temperatures the internal forces, now thought of as the interaction energy forces, maintain elementary magnets parallel over only a limited volume of specimen, usually about 10^{-8} -10^{-9} cc. and containing perhaps 10^{15} atoms. Each of these small volumes, called a domain, is magnetized to saturation but the domains are oriented in a random manner. At temperatures below the Curie temperature the domains have a vector magnetization of zero, because of the random orientation. However, when a field is applied, the domains are lined up vectorially and a resultant magnetization is shown.

The effects of domains have been demonstrated clearly. For example, colloidal iron oxide on the surface of a demagnetized silicon-iron crystal gives a microscopic powder pattern illustrating inhomogeneous magnetic fields (13,p.7).

The Weiss theory can give us information that

can be quantitatively used, but does not provide any
explanation for the tremendous internal fields causing
ferromagnetism.

An application of the Weiss theory relationship
can be pointed out by considering the magnetic energy
associated with a ferromagnetic substance.

$$E_M = -\int_0^I F dI = -\int \rho \, CI_o \, (\rho \, dI_o)$$
$$= -\rho^2 \frac{CI_o^2}{2} \qquad (12)$$

The minus sign indicates that energy must be supplied
in order to destroy the intrinsic magnetization of a
ferromagnetic material. The specific heat of a ferro-
magnetic material is greater than that for a normal
metal under similar physical conditions.

$$C_f = C_n + C_m \qquad \text{or} \qquad (13)$$
$$C_f = C_n - \frac{1}{2J} \frac{N_W}{\rho} I^2 \qquad (13a)$$

where C_f is the specific heat of a ferromagnetic metal,
C_n that for a normal metal and C_m, the specific heat for
the magnetic process. The symbol J represents the
mechanical equivalent of heat and N_W is a constant
derivable from Weiss' internal field.

As I varies with temperature then C_m will vary
as given by the equation

$$\frac{\partial C_m}{\partial T} = - \frac{1}{2J} \frac{N}{\rho} \frac{\partial I^2}{\partial T} . \qquad (14)$$

At the Curie point the intensity of magnetization will be changing very rapidly, in accordance with Weiss' curve. Therefore the specific heat of a ferromagnetic metal will rise to a sharp maximum and drop off sharply at the transition temperature if the behavior obeys the relation of equation (14).

Bates (3) has investigated the specific heat behavior of MnAs on heating and Whitmore (54) studied the behavior of the phosphide. Both workers obtained peaks of the specific heat at temperatures closely approximating the magnetic transformation point.

Bates then proceeded with other experiments in a similar manner. Since it is pointed out that the energy associated with a ferromagnetic material below the Curie temperature differs from the energy of a normal substance by the magnetic energy factor, then methods of detecting energy changes should give Curie point changes in properties. Further, since magnetization values are changing sharply, the energy factor will be changing in a manner which should give sharp peaks or breaks in their values.

An example of this is given by Bates (7), who measured the electrical resistivity of manganese arsenide.

The resistivity of a ferromagnetic substance exceeds that of a normal metal, according to this application of the Weiss theory, by a resistance related to magnetic energy. The values obtained break sharply near the transition temperature, in accordance with theory.

Heisenberg Theory of Ferromagnetism: As was pointed out earlier, the origin of the internal field is not explained by the Weiss theory. The development of the quantum theory and its application to ferromagnetism by Heisenberg provides at least a semi-quantitative explanation of the molecular field.

In the development of atomic shells, transition elements are characterized by the filling of inner shielded shells. In the iron group, the 3d shell is filling; ferromagnetic gadolinium has a partially completed 4f shell.

Iron can be taken as an example of the ferromagnetic elements. This element has a $3d^6$ shell, putting the six electrons in five orbitals. Two of the electrons will be paired or compensated in one of the orbitals and the remaining four electrons will each occupy an orbital in an uncompensated manner. The spinning of the four electrons in the same manner causes a polarization of the atom and a resultant magnetic moment can be determined.

The partial filling of the shell allows the existence of unpaired electrons, and the uncompensated electrons can then cause a magnetic moment because of their spinning. The existence of a magnetic moment must be one condition for ferromagnetism.

In the free atom, the orbital motion can also contribute to the magnetic moment, but when the metallic crystal is formed, the electron orbits are too firmly fixed to be appreciably influenced by a magnetic field. The corresponding moments do not change when the intensity of magnetization changes, so it is supposed the orbital moments of the electrons in the various atoms neutralize one another.

The magnetic moment of the atoms will be related to the number of unpaired electrons in the atom. The magnetic moment (41,p.113) is given by

$$\mu = \sqrt{n(n+2)} \quad \text{bohr magnetons} \quad (15)$$

where n is the number of unpaired electrons.

Let us now suppose that two atoms some distance apart each have a magnetic moment due to the spin action of an electron. Heisenberg shows the existence of a force of interaction between the electrons, in addition to the better known electrostatic and weak magnetic forces.

The interaction force between the electrons is due to the quantum mechanical probability of exchange of the electrons and is expressed by an exchange integral. This exchange integral will depend upon the characteristic wave equations of the atoms, the distance of separation of the electrons and the distance apart of the atoms and the exchanging electrons. The exchange integral is generally negative because the attraction between the nucleus and the exchanging electrons overrides the inter-atomic and interelectronic repulsion forces. If the conditions are correct for the exchange integral to be positive, then sufficient energy would be involved in the interaction to account for the molecular or internal field.

In summary, Heisenberg based his theory of ferromagnetism on the magnetic moment of atoms due to uncompensated electron spin action together with a positive exchange action where the interaction energy of atoms in crystals can account for the molecular field.

Exchange Integral Conditions: Several calculations have been made to determine the proper conditions that must exist if the interaction integral is to be positive. The first of these is due to Slater (46,pp.58-63).

By assuming a simple form for the wave function

as being a function of the principal quantum number and
the effective nuclear charge, a set of wave functions for
individual electrons of the various shells can be set up.
These wave functions then represent the distribution of
charge for a given shell. The maximum of the distribution
of charge will represent the effective radius of the shell,
and thus allows the calculation of effects involving
particular energy shells, as the 3d shell of the iron
group.

Slater's calculation is based upon the effective
values of the principal quantum number and the shielding
constant, both derived from presumably semi-empirical
tables, and the nuclear charge.

From these data, Slater constructed a table
giving the ratios of the distance of separation between
neighboring atoms, D, to the radius (r) of the energy
shell. He found that the ferromagnetic atoms had the
largest ratio D/r, while those which can become ferro-
magnetic in their compounds were nearly as great.
Examples of his results are shown in Table 2.

Table 2

CRITICAL DISTANCE RATIOS AS CALCULATED

BY SLATER (46,pp.58-63).

Metal	Cr	Mn	Fe	Co
Ratio D/r	2.60	2.94	3.26	3.64
Metal	Ni	Gd	Pd	Pt
Ratio D/r	3.94	3.1	2.82	2.46

Slater concluded, then, that a ratio exceeding
3.0, but not exceeding it very much will produce a ferro-
magnetic substance. That is, when the D/r ratio reaches
about 3.0 the exchange integral will be positive.

Of particular note in the above table is the
fact that the manganese ratio is very close to the
required ratio for ferromagnetism. The expansion of the
ratio by the alloying with the group V-A elements, sulfur,
boron, or a number of other elements will produce ferro-
magnetism. The loss of ferromagnetism by an alloy of
this type might then be explained by changes in bonding
influencing the magnetic moment and the effective size
of the energy shells, or from changes in the interatomic
distance.

Another calculation of the conditions for a
positive exchange integral is due to Bethe (11,pp.594-8).
His calculation is based on the forces involved as the

interatomic distance is changed, assuming an energy shell
of constant dimensions. As the separated atoms are brought
closer togather, the electron spins of the two atoms will
be made parallel, resulting in a positive interaction
energy. As the atoms are brought still closer togather,
the spin moments are held parallel more firmly until at
a certain distance the forces will diminish. Bringing
the atoms still closer can set the spins anti-parallel and
a negative interaction can result. The position of the
ratio of interatomic distance to energy shell radius on
Bethe's energy curve will then determine the paramagnetic
or ferromagnetic nature of the substance. Bethe's curve
is shown below.
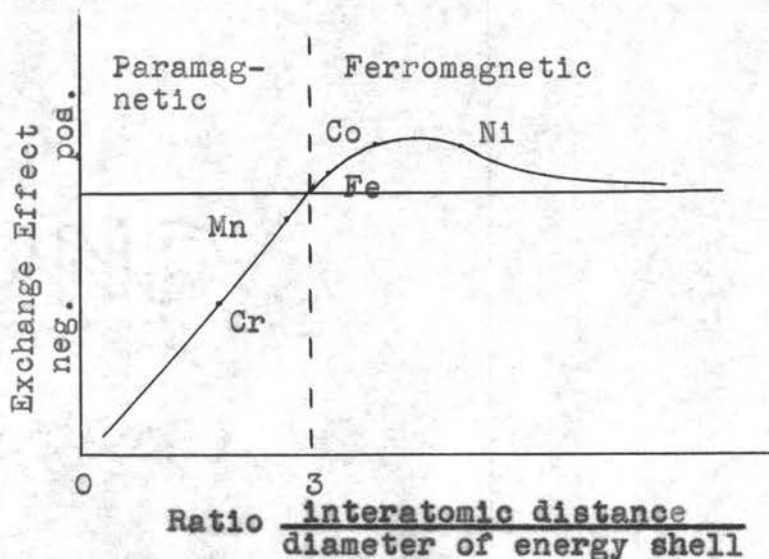
A further calculation is due to Néel (37,38).
He said that not only does the exchange integral depend
upon the D/r ratio, as given by Slater, but that the
factor for the shortest distance between the magnetic
shells should be included. Néel plots the magnetic
moment against $d - \delta$, where d is the distance between
atoms and δ is 2r corrected by the shortest distance
between the magnetic shells. Calculation of the distances
for MnAs indicate that it should be ferromagnetic while
elemental manganese is not ferromagnetic. The curve of
Néel is very similar to that of Bethe, with the points
distributed in the same manner.

The methods of calculation of the exchange
integrals would lead one to the supposition that volume
effects would be a good measure of the change involved in
a ferromagnetic material at its transformation point.
The requirement of a positive exchange integral and a
magnetic moment of the atom suggests that there should
be a definite change in volume associated with the change
in critical ratio. If the internuclear distance is changed,
or if the atomic shell dimensions are perturbed due to
bonding changes, the lattice ratio should change and the
volume would be effected.

Since the possibility exists that the effect can

be explained solely on the basis of conduction electron changes then thermoelectric action will give us an indication of effects to be noted.

The experiments are then set up to give us the following information:

i. The thermal expansion of the alloys will give indications of changes in interatomic or intra-atomic effects influencing the interatomic dimensions or the energy shell radius. Heisenberg's theory indicates that changes should be evident in thermal expansion behavior.

ii. Thermoelectric potential measurements should indicate the changes involving the conduction electrons.

iii. Thermogalvanic potentials, if obtainable with any degree of reversibility or stability, would give information regarding the energy involved in magnetic transformations.

iv. Magnetic theory indicates that the magnetic transformation should occur at a definite temperature; it should thus be possible to eliminate temperature hysteresis in all of the above effects.

PREPARATION OF THE SAMPLES

History: The first preparation of manganese
phosphide, according to Mellor (35,pp.852-3) was due to
Pelletier in 1789. He heated manganese with microcosmic
salt and charcoal to produce a white manganese phosphide
(all the phosphides produced in this investigation have
been deep black in color), and also by direct combination
of the elements. Mellor (loc. cit.) also reports prepa-
rations of phosphides by reduction of phosphates by a
number of workers during the nineteenth century. All the
products produced in that era were quite impure and are
described in general as mixtures of compounds. The
magnetic properties were not known by the early workers.

With the discovery of the Heusler alloys, in
1898, interest in the alloys of manganese developed.
Wedekind and Veit, in 1907 (52,pp.1268-9) prepared two
different "compounds" of manganese and phosphorus.
On passing phosphorus vapors entrained by hydrogen over
manganese chloride heated to a red glow, a strongly
ferromagnetic material was found. This material, after
purifying with dilute hydrochloric acid, was analyzed
and found to fit the formula Mn_5P_2.

In a similar manner, they found that direct
combination of manganese and red phosphorus in a hydrogen

atmosphere at the temperature of a gas-oxygen flame combined to form another ferromagnetic alloy, Mn_3P_2.

In 1908, Schemtschuschny and Efremoff (43,pp. 246-7) made a phase study of manganese-phosphorus alloys ranging up to about 36% phosphorus. Their study indicated two compounds in this region: Mn_5P_2 and MnP. The study does not indicate the Mn_3P_2 of Wedekind; a eutectic at 27.7% phosphorus is at almost the exact composition of Mn_3P_2. In this investigation the alloys were prepared by adding phosphorus to molten manganese protected by a film of fused $BaCl_2$.

According to Mellor (35,pp.852-3) several other investigators report the compound Mn_3P_2, though the methods of preparation (direct combination) should not rule out the eutectic.

The compound, reported by Schemtschuschny in his phase study, was also prepared by Hilpert and Dieckmann (31,pp.781-3) on heating the elements in an evacuated, sealed tube at temperatures up to 600° C. for 10-12 hours, and then removing the excess manganese with 10% hydrochloric acid.

Hilpert and Dieckmann (loc. cit.) also prepared a material of composition MnP_2 by direct combination at 400°.

This material was unstable when heated in a current of hydrogen at 400°, finally decomposing to MnP.

The properties of the phosphides, as described, are quite similar. They are insoluble in hydrochloric acid, soluble in aqua regia, some are reported somewhat soluble in nitric acid (experience of this investigation: somewhat attacked by concentrated nitric acid). The materials are grey to black powders, ferromagnetic and of density ranging from 5.12 g./ml for Mn_3P_2 to 5.39 g./ml for MnP.

The story of the manganese arsenides is quite similar to that of the phosphides. The first reported compound was the monoarsenide MnAs, reported (36,pp.70-1) by Kane in 1830. He prepared the material by heating arsenic and manganese on a platinum foil, the arsenic melting and alloying with the manganese.

As with phosphides, interest in manganese arsenides was aroused following Heusler's discovery of the ferromagnetic aluminum-manganese-copper alloys. Wedekind and Veit (53,pp.2664-9) and Hilpert and Dieckmann (29,pp.2383-5) almost simultaneously in 1911 published methods of preparation of MnAs. Wedekind found that MnAs could be prepared by heating together manganese and arsenic,freeing the regulus from excess manganese with

dilute hydrochloric acid, and removing the excess arsenic by heating with bromine or chlorine. Hilpert and Dieckmann prepared $MnAs$ similarly by heating manganese (prepared from manganese amalgam) with arsenic at about 700° C for 6-8 hours.

The compound MnAs was reported by Wedekind and Veit (loc. cit.) as being produced when the mono-arsenide was heated in a stream of hydrogen, though Hilpert and Dieckmann disclaimed the presence of either the hemiarsenide or a tritadiarsenide.

Arrivaut (2), by a method of electromotive force determinations for a series of alloys indicated that Mn_2As, Mn_3As_2 and MnAs were the compounds of manganese and arsenic.

Schoen (44) made a phase study of the manganese-arsenic system in 1911. He reports the presence of the compounds Mn_2As and, probably, MnAs. The formation of Mn_3As_2, unstable above 752° C. is also indicated. Schoen uses a rather impure manganese (97.37% Mn) in his study, and reports that MnAs and Mn_2As are not ferromagnetic (at variance with other workers), while alloys of composition near Mn_3As_2 are quite magnetically attracted. These alloys were prepared from fused mixtures of manganese and an alloy approximating MnAs.

The properties of the manganese arsenides are
quite similar to those of the phosphides. They are
attacked by nitric acid and aqua regia, and are not
attacked by, or but slowly react with hydrochloric acid.
The arsenides are black powders having a magnetic trans-
formation at about 40-45° C.

Alloys Produced By Direct Combination: A survey
of the historical methods of preparation of the ferro-
magnetic alloys of manganese suggest that direct combination
of the elements is the method most widely used.

For this research, combinations of manganese
and phosphorus or manganese and arsenic were made by
placing the finely divided mixed elements in a heavy
quartz tube, evacuating to a pressure of about 2 mm. Hg,
sealing and heating in an electric furnace. Because of
the danger of explosion, the tubes were placed in iron
pipes.

The phosphides were prepared by heating the
samples to 400°, following the procedure of Hilpert and
Dieckmann (31,pp.781-3). The result in a significant
number of cases was rupture of the tubes. Since drying
the samples after insertion in the tubes did not make the
method more satisfactory, it is supposed that local
temperatures, considerably exceeding the furnace temper-
atures, gave rise to high phosphorus pressures. The

vapor pressure of phosphorus increases rapidly to an intermediate high pressure near 400° although the vapor pressure at 400° is not very great. Since it is reported the reaction proceeds with incandescence (35,p.852), the explanation given must be reasonable.

Similar results were obtained with the combination of manganese and arsenic. The method of Wedekind (53,p.2664,2669) was used, combining the elements at $400-500^\circ$ C. Although explosions were common in producing the arsenide, just as with the phosphide, another difficulty arose. Since the alloys were produced much below their melting point, the unreacted material must be removed in order to produce a homogeneous alloy. The excess manganese can be easily removed with hydrochloric acid, but the removal of the unreacted arsenic by heating with bromine or chlorine resulted in the burning of the alloy to the chlorides (or bromides) in many cases.

Most of the direct combination alloys were produced from an impure manganese and arsenic (qualitatively they contain about 1% iron). It was extremely difficult or impossible to dissolve these alloys in aqua regia or nitric acid. Substitution of a pure electrolytic manganese (99.99% Mn) and Eimer and Amend purified arsenic

resulted in an alloy soluble in aqua regia and somewhat attacked by nitric acid.

Manganese-antimony alloys could be easily prepared by heating the mixed elements under a layer of fused NaCl, KCl or $BaCl_2$. This method was used by Schemtschuschny (43,p.245) with manganese-phosphorus preparations, and Ageev (1) with manganese-antimony alloys. The method was not found during this investigation to be satisfactory for the purpose of preparing the phosphides or arsenides; the non-metallic elements would burn out or evaporate through the fused salt, leaving but little combined non-metal in the alloy.

Chemical And Electrolytic Preparations of Alloys: In considering the preparation of manganese alloys, the possibility of metathetical reaction and of the reduction of manganese salts must be considered. Such methods might have a particular advantage in preparing pure materials which would not have been heated to the magnetic transformation region.

Manganese pyrophosphate was prepared and its reduction to the phosphide was attempted. Reduction with zinc, heated, or with zinc and acid, were not successful in producing the phosphide. Heating of the pyrophosphate with carbon to a red heat did produce some magnetic activity, though minor compared with materials produced by

direct combination.

It was thought that perhaps a reaction of the type

$$MnCl_3 + PH_3 \longrightarrow MnP + 3HCl$$

would produce the material desired. A manganese tri-
chloride was produced in ether solution by bubbling
hydrogen chloride onto the trioxide -- a dark green to purple
solution was produced. The bubbling of phosphine into
the solution resulted in the formation of a non-magnetic
brown precipitate.

The reduction of the pyrophosphate with thermite
was tried, and produced but a slightly magnetic product.

According to Chêne (15,pp.198-202,265-9),
electrolysis of molten salt mixtures can result in the
reduction of manganese phosphates to phosphides in small
crystalline quantities. He reported MnP or Mn_2P to be
produced in yields of about four grams from a 100 gram
crucible charge. This method would seem to be a general
method that might be applied to the preparation of arsenides
and antimonides as well as the phosphides. This method was
tried, using a four inch graphite crucible as the anode and
electrolyte container, and a graphite rod as the cathode.
Four parallel-connected 12 volt light storage batteries
formed the current source. It was found necessary to place
the crucible anode in a gas-fired pot furnace in order to

keep the bath molten and conducting.

When approximately 100 grams of the crucible mixture ($MnCl_2$ + 2 $NaPO_3$ + KCl) was heated to 650° C and current of 10 amperes at 12 volts potential was passed through the cell for one hour, only a trace of the magnetic product, not in visibly crystalline form, was produced.

Electrolytic reduction of Mn PO_4 in concentrated sulfuric acid solution did not produce the phosphide.

Crystallization Experiments: Ferromagnetic crystals are generally magnetically anisotropic (8,p.160); that is the magnetization is easier along a certain crystal axis. This phenomenon, intensively investigated by Guillaud and others, suggested that it might be desirable to make measurements with single crystals of the alloys, if possible.

Gwathmey and Benton (26,pp.35-7) report the growth of large single crystals of metals with melting points as high as 1500° C. Their method consists of very slowly passing molten metal through the hot zone of a vacuum furnace, the metal passing from a zone heated to about 50° C. above the melting point to an area heated to slightly less than the freezing point in some 14 hours. Mechanical leveling bulbs allowed the slow, uniform and

non-vibratory movement of the metal in a crucible.

This method of preparation would seem satis-
factory for preparation of single crystals of the alloys
having a melting point quite similar to that of copper.
Preliminary experiments were made in which the sample was
held in position in the furnace and the temperature was
slowly and uniformly reduced by manual control. Available
was a quartz tube furnace fitted with a thermocouple well
and wound with an insulated heating element. A vacuum
connection was attached. The entire furnace was insulated
by two inches of MgO. Temperature measurements were made
with a thermocouple and potentiometer.

A sample of Mn_2Sb prepared by direct combination
was placed in a graphite crucible (1/4 inch by 2 inch hole
in a 1/2 inch by 5 inch graphite rod), and inserted in the
furnace. The furnace was operated at about three mm.
of mercury pressure. The sample was cooled from a temper-
ature of 940° C. to 830° C. in a period of 11 hours. The
melting point of Mn_2Sb is 919° (36,p.412).

Upon removing the sample from the furnace, micro-
scopic examination revealed very small crystals, of in-
determinate shape. The crystals were quite magnetic, and
qualitatively anisotropic: that is, the crystals would tend
to line up with the long axis perpindicular to the magnetic

field. The crystals were of the order of 0.1 mm. in diameter and perhaps twice as long.

It was not definitely determined that the sample had been heated to melting, since the sample did not appear fused, so a new crystallization attempt was made with a higher temperature of the furnace. The same apparatus was used with the exception of the sample crucible. A small quartz tube contained the alloy. The sample was heated to 1060° C and the temperature was evenly lowered from 1050° C to 880° C in a period of six hours.

When the sample was withdrawn from the furnace, it was noted that two types of materials were present: black microcrystals some of which were as large as 0.5mm. in one dimension and some brilliant green crystals of the same size. Magnetic investigation of the crystals indicated that the black crystals were quite strongly attracted to a magnet while the green ones were but slightly attracted. The attraction of the two types was clear cut enough to allow magnetic separation of the crystals. Analysis indicated the presence of some silicon in the green crystals perhaps as a ternary silicide. The green crystals were most prominent at the sides of the quartz tube; the tube appeared etched after removal of the samples.

The results of the above experiments indicated that the crystallization attempts did not yield large enough crystals to be of value in the determinations to follow, and the experiments would not yield enough additional information to justify the expense of constructing the apparatus needed for a more refined growing of these crystals. The stability and melting point data also indicated that attempts to grow arsenide and phosphide crystals would be even less likely to succeed.

Tube Furnace Method of Preparation of Alloys: The methods of preparation of the alloys used by previous investigators was, in general, that of direct combination of the elements in an evacuated tube.

Experience has shown, however, that this method offers several disadvantages: (1) the reaction seems to take place with considerable heat evolution, which may raise the vapor pressure high enough to cause tube fracture. This result was obtained in a significant percentage of trials. The burning of arsenic or phosphorus from a tube fracture offers a serious safety hazard. (2) It seems difficult to free the sample of excess arsenic (or phosphorus) without using means drastic enough to permit breakdown of the alloy into the corresponding chlorides. (3) It has been the result of previous workers that the arsenidation

was limited at the composition MnAs (eg.2,p.284); it has
been reported that phosphorus alloys produced in high
pressure bombs could not be made with phosphorus content
as high as that corresponding to the formula MnP (24).
Heating at the temperatures indicated for the preparation
of the alloys results in the loss of arsenic; arsenic
starts to be volatilized above about 400° C. Similar
results are to be presumed with phosphorus alloys.

Arrivaut (2,p.284) mentioned that it is possible
to prepare MnAs by passing $AsCl_3$ vapors over manganese
heated to 400° C. This method would seem to offer the
advantages of operating at atmospheric pressure, thus
eliminating the danger associated with heating sealed,
evacuated tubes near the boiling point of one of the
materials enclosed in it. In addition, the group V-A
chlorides are available in purer forms than the elements,
since they are common laboratory reagents.

The method has been tested and found to be a
good general method for the preparation of manganese-
phosphorus, manganese-arsenic, and manganese-antimony
alloys.

The furnace used in heating the manganese was an
Eimer and Amend 1300 watt tube furnace, having a bore of
two cm. and a heating area of 35 cm. long. Rheostats and

an ammeter were provided for the regulation of temperature through control of furnace current.

The vaporizing flask, the furnace combustion tube and the vapor traps were connected together in an all-glass system. The group V-A chloride was vaporized in a 100 ml. boiling flask; the furnace combustion tube was generally of pyrex though a satin quartz tube was used for some higher temperature preparations. The vapors after passing through the furnace were collected in a trap cooled with ice, followed by a gas washing bottle to scrub out remaining vapors. This was necessary because of the unpleasant and corrosive nature of the PCl_3 and $ASCl_3$ vapors, even at room temperature.

The manganese used was produced by the Electro Manganese Corporation of Knoxville, Tennessee. The purity of the material according to the supplier[1] was:

Table 3

IMPURITIES IN METALLIC MANGANESE

Sulfur as Sulfide	0.011%
Sulfur as Sulfate	0.001%
Iron	less than 0.001%
Heavy metals	spectroscopic traces, none greater than 0.005%.

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1. Personal communication from William L. Hammerquist, Electro Manganese Corporation, Knoxville, Tennessee, March 11, 1948.

The phosphorus chloride used was a Bakers C.P. product, the iron content given as 0.0003%. The arsenic chloride was also a Bakers product, though no analysis was given.

The procedure adopted as best was as follows: The manganese was finally ground in a mortar and pestle to approximately -100 mesh. The manganese powder was next mixed with about ten volumes of C.P. light grade MgO and thoroughly mixed. The resultant mixture was then placed in a uniform layer to about half fill a pyrex tube closely fitting into the furnace combustion tube. The tube was then placed in the furnace and heated for 20 minutes at the desired furnace current. The group V-A chloride was then vaporized over the heated manganese. The reaction proceeds with incandescence.

The sample, when cooled, was treated with dilute hydrochloric acid which removed foreigh substances pro- duced in the furnace. The sample would contain, other than the manganese alloy, varying amounts of MgO, $MgCl_2$, $MnCl_2$, Mn, and PCl_3 (or $AsCl_3$). These are all soluble in hydrochloric acid solution, while the alloy is the unattacked so a simple separation of pure alloy can be made. The alloy was twice treated with the acid, then washed thorough- ly with distilled water and dried.

Since the thermal history of the samples was important, care was taken to see that the magnetic transformation region was traversed but once in the preparation of the alloys. If repeated heatings of the sample should be necessary, the samples were stored above the Curie point until all heat treatment had been completed. The manganese phosphide alloys were stored in a deep freeze at -30° C before and after use; the arsenides could be kept at room temperature.

Addition of the MgO powder was found necessary in order that the reaction proceed with the use of most of the manganese. If the manganese was not diluted, a fused coat of $MnCl_2$ would form at the surface of the metal and the action would cease. Sodium chloride was tried as a diluent but was not successful.

Increasing the temperature of the tube furnace resulted in an alloy with a higher ratio of manganese to phosphorus (or arsenic). This is shown by the following table:

Table 4

EFFECT OF TUBE FURNACE TEMPERATURE ON ALLOY COMPOSITION

Temperature of Furnace, $^{\circ}$C.	Ratio
370	Mn:P = 1:1.39
460	1:1.30
660	1:1.02
460	Mn:As= 1:1.34
660	1:1.03

Manganese powder was refluxed with arsenic tri-chloride (b.p. 130°) producing a black powder which was non-magnetic. Qualitatively it contained but a trace of manganese. Refluxing antimony trichloride (b.p. 220°) with manganese gave a black powder which was somewhat magnetically attracted. Qualitatively the sample contained a minor quantity of manganese. A manganese-antimony alloy formed at about 400° C. was considerably more attracted to a magnet, and qualitatively contained more manganese than the reflux prepared sample.

Phosphorus (or arsenic as the case may be) precipitates in the cool portions of the combustion tube, but none collects in the heated sample zone of the furnace.

All of the samples used in the investigations to follow were prepared by the tube furnace method. The furnace temperatures used were those given in Table 4. Alloys richest in manganese were prepared by burning the arsenic or phosphorus out of the alloys by heating in air to about 750° C. for an hour. The results of analyses of the samples used in the investigation of the manganese-phosphorus system is given in Table 5; these are the samples used in the runs given by figures 3,4,5 and 6. Table 6 shows the result of analyses of the manganese-arsenic alloys used in obtaining the data of figures 7, 8 and 9.

Table 5

RESULTS OF PREPARATION OF MANGANESE-PHOSPHORUS ALLOYS

Manganese,avg.%	66.57	62.80	57.71	56.02
Phosphorus,by diff %	33.43	37.20	42.29	43.98
Chloride	neg.	neg.	neg.	neg.
Magnesium	neg.	neg.	neg.	neg.
Silica	neg.	neg.	neg.	neg.
Iron	trace	sl.trace	sl.trace	sl.trace
Ratio P:Mn	0.89	1.02	1.30	1.39

Table 6

RESULTS OF PREPARATION OF MANGANESE-ARSENIC ALLOY

Manganese,avg.%	44.97	41.71	35.45
Arsenic,by diff.%	55.03	58.29	64.55
Chloride	neg.	neg.	neg.
Magnesium	neg.	neg.	neg.
Silica	neg.	neg.	neg.
Iron	sl.trace	trace	sl.trace
Ratio As:Mn	0.90	1.03	1.34

Note: In the analysis for iron, the notation "sl.trace" designates color reaction about equal to the manganese of the original sample (0.001%). A "trace" designates an amount of about 0.005% or less.

Analysis of the Samples: The samples of the manganese-phosphorus and manganese-arsenic alloys were not too soluble. They are but partially attacked by concentrated nitric acid, are unattacked by concentrated or dilute hydrochloric or sulfuric acids. Alkalies do not

dissolve the materials. The following procedure was found to be the best method of dissolving the alloys: concentrated nitric acid was added and the samples were brought to a boil. Concentrated hydrochloric acid was then added until aqua regia was formed, and the samples were again brought to a boil. The boiling was continued until the samples dissolved. The ease of solution of the samples seemed to be a function of the non-metal alloying constituent; samples rich in phosphorus, for example, were more readily dissolved than samples poorer in phosphorus. Although solution could be achieved with the chlorinating agents, such as $KClO_3$ and HCl, the above procedure gave the best results, since solution was frequently quite difficult.

Once solution was achieved, the elements were separated for analysis. A survey of methods of analysis indicated the method of separation of manganese as the dioxide was the best method. The dioxide was separated by the method of Scott (21,pp.559-60) using $Zn(NO_3)_2$ as the reagent to promote consistent results. The precipitated manganese dioxide was then filtered through an asbestos mat in a Caldwell crucible, and washed well with hot distilled water.

The preferred method of analysis (21,p.574) for manganese was the dissolution of the manganese dioxide precipitate with an excess of standard ferrous sulfate solution, in the presence of sulfuric acid and phosphoric acids. The excess ferrous sulfate is back titrated with standard potassium permanganate to the permanganate end point.

Standardization of the permanganate was against weighed amounts of the electrolytic manganese, precipitating and titrating the manganese by the methods used above.

Titrations were also made by the iodometric method (21,pp.570-1), but the titration was not as sharp as the ferrous sulfate-permanganate method.

In the case of phosphorus alloys, the phosphate can be determined in the filtrate of the manganese dioxide precipitate. The standard method (21,pp.614-6) of precipitating the phosphate as ammonium phosphomolybdate, dissolving and reprecipitating as magnesium ammonium phosphate was used. The precipitate was then ignited in an electric furnace and weighed as magnesium pyrophosphate. The method was very satisfactory.

Arsenic determinations, in the case of arsenic alloys, were made by the gravimetric method of Scott (21,pp.96-8). The precipitation was made as magnesium ammonium arsenate, being ignited to and weighed as magnesium pyroarsenate.

Because of the volatility of PCl_3 and $AsCl_3$, and the drastic treatment necessary for sample solution, it is very difficult to get complete analysis of the sample, some PCl_3 (or $AsCl_3$) will be lost through volatilization. Therefore, in determining the ratio of phosphorus to manganese, the phosphorus was determined by difference.

The samples were qualitatively analyzed for iron by the usual colorimetric thiocyanate method. The iron content was scarcely detectable with all samples.

Magnesium content of the samples was determined qualitatively with paranitrobenzene azoresorcinol (S. and O. reagent) but was negative in all cases.

A sample of each of the alloys was leached with boiling concentrated nitric acid, diluted somewhat with water, and tested for chloride by the addition of silver nitrate solution. The results of the test showed chloride ion to be absent.

Since the samples completely dissolved in the acid mixture used for solution, silica (from the combustion tubes) must be absent.

Rhenium-Antimony Alloy: Since the possibility exists that ferromagnetism of manganese-group V-A alloys is due to the peculiar electronic arrangement of these

elements, then other group VII-B alloys with the group
V-A elements should also exhibit ferromagnetism.

In group VII-B with manganese are found
technicium and rhenium; of these only rhenium is com-
mercially available at a cost of $3.50 per gram.

The rhenium-phosphorus system was studied by
Haraldsen (27) and the rhenium-arsenic system was inves-
tigated by Weichmann and Heimburg (55); but no ferro-
magnetic alloys are mentioned in their work, though the
alloys may not have been tested for magnetic behavior.

A small amount of rhenium was procured to
test the ferromagnetism of a rhenium alloy. Antimony
was chosen as the alloying group V-A element since it
is easily combined, has a strong effect when alloyed
with manganese and has a high Curie temperature with
manganese.

Rhenium and antimony powders were mixed in
equi-molecular ratios (2.7 millimoles of each), covered
with barium chloride crystals, and heated to 800° C. in
the furnace for an hour. The resulting alloy was leached
with water to remove the barium chloride, washed and
dried. A qualitative test showed the presence of antimony
in the alloy; no quantitative test of composition was made.

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The rhenium-antimony alloy was tested for magnetic attraction by observing its behavior with a large alnico permanent magnet (1831 gauss) but no visible attraction of the alloy particles were noted. The sample was cooled to 0° C. before testing for the magnetic action; manganese-antimony alloys remain ferromagnetic up to 275-330° C.

The results obtained with the rhenium-antimony alloy are not unexpected since iron, cobalt and nickel of group VIII, following manganese are ferromagnetic, but the group VIII elements of other periods are not ferromagnetic.

EXPERIMENTAL

The apparatus was constructed with the aim of making simultaneous determinations of the relative permeability, thermal expansion, thermoelectric potential and thermogalvanic action of samples of the alloys of manganese and phosphorus or arsenic.

A unitized thermostat assembly proved convenient for the measurements. A small table with a thermostat mounted in the table top allowed control of the thermo-regulator, thermometer bridge, thermogalvanic potentio-meter and thermoelectric voltmeter from one position; the cathetometer for reading dilatometer height was necessarily mounted across the room.

The thermostat bath was of five gallon capacity and was thermally lagged with magnesia-asbestos insulation. Water was used as the bath liquid for all of the measure-ments. Efficient stirring was accomplished with a variable-speed stirrer.

Thermostat heaters ranging from 10 to 250 watts were used; light bulbs proved to be convenient small heaters. The heating was divided between continuous and intermittent heaters. Cooling of the bath liquid was conveniently accomplished with a coil circulating cold water; pressure fluctuations of the cold water were necessarily cut down with a pressure regulator.

Temperature Measurement: It was desired to
have a system of temperature measurement which would be
sensitive to changes of temperature of the order of 0.01°C.
over the range from 0° C. to about 375° C. The sensitivity
and range desired suggested the use of a resistance thermo-
meter. Although platinum is most commonly used in resist-
ance thermometry, Maier (33,pp.2860-6) has found copper to
be a stable material having a slightly higher coefficient
of resistivity than platinum.

The thermometer used consisted of two layers of
close wound No. 40 gage Formvar covered copper wire
wound on a 6 mm. pyrex tube 12 cm. long. This was placed
in a close fitting pyrex glass sheath and connected to the
measuring bridge with No. 18 gage copper wire. An addit-
ional thermometer consisting of bare No. 40 copper wire
interwound with glass yarn was constructed to cover the
range up to 375° C; the Formvar insulation will start to
break down at about 125° C.

The resistance of the thermal sensitive unit was
measured with a standard Wheatstone bridge circuit,
employing a Leeds and Northrup precision type Kohlrausch
Slide Wire and a Leeds and Northrup Lamp and Scale type
galvanometer in the measuring circuit. The resistance

box was set at a constant value of 140 ohms so that temperature could be determined as function only of slidewire drum setting. By using the slide wire with the end coils, the entire range was needed to cover temperatures from 0° to 100° C.

The resistance thermometer unit was calibrated at the ice point, the steam point, the transition temperature of C.P. sodium sulfate, and the boiling point of 100% ethanol. Standardizations were made by the methods of the U. S. Bureau of Standards (20,p.278) and Daniels, Mathews and Williams (18,pp.147-9). The plot of temperature against resistance was very nearly a straight line. The resistance corresponding to temperatures for 10° intervals was determined and the intermediate temperatures could then be calculated by linear interpolation. The ice point resistance of the thermometer was 115.44 ohms, the steam point 164.24 ohms, with 15 cm. immersion of the thermal sensitive unit.

Thermoregulator: A survey of methods of temperature control sufficiently sensitive to give control of the order of ±0.02^o C. and capable of continuous regulation at temperatures ranging from 0° C. to about 375° C. indicated the best method seemed to be the resistance thermometer A. C. bridge type of controlling

unit. The apparatus chosen was that due to Coates (17),
adapted to American components. The circuit,as finally
evolved, is shown by figure 1, and the electronic
components used are given by Table 7.

The assistance given by Prof. J. J. Wittkopf
of the Electrical Engineering department in designing
the apparatus and of Mr. Ben Ballard of Radio Station
KOAC in adjusting the thermoregulator is gratefully
acknowledged.

In this type of regulator, the resistance thermo-
meter and a sensitive setting or balancing resistance
form two arms of a bridge, the other two arms of which
are formed by a 15V. center-tapped A.C. transformer.
When the bridge is unbalanced, a voltage will be impressed
upon the grid of V-1, the value of the current being
related to the extent of unbalance of the circuit. The
current due to unbalance if the thermal unit is "too
hot" or "too cold" by the same amount will be equal.
That is, if the sensitive unit is either "too hot" or
"too cold" by 0.01^o, a current of "a" amperes will be
impressed upon the grid of V-1, but there will be a
phase difference of 180° between the "too hot" and "too
cold" voltages. The grid voltage is then amplified by
V-1, V-2 and V-3, though V-3 plays the additional role
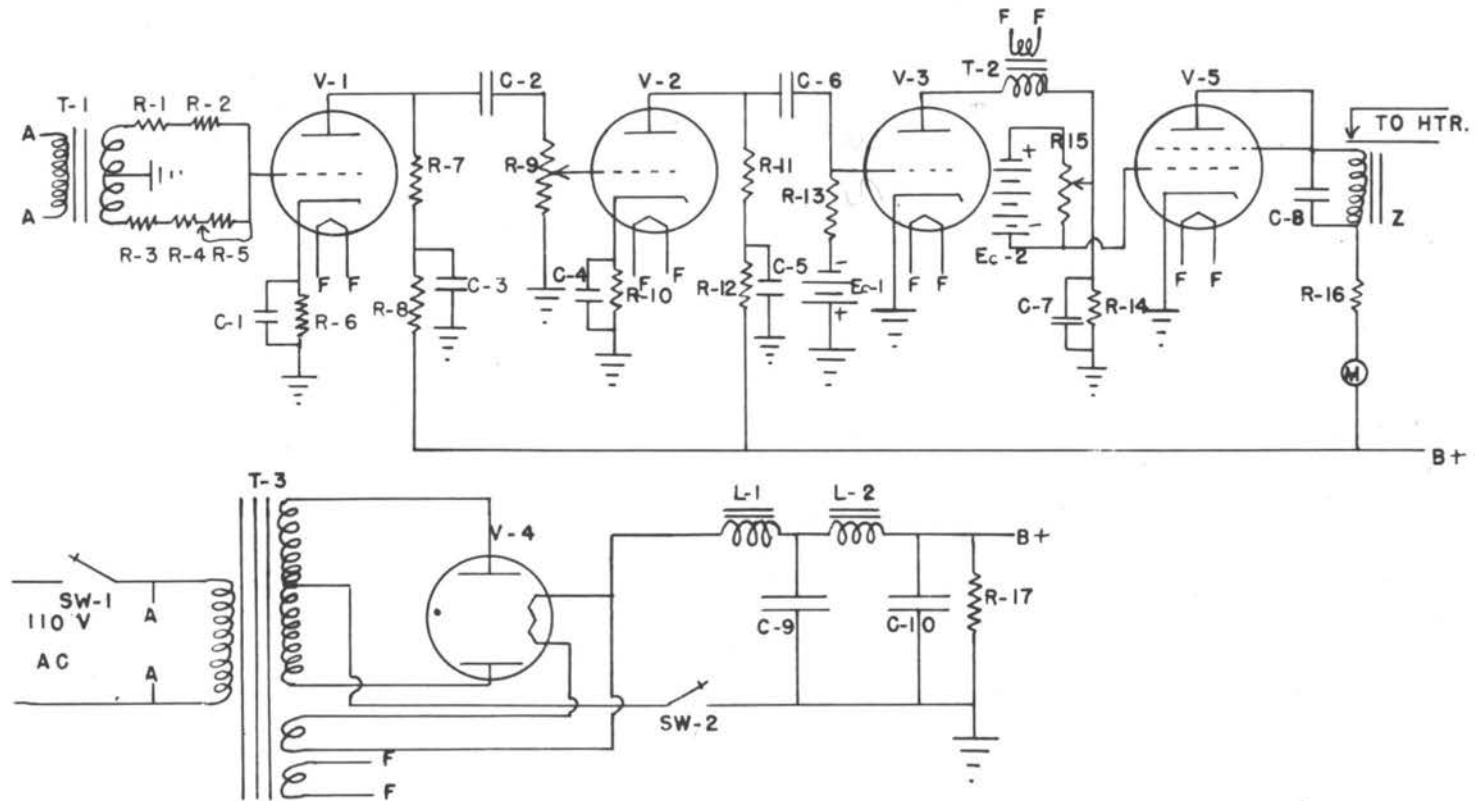of selecting between the "too hot" and "too cold" signals.

Fig.1   Circuit Diagram, Electronic Thermoregulator.

Table 7

Parts List for Electronic Thermoregulator

R-1	Thermistor, Western Electric type 15-A
R-2, R-4	250 ohm, 1 W. carbon resistors
R-3	200 ohm Helipot, Beckman type 200 AZ
R-5	75 ohm, 1 W. resistor
R-6, R-10	2400 ohm, 1/2 W. carbon resistors
R-7, R-11	100,000 ohm, 1/2 W. carbon resistors
R-8, R-12	10,000 ohm, 1/2 W. carbon resistors
R-9	250,000 ohm potentiometer
R-14	68,000 ohm, 1 W. carbon resistor
R-15	500,000 ohm potentiometer
R-16	1000 ohm, 10 W. wire-wound resistor
R-17	20,000 ohm, 10 W. wire-wound resistor
C-1, C-4	10 microfarad, 25 volt electrolytic condensers
C-2, C-6	0.1 microfarad, 600 volt paper condensers
C-3, C-5	8,8 microfarad, 450 volt dual electrolytic condenser
C-7	0.1 microfarad, 400 volt paper condenser
C-8	8 microfarad, 450 volt electrolytic condenser
C-9, C-10	8,8 microfarad, 450 volt dual electrolytic condenser
T-1	Bridge transformer: secondary of 6.3 W filament transformer rewound so as to deliver 15.4 RMS. volts at 100 ma., tapped at 7.5 volts.
T-2	Plate transformer: 220 volt to 10 volt bell-ringing transformer reversed and primary rewound so as to operate from 6.3 volt filament transformer. Out put 155 volts RMS.
T-3	Power transformer, rating 350-350 volts at 120 ma., 5 volts at 3 amps, 6.3 volts at 4.7 amps.
L-1	Choke, rating 4-16 henry, 15-150 ma.
L-2	Choke, rating 10 henry, 150 ma.
Ec-1	Bias battery, 3 volts
Ec-2	Bias battery, 22 1/2 volts.
Z	Relay, 175 ohm. Spring adjusted to short range: close 10 ma., open 5 ma.
M	Milliameter, 0-50 ma. D.C.meter
V-1, V-2	Vacuum tube, type 6SN7-GT
V-3	Vacuum tube, type 6J5-GT
V-4	Vacuum tube, type 83
V-5	Vacuum tube, type 6L6-GT
SW-1	Power switch
SW-2	High voltage switch

The alternating current potential developed by the bridge upon unbalance will result in an A.C. potential at the grid of V-3. Since an A.C. potential is also impressed on the plate of V-3, the tube will only conduct when the plate of V-3 is positive as the bridge signal is received at the V-3 grid. Therefore, if the phase is such that the plate of V-3 is positive as the error signal from a "too cold" voltage reaches the V-3 grid, the tube will conduct and the amplified voltage is passed on to tube V-5. But should a "too hot" signal be impressed upon the grid of V-3, now 180° later in phase, then the plate will also be 180° later in phase. Since the plate is negative, the tube will not conduct and the "too hot" signal is rejected. The signal from V-3 is filtered somewhat by C-7 and R-14 and passes on to V-5 where a relay is controlled by the plate circuit response of the tube to the error signal passed on from V-3.

The phasing of T-1 and T-2 can thus be adjusted to fit the type of control needed; the control can be used for thermally sensitive units with either a positive or negative coefficient of resistivity, or for normally open or normally closed control circuits by proper adjustment of phase of T-1 and T-2.

The thermoregulator circuit as finally evolved was used with a Western Electric thermistor as the sensitive unit; a copper resistance thermometer had previously been used but the thermistor gave a more sensitive response. The thermistor was kindly furnished by Western Electric Co., New York, N.Y.

The thermistor used, a Western Electric type 15-A, had the following characteristics (19,pp.84-91): Resistance at 0° C. about 283 ohms, at 25° C. about 100 ohms and at 50° C. about 41 ohms. It was furnished in the form of a 0.4 inch diameter disk with radial leads. The thermistor was covered with ceresin wax and placed in a glass protective tube with some water added to aid in heat transfer.

The bias potential from EC-2 was adjusted to 18.5 volts by means of R-15, for best operation of the thermoregulator.

The type of thermoregulator used had an added advantage in that it is quite insensitive to line voltage fluctuations.

Dilatometer: The use of a bulb and capillary dilatometer suggested itself as the best means for measuring the density of the alloy powders as a function

of temperature. This is brought out by Reilly (42,pp. 467-8), and was the method used in previous work with MnAs by Guillaud (25,p.394) and Smits, Gerding and Vermast (48,pp.358-60).

The dilatometer consisted of a spherical bulb of about 13 cc. capacity which was connected by a 10/30 $ joint to a section of pyrex capillary tubing 90 cm. long, and with a bore of about 0.8 mm. An additional capillary was available with a bore of about 0.2 mm.

The proper choice of containing liquid and sealing material at the ground joint was very important. The conditions that must be met by the containing liquid and sealing cement were:

    i.   The containing liquid must be inert towards the alloys to be measured.

    ii.   The vapor pressure should be low; the combination should be sealed so that loss of material will be 1 mg. or less per week.

    iii.   Thermal expansion of the containing liquid should be low so as not to mask alloy expansion.

The conditions set forth were properly fulfilled by using a treated mineral oil as the containing liquid and General Electric glyptal cement as the sealing medium. The mineral oil used was U.S.P. White Oil

No. 7, light grade, which was heated to 150° C. at 3 cm.
pressure for one hour, in order to remove the more
volatile components. As a further precaution, the ground
glass joint was polished with levigated alumina (sapphire
dust). The dilatometer capillary tip was sealed off
from the atmosphere with a rubber policeman tip.

A number of other media were tested before the
proper combination was discovered. Some unsatisfactory
media were n-dibutyl phthalate, water, and xylene.
Some sealing cements which were not successful included
picein, sealstix, silicone grease, ceresin wax, apiezon,
lubraseal, and tetraethyleneglycol citrate.

The capillary tube was calibrated with weighed
slugs of redistilled mercury. The length of slugs of
mercury about 30 mm. long was measured with a travelling
microscope (read to 10^{-3} mm.) at short intervals along
the capillary, allowing the average area to be obtained.
A large graph of the closely agreeing values of the
capillary area as a function of length along the tube
was then constructed. Volume of liquid in the capillary
could then be calculated by the method of summation of
trapezoids.

The volume of the bulb was determined from the
weight of redistilled mercury required to fill the bulb,
after correcting for the volume held in the capillary.

The volume of the bulb was determined at intervals from 0° C. to 55° C. and a large graph of the volume against temperature constructed for interpolation of the volume.

The specific volume of the oil used as a containing liquid was determined over the range of temperature to be used, as described above.

The procedure in filling the dilatometer was as follows: The finely divided alloy powder was weighed into the dilatometer; from 5 to 10 grams of sample were used. The oil was added to about fill the bulb and the dilatometer bulb was placed in a vacuum dessicator and evacuated to remove the occluded air and gases from the sample. Oil was added at intervals to keep the oil level at the top of the bulb neck and the bulb was frequently tapped to aid in gas evolution. When gas evolution had ceased, the capillary was partially filled with oil and attached to the bulb. The joint was sealed with the glyptal cement after weighing the dilatometer plus contents. A clamp was attached to the dilatometer neck holding the capillary by small springs or rubber bands in order to take the strain of holding the dilatometer off of the sealed joint. A rubber policeman was placed over the capillary tip to cut down evaporation loss.

All weights of samples, containing oil, and calibrating materials were converted to weight in vacuo.

Although all calibrations of the capillary were referred to a reference scratch at the base of the tube, a second fiducial scratch a known distance from the first mark and near the middle of the tube was added as a reference for the dilatometric reading.

Measurements of the oil level were made with a Gaertner cathetometer, read to 0.01 cm.

The volume of the sample V_s at a given temperature was calculated by the following equation.

$$V_s = V_b + V_c - W_0 SV_0$$

where V_b is the volume of the bulb, a function of temperature. The symbol V_c represents the volume of oil in the capillary and is obtained by graphically integrating the area under the capillary area-oil height curve. The methods of trapezoids was used in summing the capillary volume. The symbol W_0 represents the weight of the oil used as a containing liquid, and SV_0 is the specific volume of the oil at the temperature of the measurements.

Thermal expansion of the capillary was disregarded since measurements indicated its temperature to be the same as the air temperature of the room.

Permeameter: Correlation of magnetic behavior
with thermal expansion, thermoelectric potential and
thermogalvanic action made it necessary to provide some
means of measuring the magnetic effects. The require-
ments were that the device would give at least relative
values of magnetic permeability and that the device be
small so that it could fit into the thermostat used, so
the sample could be measured at the variable temperatures
of the bath. In addition, the apparatus should use but
small quantities of powdered sample.

Since conventional magnetometers (45,p.18,239),
(8,pp.59-60) do not completely satisfy the conditions
of the experiment, a search was made for a new method
which would be satisfactory.

The properties of a tuned inductance in a
resonant circuit seemed to be a good possibility for
relative measurements of permeability.

For a resonant circuit (28,p.222,312)

$$2 \pi fL = \frac{1}{2 \pi fC}$$

or $$L C = \frac{1}{4 \pi^2 f^2}$$

and at a constant frequency,

$$L C = constant$$

Now the inductance of a coil is proportional to the
permeability of the medium enclosed

$$L = \mu L_0$$

where L_0 is the inductance of the coil in vacuo,
where $\mu = 1$.

Then, at constant frequency

$$\mu C = \text{constant, or } \mu \propto \frac{1}{C}$$

Therefore, if the coil and condenser represented the
entire capacitance and inductance of the circuit, the
above relationship would hold. Since other stray
capacitances and inductances are present in the circuit,
it should be possible to use the change in capacitance
on inserting the sample as an indication of changes
of permeability.

The apparatus used for the determination was
a heterodyne-beat dielectric-constant apparatus (16,pp.
494-7) kindly furnished by Dr. J. C. Decius. In this
apparatus, the frequency of a variable frequency
oscillator is balanced with that of a crystal-controlled
fixed frequency oscillator, balance being as close as one
cycle per second under optimum conditions.

In order to use the apparatus for permeability
measurements, the internal coil of the variable frequency
oscillator must be replaced by a coil which could be

thermostated in the bath and which could contain the sample. A coil was constructed as shown in Figure 2.

The coil was constructed of 500 turns of No. 25 gage double silk covered wire wound on a section of glass tubing 13 mm. in diameter with the coil five cm. in length, three layers being required for the coil. This coil was placed in a cylindrical copper shield two cm. in diameter and seven cm. long, the coil being centered in the shield with lucite spacers. Connection to the oscillator was made with type RG8/U coaxial cable. Mineral oil was added to both the copper shield can and the glass sheath to improve thermal equilibrium.

The inductance of the coil, according to the formula of Harnwell (28,pp.436-7) was about 300 micro- henries, closely approximating the inductance used internally when the apparatus was used for dielectric measurements.

The exaggerated long slim shape of the coil was made so as to better fit a sample of the alloy to be tested. The sample was contained in a test tube one cm. by seven cm. The volume of alloy contained in the test tube was about three ml.

The variable frequency oscillator circuit was tuned with a General Radio precision type 1500 micro-

COAXIAL CABLE
TO OSCILLATOR

SAMPLE TUBE

COIL WOUND OVER
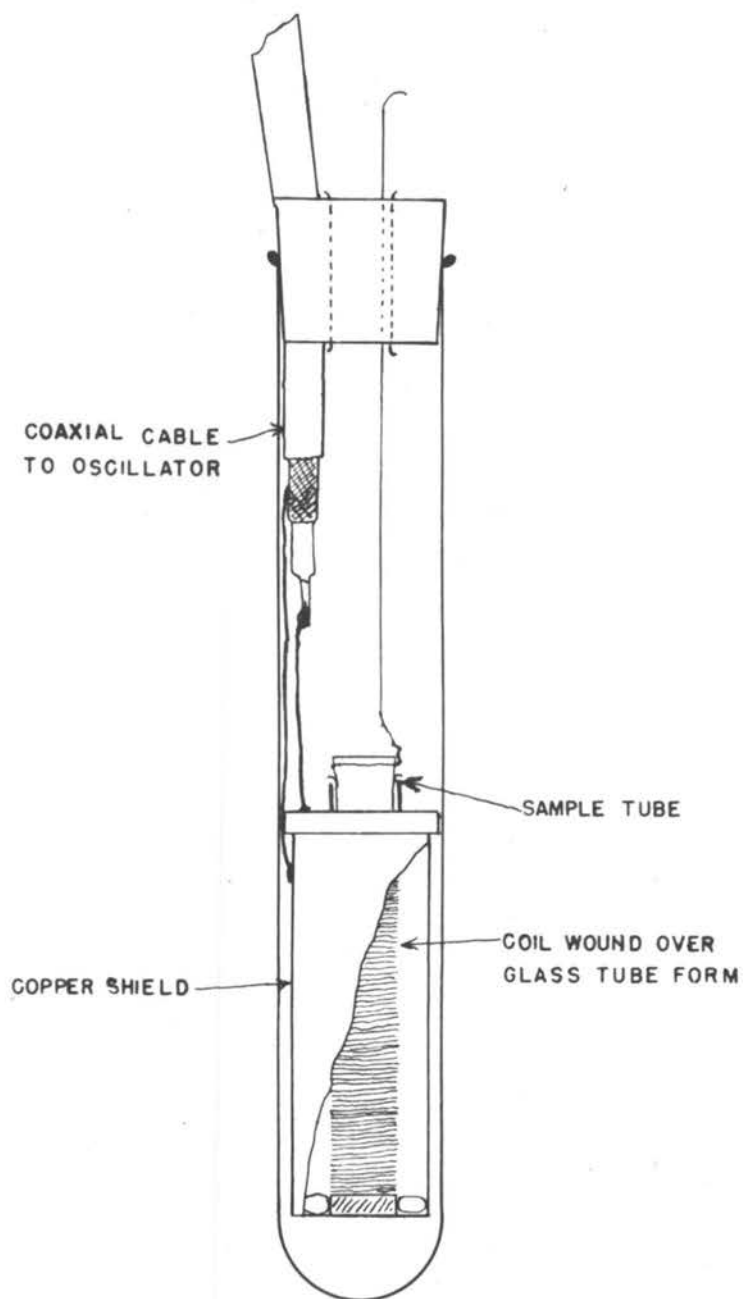GLASS TUBE FORM

COPPER SHIELD

Fig. 2 Inductance Cell Used for
Permeability Determinations

microfarad condenser, connected to the oscillator unit with coaxial cable.

Determinations of the magnetic behavior of the samples was made by filling the test tube sample holder with the alloy and obtaining the condenser readings corresponding to heterodyne null with the sample inserted in the coil and removed from the coil. This procedure of finding the actual change of capacitance necessary to balance the change in the permeability of the medium enclosed was necessary to correct for ambient temperature effects on the inductance of the coil; these effects were of consequence. The capacitance to tune the empty coil at 25° C. is about 2 1/2% more than that required to tune the empty coil at 50° C.

No attempt was made to eliminate a possible error due to differences in packing of the samples. This would not effect the sharpness of the changes at the magnetic transformation temperature but would only effect the magnitude of the changes.

For the same reason, absolute calibration was not attempted. The magnitude of the permeability of the samples is told, however, by the change in capacitance for powdered nickel produced by the carbonyl process. The change in capacitance for the nickel powder varied

from 115 to 254 $\mu\mu$ f., depending on the particle size.
A 29% solution of C.P. $NiCl_2$, with a molar susceptibility
of 4433 $\times$ 10^{-6} C.G.S units (45,p.29) gave a value for
ΔC of 1.3 $\mu\mu$ f. The data of Figures 3 through 9 show
that the permeability of the alloys approaches that of
nickel.

The apparatus was found to be very sensitive
and reproducible. Readings for change of capacitance
are believed accurate to better than 0.1 $\mu\mu$ f.

Thermoelectric Potential: The thermoelectric
potential of MnAs alloy was first studied by Bates (5).
In his investigation, rods of the manganese arsenide
alloy were cast and the potential was measured between
the two ends of the rods kept in thermostats with a
temperature difference of 2° C. between the two ends.
The rods as cast had a resistance of but a fraction of
an ohm and the potential was measured by the deflection
of a galvanometer connected between the two ends of the
alloy junction. The junction was MnAs alloy-copper.

The method of Bates has the rather serious
disadvantage in that the alloys break down as they are
heated to melting for the casting process; the alloys
tend to become unstable with regard to arsenic (or
phosphorus) at temperatures exceeding about 400° C.

It was therefore decided to see if satisfactory alloy junctions could not be prepared by pressing the alloys to form compacted rods.

The junctions were made by adding the alloy to a glass tube of three mm. inside diameter and 16-20 cm. long. The alloy was tamped in place and then firmly compacted by hammering with a close-fitting brass rod. The tamping and driving process was repeated with each small addition of the alloy, thus building up a firm, though brittle rod. Copper wire leads were compacted into the alloy at each end of the rods. The copper leads and alloy were kept tightly in place with wooden plugs. The resistance of the rods varied from about 10 to 100 megohms.

Since the resistance of the rods is so high, neither a conventional microvoltmeter nor a potentiometer was sufficiently sensitive to measure the potential of the thermal junctions. Because of the very high resistance of the rods, the use of a vacuum-tube micro-voltmeter was suggested.

One of the most sensitive and stable types of vacuum-tube voltmeters is the Wynn-Williams bridge type. The version used by Burr, Lane and Nims (14,pp.66-74) had, for example, an input impedence up to 100 megohms with a sensitivity of about three microvolts. Such a circuit

would be satisfactory for the measurement of the potential
of the alloy thermals.

A stable, sensitive vacuum-tube millivoltmeter
had been constructed by Keilholtz (32,pp.40-43,44c).
This instrument had a sensitivity of 0.3 millivolt with
an input impedance of 10 megohms. Since the galvanometer
used in the millivoltmeter was a panel-type 0 - 100 micro-
ammeter, the sensitivity could be improved by simply using
a more sensitive galvanometer. The instrument was used
by substituting 120 megohms resistance for the input
resistance R-4 of figure 11 (32,p.44c) and by using a
Leeds and Northrup type P wall-type galvanometer for
the galvanometer of the circuit. When used in this manner
the scale was expanded to sufficient sensitivity for the
measurements desired.

The instrument was calibrated against a
chromel-alumel thermocouple which could be measured with
a Leeds and Northrup type K-1 potentiometer. The
calibration value was 37 mm. deflection per millivolt at
one meter, with the galvanometer used.

The cold junction was maintained at the ice
point for these readings. The procedure differed from
that of Bates in that the temperature of but one of the
junctions was varied while the other junction was main-

tained in a constant state.

A positive potential was indicated when the cold junction was connected to the positive terminal of the microvoltmeter and the hot or variable temperature junction was connected to the negative terminal.

Thermogalvanic Potential: Measurements of the potential of the cell

$$Pt, MnAs\ (T_1)\ \bigg|\ MnCl_2,\ HCl\ \bigg|\ MnAs\ (T_2),\ Pt$$

were made by Bates (4) using an "H" type cell with the manganese-arsenic alloy covering a platinum wire contact tip.

Arrivaut (2), in an earlier work, measured the potentials developed between a number of manganese-arsenic cast rods and a pure manganese electrode; the electrolyte was normal manganese sulfate solution.

The method of Bates does not seem to assure good electrical contact; the method of Arrivaut, in casting the rods, must result in some decomposition of the samples. Pelleting buttons of the alloys around copper wire contacts should make electrodes without the objections made above, and a cell similar to the one of Bates could be used.

Buttons of the alloys about five mm. in diameter and five mm. thick were made in a modified pellet press. The buttons were compacted onto copper

wire electrical leads.

The electrolysis cell was an exaggerated "H" type, with legs about 25 mm. by 15 cm. and the connecting leg 15 mm. by 18 cm. and with a stopcock for filling the cell in the connecting leg. The electrodes were cemented into glass tubes and inserted in the legs of the cell by standard taper joints.

The electrolyte used in the cell was 0.1 molar in manganous chloride and 0.025 molar in hydrochloric acid. About 100 ml. of electrolyte solution was required to fill the cell.

The constant temperature junction of the cell was maintained at 0° C. by an ice-water mixture.

Potential measurements of the cells were measured with a Leeds and Northrup type K-1 potentiometer. Positive readings of potential were indicated when the cold junction was connected to the positive terminal of the potentiometer and the hot junction was connected to the negative terminal.

Suggested Improvements in the Apparatus: If a greater temperature sensitivity of the thermometer is desired, the use of thermistors as the temperature sensitive unit should give a sensitivity about ten times as great as now obtained with copper or with platinum.

The upper temperature limits now given for thermistors, however, is about 300° C. (19,pp.84-90) and so might not be suitable for use in studying manganese-antimony or manganese-bismuth systems or others having thermal changes at about 300° C.

Improvement in temperature control, if needed, could be had by adding voltage amplification in an additional stage or by using a heat regulating load circuit. The phase shifting thyratron circuit of Benedict (10) is an example of a circuit where proportional heat control, rather than a simple on-off heater, is used.

Measurements of the thermoelectric junctions could be improved by forming lower resistance thermal elements. The process of powder metallurgy suggests that moderate temperature, below the decomposition temperature of the alloy, together with exerted pressure may form units of a moderate resistance. More refined methods of measurement at moderate resistances might yield more stable readings than obtained with the present instrument and may show trends not apparent with the method employed.

An oil with extremely low vapor pressure and

and low viscosity, such as the phthalate ester oils
used in diffusion pumps, should make an ideal dilatometer
fluid, but the cements and greases tried would not hold
the n-dibutyl phthalate. A better cement and oil
combination might be obtained, since the mineral oil is
rather viscous and does not drain as rapidly as might be
desired in the dilatometer. A dilatometer constructed
with precision bore tubing would also reduce the
corrections due to irregularities of the capillary. The
general character of the dilatometer is good, but no
containing oil has been found that would allow the use
of a dilatometer of this type with the manganese-
antimony or manganese-bismuth systems. The silicone
oils, especially General Electric 9981LTNV-70ot, offers
hope of providing a containing liquid with a satis-
factorily low vapor pressure to be used in the study of
alloys from 250 to 375° C.

The thermogalvanic effect does not offer too
much hope of giving reproducible or reversible potentials
unless a scheme is evolved for measurement of the mangan-
ese electrode which would be applicable to these measure-
ments.

EXPERIMENTAL RESULTS

Introduction: The usual procedure for the runs
to follow was to make all determinations with a given
alloy simultaneously. The cases where that has not been
the case are given.

The rate of temperature rise was regulated by
the rate of change of the reaction. That is, the
temperature was not raised or lowered until equilibrium
values for the determinations at the temperature were
reached. Readings were usually taken every 15-20
minutes, and three to four sets of readings identical
to within experimental error were required for equilib-
rium conditions. In some cases, equilibrium was
reached in an hour, in one case as long as four days was
required. In general, equilibrium was reached much
faster at a temperature removed from the magnetic trans-
formation region.Also, equilibrium of the manganese
phosphides was much faster than for the arsenides.

The fast runs were conducted by applying
a heating (or cooling) source sufficient to pass
through the range of temperatures desired in a period
of about four hours. Readings were then taken about
every ten minutes, with readings at five minute intervals
in the magnetic transformation region.

Preparation of the samples for the particular
measurements are described previously under the heading
of the measurement made.

Continuous readings were taken during about
18 hours each day; in general readings were not taken
for a six-hour period each night.

Manganese-Phosphorus Alloys: Results of the
analyses of the alloys used are given in Table 5 (page 39).

The results obtained with the alloy richest
in manganese, of composition Mn:P= 1:0.89, are given
by figure 3.

The slow run for this alloy was conducted
during a period of 124 hours, the fast run required
7 1/2 hours for completion.

The magnitude of the permeability differences
is considerably reduced because of the fact that insuf-
ficient alloy was available for the determination; the
sample tube was only one-third filled.

The permeability curve for both fast and
slow heating and cooling cycles seems to follow the
same curve indicating the absence of temperature hys-
teresis. At about 16.8° C. the susceptibility begins
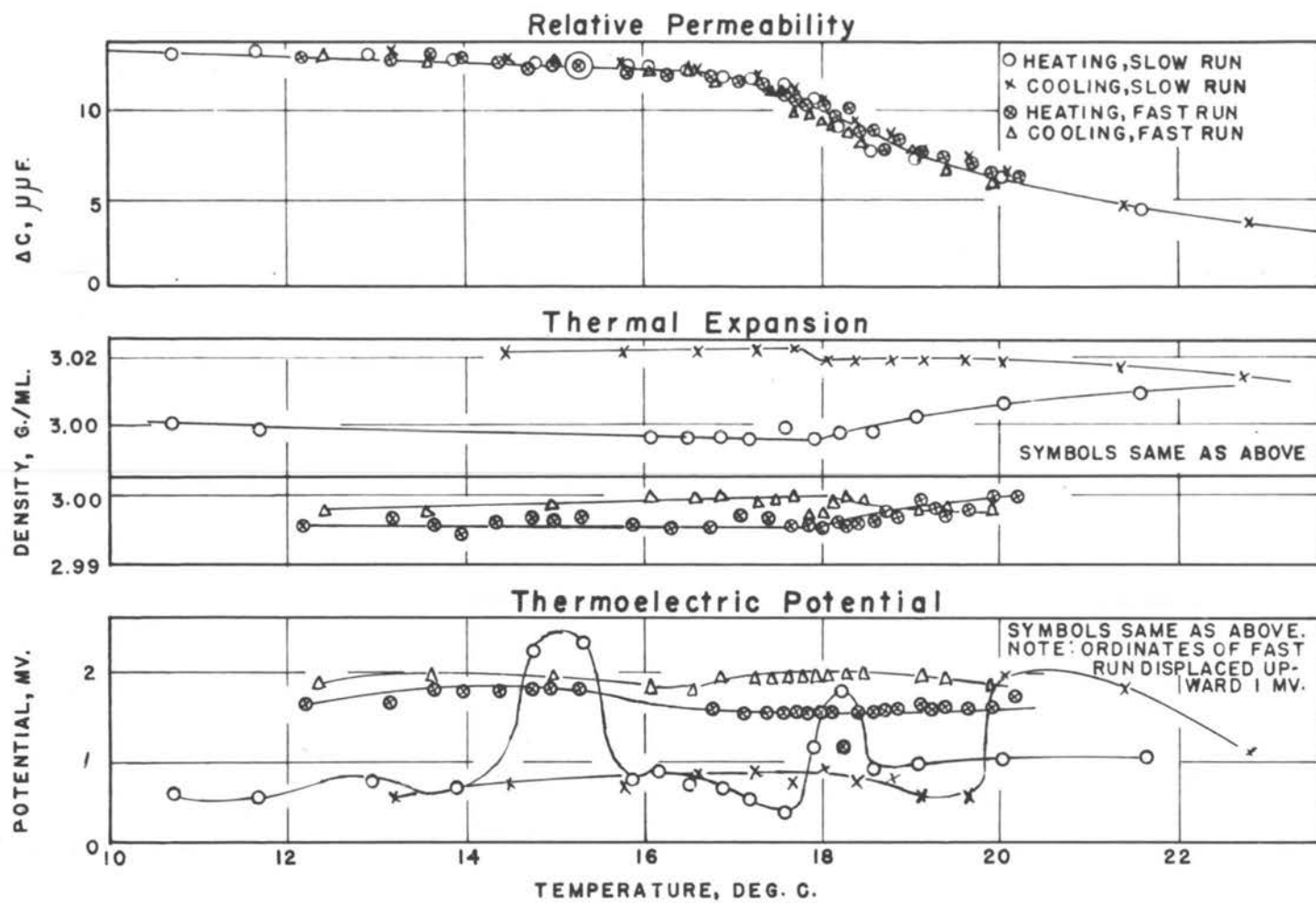to decrease, and the point of inflection, which would

FIG. 3   Transition Results for Alloy Mn P$_{0.9}$

be the point of greatest change of magnetic properties is seen at 18.1° C.

Thermal expansion, as given by the dilatometer results, shows, with slow heating a very definite point of inflection at 17.9° C. On cooling the same sample, the density of the sample was seen to break, discontinuously or nearly so, increasing by about 0.003 g./ml. at 17.9° C. The temperatures of the magnetic transformation were the same, as nearly as could be detected, for both the heating and cooling cycle. When the samples were heated and cooled more rapidly in the 7 1/2 hour heating and cooling cycle immediately following the slower experiment, the results obtained were quite similar to those of the slower determination. The density remained sensibly constant, upon heating, until a temperature of 18.0° C. was reached and then the density started to increase. Upon cooling, the reverse process was noted. The density increased up to a temperature of 18.0° C. at which it remained nearly constant, though decreasing slightly.

Two particular factors in the faster run should be noted. One is that the density curves cross above the transition point. Since about two hours and forty-five minutes elapsed between the heating cycle and

the cooling cycle, the effect may well be one of non-equilibrium in the alloys. The scattering of the points may also be due to this same effect. The second point of note is that the magnitudes of the changes at the transitions are somewhat diminished from that of the slower determinations.

The thermal expansion slow runs show that the density increases on heating and also increases on cooling. This anomalous result may possibly be explained by the fact that the readings at the transition temperature were slower and the longer time resulted in a larger loss due to evaporation. This tends to override the volume change. That is, a small volume change in the opposite direction from the cooling cycle increase in density may have impressed upon it an evaporation loss effect which overcomes the density decrease and shows an apparent volume increase. This could also account for the density values not being the same at the start and end of the run.

The thermoelectric potential produced by the alloys is indeed an unusual curve. Slow heating of the alloy produced a large increase in the neighborhood of 15° C., with a smaller bump at about 18.2° C. The increase at 18.2° C. also resulted in a change in the

base value of the potential; that is, the potential
before and after the 18° increase changes by about
0.5 millivolts. This was not the case for the peak at
15° C. Upon cooling the sample slowly, a peak at
about 20.5° C. followed by a sharp dip at 19.8° C. was
the most prominent factor observed. A very flat rise
reaching its maximum at 18.0° is observable. The
readings in the neighborhood of 18° C. are quite steady
and do not fluctuate as much at a given temperature as
do some to be mentioned later. The results of the fast
heating and cooling runs do not seem to show any
significant trends, though the fast heating run has one
point at 18.2° C. which dipped sharply. The authenticity
of a dip at this point is not known, though, since the
points immediately preceeding and following the point
at 18.27° C, and separated from them by only five
minutes did not show any deflection. All values of the
thermoelectric potential and the increases are in the
positive direction.

Thermogalvanic potential measurements were
not made with this alloy.

In figure 4 are shown the results obtained
with an alloy with a composition nearly that corresponding
to MnP.

Relative Permeability

○ HEATING, SLOW RUN
✕ COOLING, SLOW RUN
⊗ HEATING, FAST RUN
△ COOLING, FAST RUN

ΔC, μμF.

Thermal Expansion

DENSITY, G./ML.

SYMBOLS SAME AS ABOVE

Thermoelectric Potential

POT. MV.

SYMBOLS SAME AS ABOVE

Thermogalvanic Potential

POT. MV.

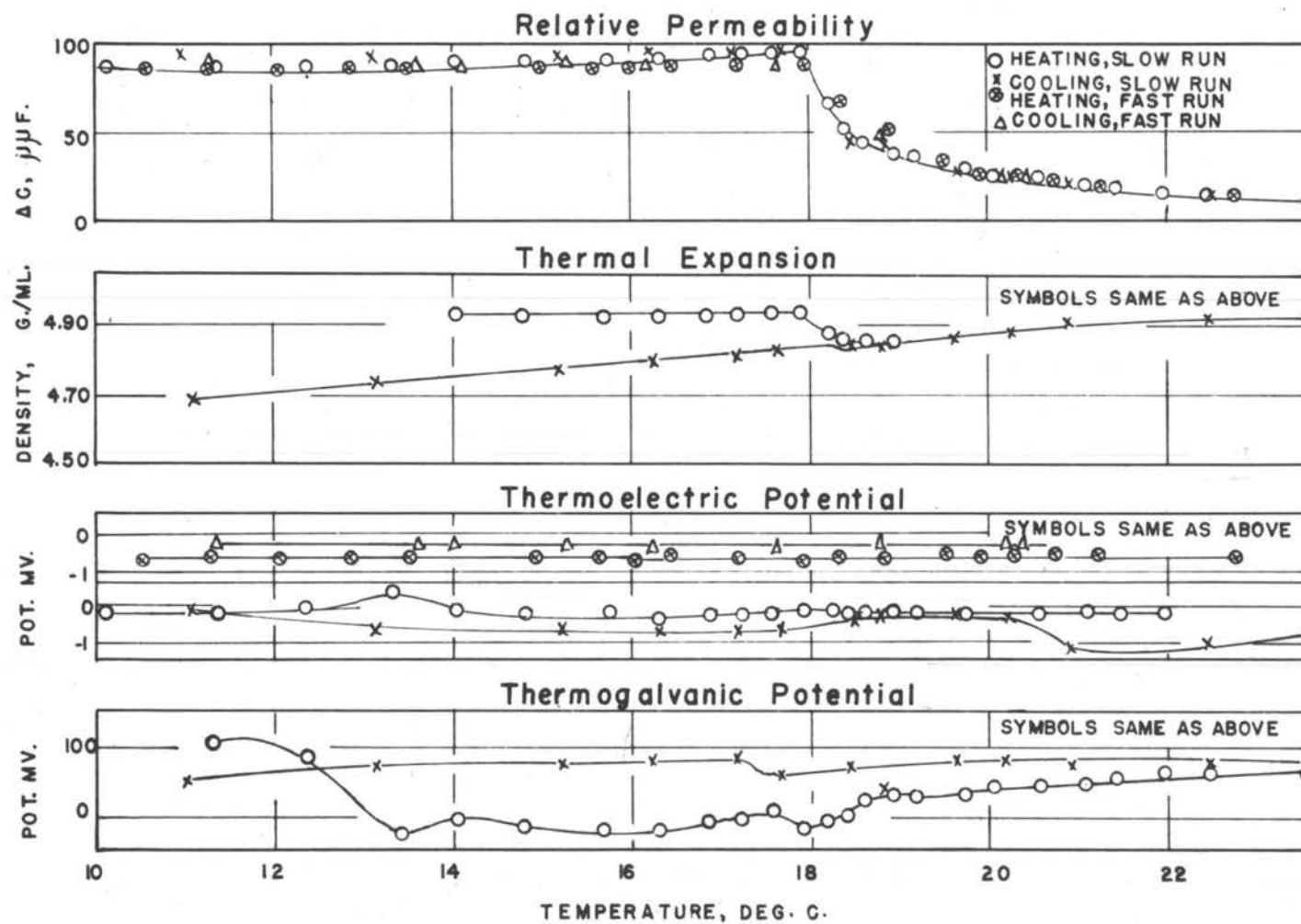SYMBOLS SAME AS ABOVE

TEMPERATURE, DEG. C.

FIG. 4   Transition Results for Alloy Mn P$_{1.0}$

The permeability determination again showed
the results of a slow run (295½ hours) and a fast run
(in which the sample was heated from 10° C. to 22° C.
in four hours and cooled in five hours) followed each
other very closely. The only particular trend difference
noted was that the cooling cycle values below the trans-
ition temperature are in general somewhat greater than
for the heating cycle, but this may well be due to
packing of the powdered sample.

As can be noted from the graph, the values
of the relative permeability started to change sharply
at a temperature of 17.9° C. The results from a temper-
ature of 17.6 to 18.7° C. were very sensitive to temper-
ature differences and fluctuated quite markedly. At a
temperature of 17.59° and 17.91° C., the behavior
noted was for the change in capacitance to dip and rise,
as the example shown in the table.

Table 8

Fluctuations of $\triangle C$ as a Function of Time

Date 3-14-50   Temp. 17.59° C.

Time	$\triangle C$, $\mu\mu$f.
5:20 P.M.	93.36
5:40	92.82
5:55	91.80
8:20	94.80
8:40	94.80

as a temperature of 18° was reached, the readings became even more sensitive to temperature change and a change of temperature of as little as 0.01° C. could reverse the drift in values of the change of capacitance. That is, if the value of ΔC is decreasing, an increase of temperature of 0.01° could increase the value of ΔC.

The value of the density changed quite significantly at the temperature of 17.9° C. too. In the range 17.91° to 18.43° C, the density decreased from 4.922 to 4.859, at which value it remained about constant. Upon cooling the same sample, the density value very slightly increased. The actual values of the density decreased from 4.857 at 18.90° to 4.828 at 17.67° C., but the extrapolation of the smooth lines above and below 18° C. indicated a slight increase in density in going from above 18° to below 18° C. The break was not nearly as pronounced as with the heating cycle. No fast determination of the volume expansion was made.

Slow determination of the thermoelectric potential revealed a slight rise of the value at 18° C. with a corresponding dip in the value on the cooling curve. A bump at 15.4° C. on the heating curve and 20.4° on the cooling curve is also shown. No trend or change of any type was shown with the same samples with a faster heating

and cooling cycle. It should be noted that most of the values of the thermoelectric potential are negative, whereas the preceeding run had positive values of potential. The break in potential noted was in the positive direction, however, as was the result of figure 3.

The result with a sample richer in phosphorus content, having a ratio of 1.3 phosphorus atoms per manganese atom is next shown in figure 5. This was the first sample determined by the dilatometric method. The permeability determinations and thermoelectric potential were measured in a separate experiment. The slow run of permeability and thermoelectric potential were made concurrently with the sample of figure 6, and required 198 hours. The fast runs were made in nine hours. The slow determination of thermal expansion and thermogalvanic potential required 36 hours.

The relative permeability result was not as sharp as that for the alloy MnP, though the result of slow and fast determinations of permeability falls on the same line. The magnitude of the magnetic effect is not as great as with the alloy MnP; the difference in magnitude between the sample of figure 4 and of figure 5
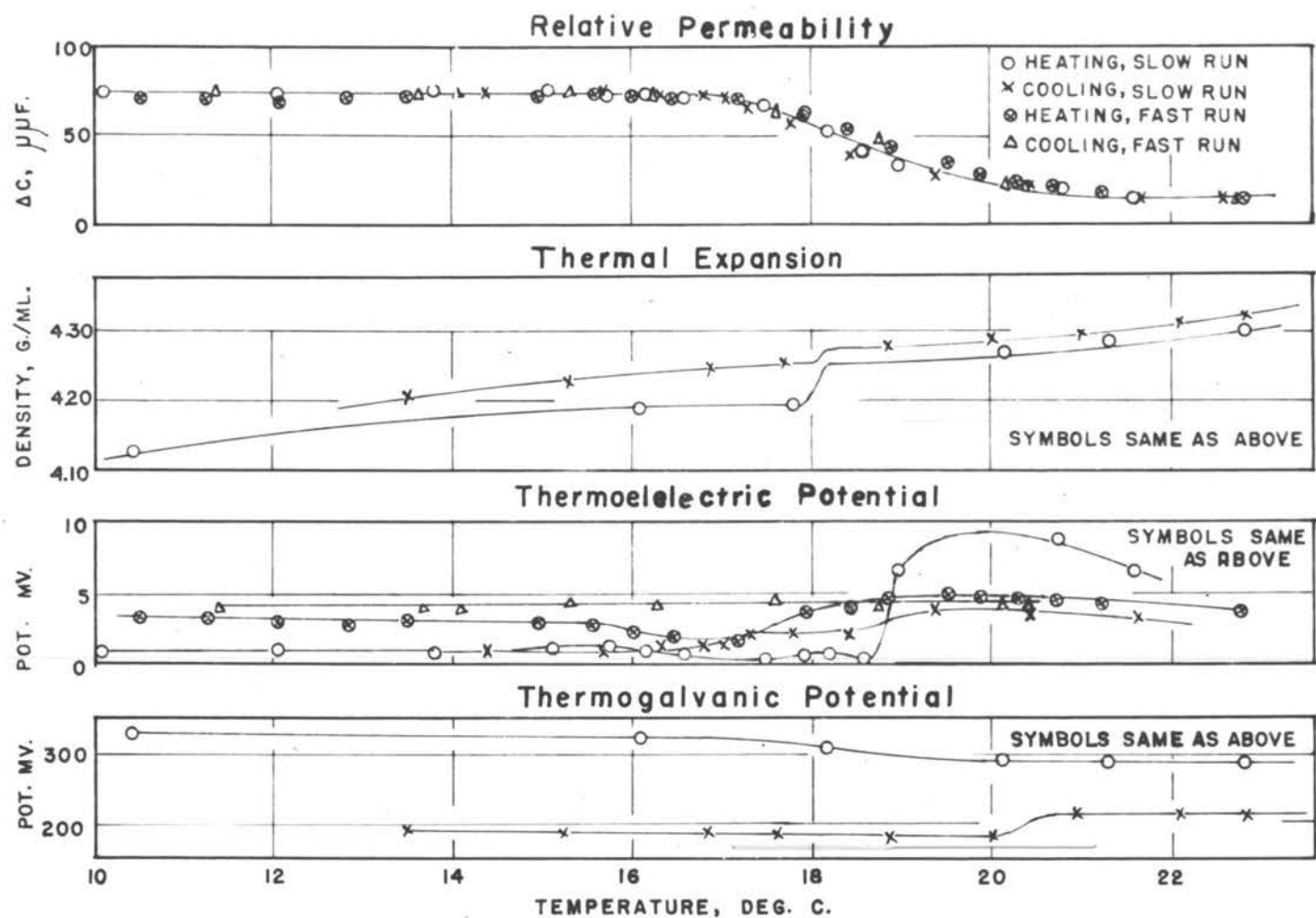
FIG. 5   Transition Results for Alloy MnP$_{1.3}$

is too great to be due simply to differences in packing
of the sample. The maximum change of slope of the perm-
eability curve lies at 18.3° C, though the decrease of
magnetic effect is first noted about 16.8° C.

The thermal expansion determination was made
as the first determination on a manganese phosphide
alloy and hence is not as well mapped as some succeeding
ones. However, definite breaks in the density at 18° C.
are noted. Extrapolation of points above and below the
transformation point would indicate that the heating
cycle change in density is from 4.20 to 4.27 g./ml. and
from 4.28 to 4.25 g./ml. on the cooling cycle. The
determination was made fairly rapidly (36 hours); no
faster determination was made.

The thermoelectric potential determinations
indicates a small bump in the positive direction at
18.1° C. followed by a much larger rise beginning at
19°. Upon cooling the sample, the trend is quite
indefinite at 18°, though a fairly sharp change of
inflection occurs at 17.2° C. The cooling run of the
fast determination shows no breaks at all, though the
fast heating cycle dips and rises to a maximum with a
point of inflection at 17.6° C. Of more significance

than the slight rise in the slow heating curve is the
fact that at a temperature in the region of 18° C. the
values would be rather sporadic and unsteady as compared
with readings at other temperatures. In general, however,
the thermoelectric potential would rise to a more positive
value and then decrease, the temporary rise amounting to
about three millivolts at 17.9° C.

A rather large thermogalvanic potential was
noted, though the asymmetry potential is quite large
for this alloy cell. The heating curve shows a point
of inflection at about 18.2° C., with a break in the
opposite direction occuring in the cooling cycle at
about 20.4° C. The opposite directions of the galvanic
potential breaks indicate the extreme irreversibility
of the reaction.

The sample richest in phosphorus, with 1.4
phosphorus atoms per manganese, is next shown.

The result of this experiment is shown in
figure 6. The slow run occupied 198 hours, while the
fast run was conducted in 9 hours.

As with the previous experiments, the
permeability determinations for both the fast and slow
runs followed the same curve. The magnitude of the

Relative Permeability

O HEATING, SLOW RUN
X COOLING, SLOW RUN
⊗ HEATING, FAST RUN
△ COOLING, FAST RUN

Thermoelectric Potential

SYMBOLS: SAME AS ABOVE

Thermogalvanic Potential
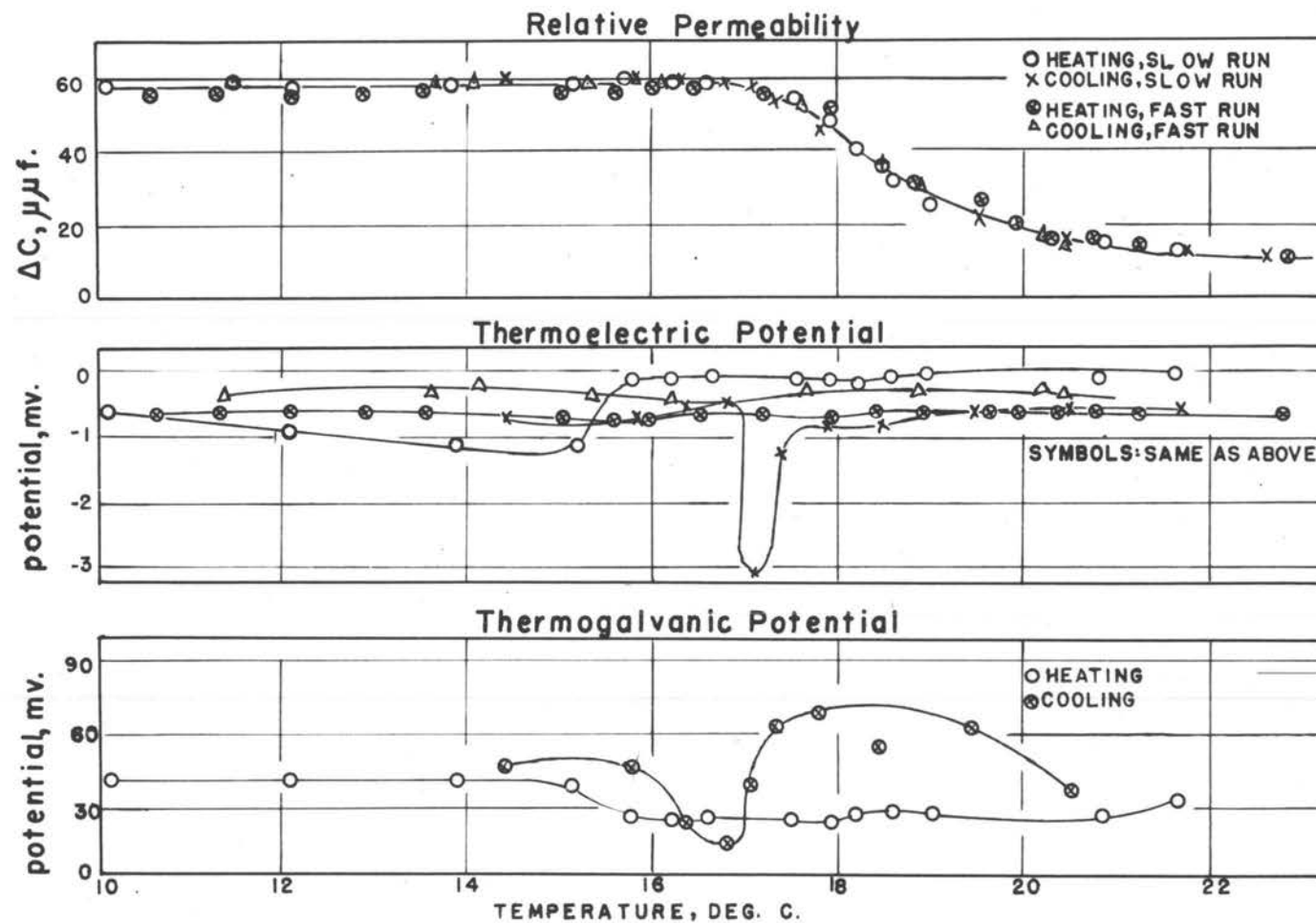
O HEATING
⊗ COOLING

TEMPERATURE, DEG. C.

FIG. 6   Transition Results for Alloy MnP$_{1.4}$

permeability capacitance difference is less than with either the alloy shown in figures 4 or 5. The permeability starts to decrease at a temperature of 16.8° C. and the point of inflection of the curve appears at 18.2° C.

Several attempts were made to run the thermal expansion of this alloy, but all efforts were unsuccessful. The alloy would decompose with the evolution of gas, apparently phosphine, at room temperature, and hence the bubble formation in the dilatometer would allow no reasonable values for the density of the samples. The unstable nature of the alloy would have no apparent effect on other measurements.

The results shown by the thermoelectric potential determinations is that when the alloy junction is slowly heated a sharp rise towards a more positive value occurs at about 15.2° C. and, after being sensibly constant until 18.2° C., started to rise slightly. The same junction, upon being slowly cooled dipped slightly at about 18.6° and sharply to a distinct minimum at 17.2° C.

More rapid heating of the thermal junctions

indicated only an instability in the region 15° to 19° C.; no trends were apparent. Fast cooling shows a slight dip, perhaps not significant, at about 17° C.

Thermogalvanic action of the cell used shows a maximum at about 18° with the cooling cycle, dipping to a minimum at 16.8° C. The heating curve shows a faint minimum at about 16.4° and an indistinct maximum at about 18.6° C.

It should be pointed out that the thermogalvanic cell readings obtained with all samples drifted considerably. Readings were almost never constant to a millivolt, but varied quite continuously in a scattered manner.

The results of the manganese phosphide runs can be summarized in the following statements:

i. The magnetic transformation occurs at $18.1 \pm 0.2^\circ$ C. and occurs without temperature hysteresis. Results for fast and slow heatings coincide.

ii. The permeability break is both sharper and of greater magnitude with the alloy having composition approaching MnP. The permeability magnitude decreases as the ratio of composition goes from 1:1.

iii. The volume of the sample, as evidenced by the
density, changes definitely at a temperature
the same as that for the magnetic transfor-
mation. All of the density changes were not
in the same direction, however.

iv. The thermoelectric action with slow runs
generally shows an instability at the magnetic
transformation though peaks on the curve are
generally quenched. Fast determinations of
the thermoelectric potential generally show
no trend.

v. The thermogalvanic action of the alloy goes
through rather indefinite changes which are
difficult to correlate.

Manganese-Arsenic Alloys: Analyses for all
manganese-arsenic alloys used are given in table 6,
(page 39).

The results for the manganese-arsenic alloy
richest in manganese are shown in figure 7.

The heating and cooling cycle for this sub-
stance occupied a period of 380 hours; one of the most
noticeable items with the arsenic alloys is the slowness
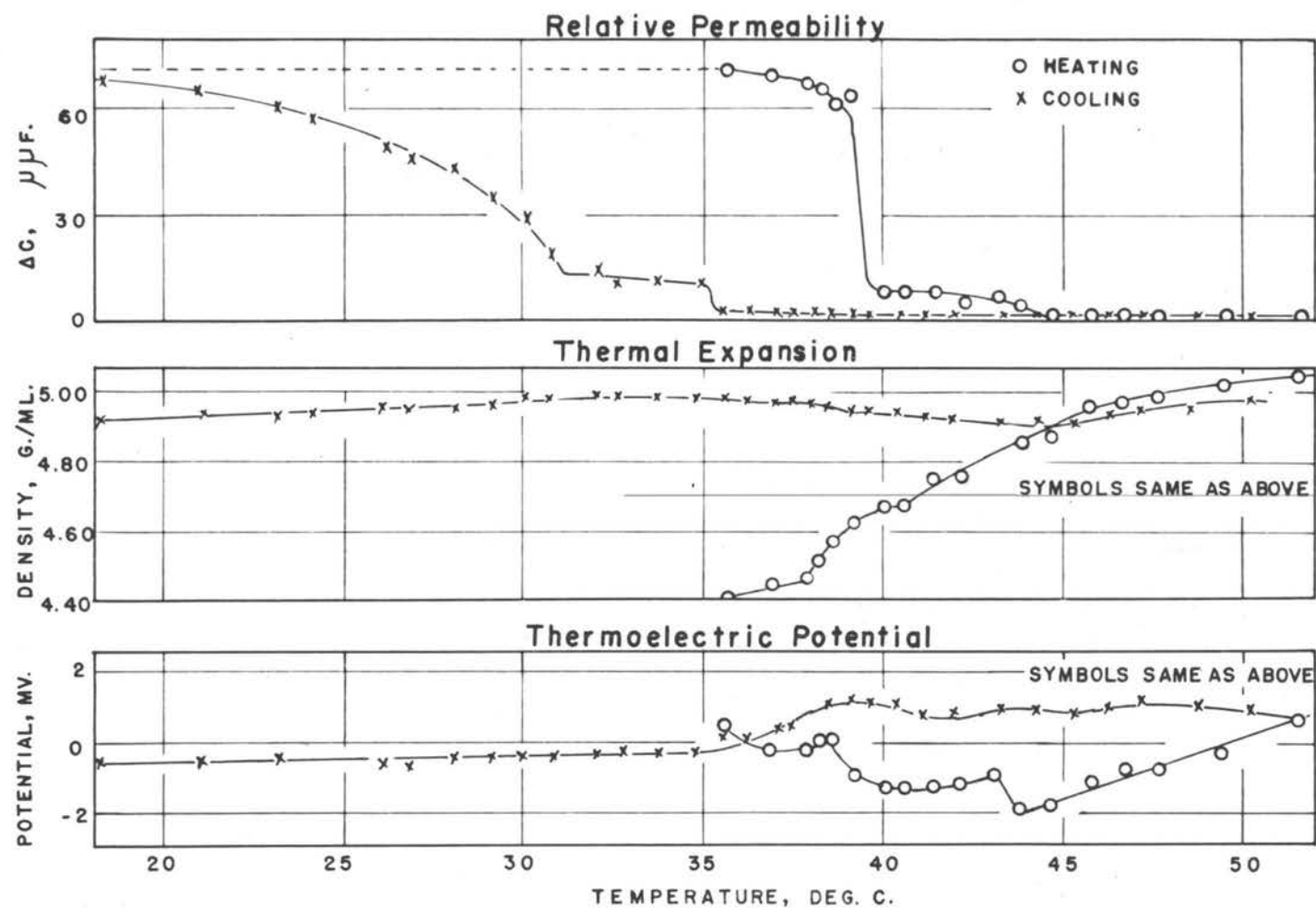with which transitions occur. No fast runs were made

FIG. 7   Transition Results for Alloy MnAs$_{0.9}$

with the arsenic alloys, with the exception of the
volume determination cited in figure 9.

The permeability determination shows a
capacitance difference of the same order as that for
the phosphides. A more interesting feature, perhaps,
is the existence of two separate breaks in the curve.
At a temperature of 39.2°, the permeability dropped
sharply. From 43° to 45° C. the capacitance difference
again dropped, though not as sharply as the previous
jump and of much less magnitude. The point of
inflection was 44.5° C. The cooling cycle indicated
that the small break in permeability occurred on
cooling at 35.5° C., and was slightly larger than the
break downward on the heating cycle. The temperature
hysteresis of about 9° C. was then evident with the
small break. At a temperature of 31.2° C., the
capacitance difference started to increase gradually
and at 18° C., had about reached the value shown by
the sample initially. The hysteresis from the sharp
transition on heating to the beginning of the more
gradual transition on cooling was 8° C.

The graph showing the results of the thermal
expansion of the alloy indicates two changes of in-
flection upon heating the sample. The first occurred

at 38° and the second sharp change of slope occurred at 40.6° C. When the sample was cooled, the breaks in the thermal expansion curve become much less pronounced. The first break in the cooling curve appears at 39° and the second at 36.3° C. These values would indicate hysteresis of 1.7° and 1.6° C. respectively, for the two transitions. It is to be noted that the transitions do not appear at the same temperatures, either with the heating or cooling cycle, as the permeability changes.

Also of note is the fact that the density value of the sample after heating does not return to the value found before the transition, but remains sensibly constant as the temperature is decreased.

When the sample was heated, the thermo-electric power showed two sharp changes in curvature, corresponding quite closely with the changes of the permeability function curve. The first break occurred at 38.6° (permeability 38°) and the second at 43.1° (permeability 43.8°). Upon cooling the thermoelectric sample, the curve obtained is not as well defined as was the heating cycle curve. The curve has several waves from about 45° to 35°, but the main points of

inflection seem to be at 42° and 37°. These results would indicate a temperature hysteresis much smaller than that appearing in the permeability determinations. The hysteresis results would be, respectively, 1.1° and 1.6° C.

In figure 8 are shown the results obtained with an alloy of composition approximately MnAs.

The heating and cooling cycle for this determination took a total of 29 days; the total time elapsed was 694 hours. This illustrates the extremely slow action observed with some of the alloys studied.

The permeability values started to drop at 42° and reached a point of inflection at 47.4°C. Upon cooling the sample, capacity difference increased slightly at 37.3 ° and started to climb up to the starting value at about 31°. At zero degrees the permeability had not reached the original value, and by extrapolation of the converging curves would not reach the starting value until about -25°C.

The thermal expansion results as shown in the graph of figure 8 show one of the sharpest and bestdefined breaks obtained in this investigation. The volume level in the dilatometer changed continuously over a period of 114 1/2 hours. Some of the

values of the oil level in the dilatometer are given in
Table 9, to illustrate this slow transition. The density
increased from 4.354 at 37.98^o to 4.411 at 38.52^o. The
permeability results remained very constant during the
volume transition. Further heating of the sample
reveals very small apparent breaks in the curves at
about 43° and 47°. These small inflections agree pretty
well with the beginning and end of the permeability
decrease.

Upon cooling the sample, no sharp break is
shown, though changes of inflection are shown at 43°
and 47°, in agreement with small changes during the
heating cycle. A third point of inflection occurs
at the same temperature (38.5^o C.) as the large change
on heating. The final and initial densities agree
quite well, indicating a complete volume expansion
and contraction process.

The thermoelectric potential of the junction
on the cooling curve rose to maximum at 40.6^o and
43.8^o C. Maxima for the heating curve occur at 41.0^o
and 44.7^o C. The curve is rather irregular, though the
readings at a particular temperature do not fluctuate
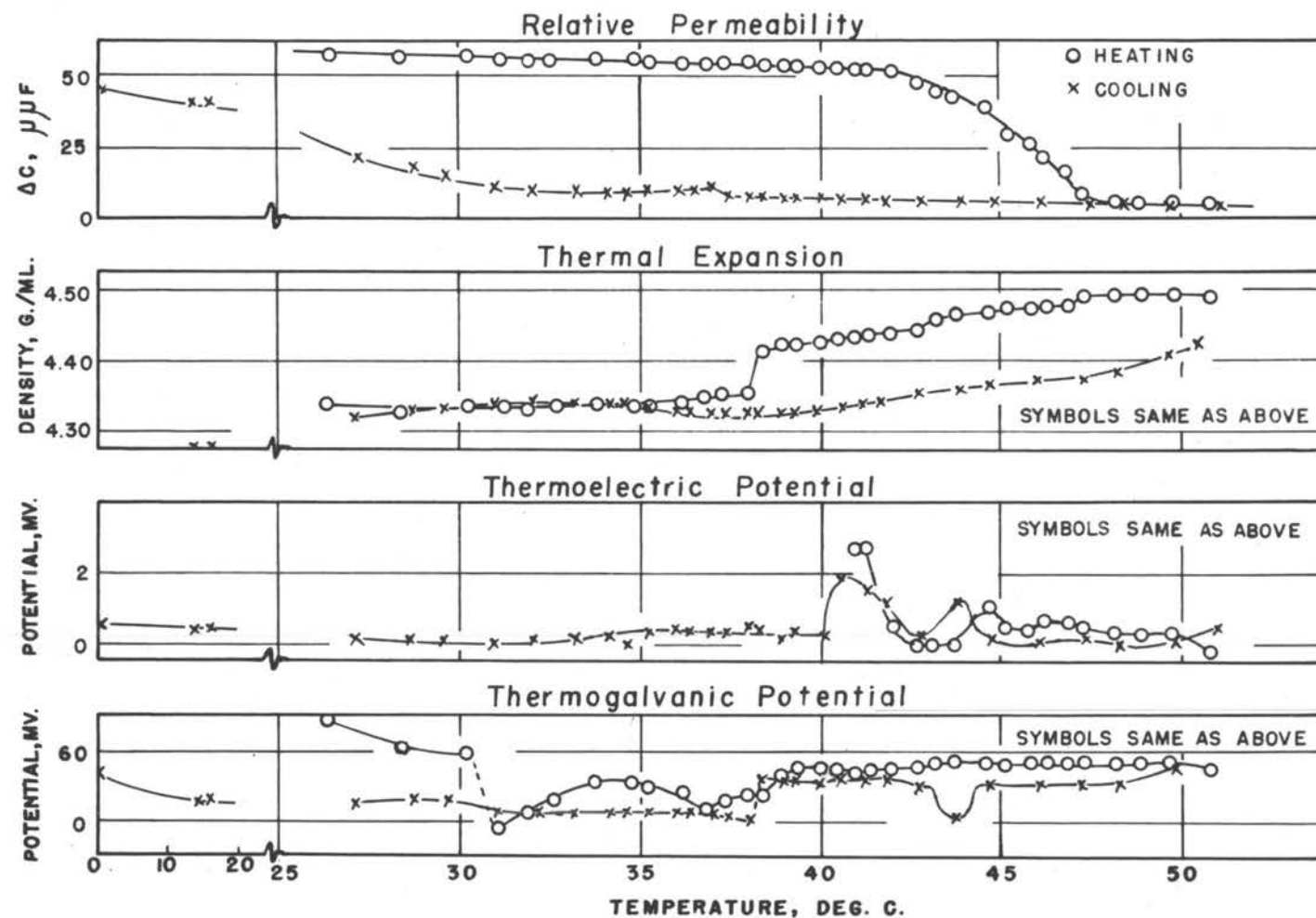very much. Unstable fluctuations finally settling down

FIG. 8.　　　　　Transition Results for Alloy MnAs₁.₀

Table 9

Slow Transition of Volume for MnAs

Date	Time	Temperature, $^\circ$C.	Oil Level Cm.
2-8	2:50 P.M.	38.37	41.72
	7:30 P.M.	38.52	41.50
	8:50 P.M.	38.52	41.46
	10.35 P.M.	38.52	41.19
2-9	6:50 A.M.	38.54	40.44
	7:55 A.M.	38.52	40.40
	8:35 A.M.	38.52	40.20
	10:25 P.M.	38.52	39.31
2-10	7:30 A.M.	38.52	38.52
	12:00 Noon	38.54	38.82
2-11	11:55 P.M.	38.52	38.18
2-12	12:50 P.M.	38.54	37.97
	4:10 P.M.	38.52	37.70
	7:10 P.M.	38.52	37.51
2-13	6:55 A.M.	38.52	37.05
	8:20 A.M.	38.52	37.06
	9:35 A.M.	38.52	37.05

to a mean value (such as was noted with some manganese phosphide samples) were observed at 47° C., the temperature of the point of inflection of the magnetic effect.

The thermogalvanic potential shows a break in potential at about 31° and a point of inflection at 37° C. There is no deflection at the magnetic transformation point at 47° C. on the heating cycle. The cooling cycle reveals a dip at 43.5°, corresponding with the thermoelectric potential peak on the cooling curve. The cooling curve also shows a break at 38° which corresponds quite nicely with the sharp increase of the heating curve for the thermal expansion of the alloy. It must be mentioned though, that the breaks in the galvanic potential curves are so irregular that correlation with other effects is rather unsure.

The curve for the alloy richest in arsenic is shown in Figure 9.

The first run of the thermal expansion was quite rapid, 32 hours being required for the determination. The slower run of thermal expansion required 110 1/2 hours. The permeability determination and thermoelectric potential were separately determined in a run lasting 380 hours. The thermogalvanic potential
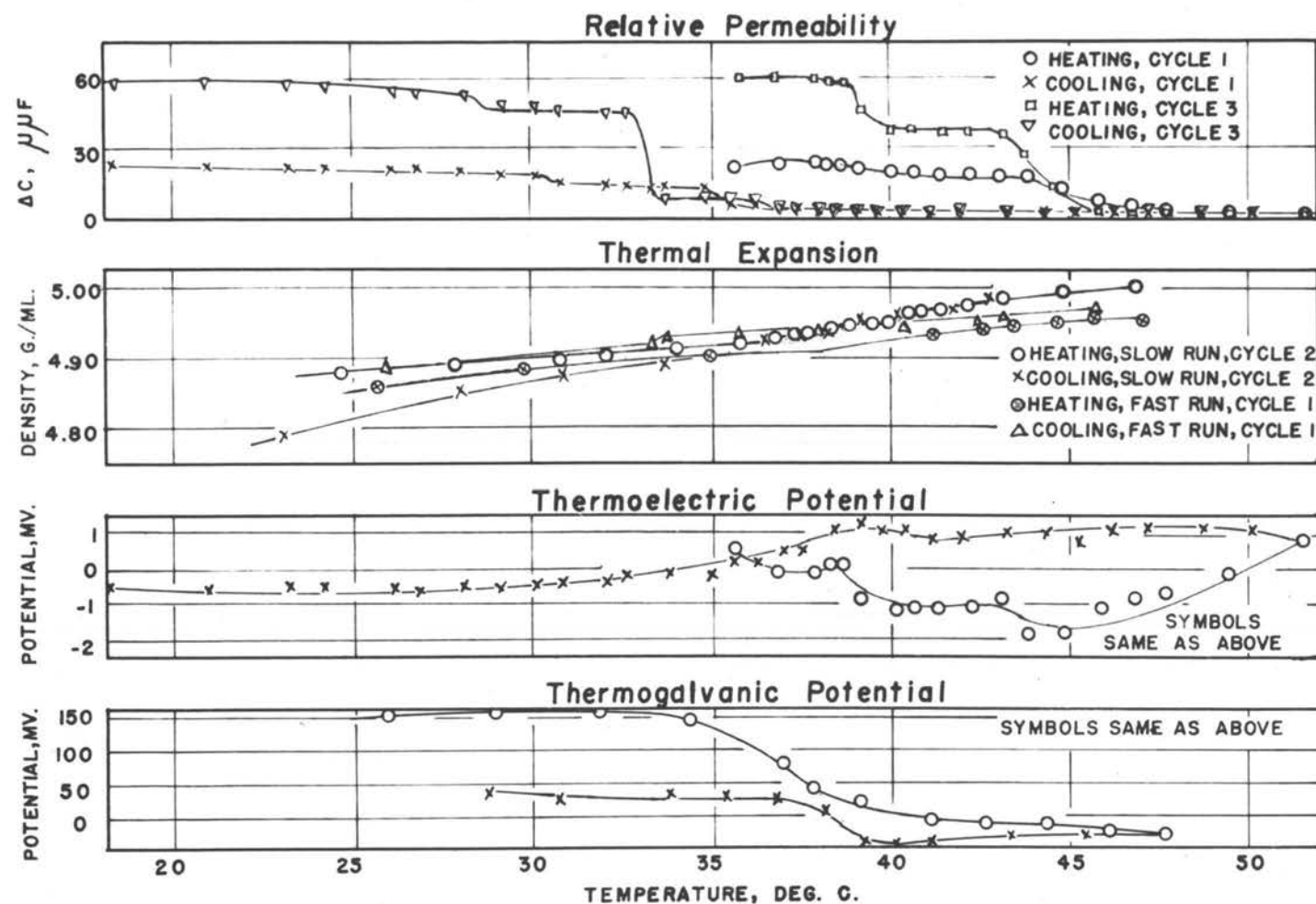
FIG. 9   Transition Results for Alloy MnAs$_{1.34}$

was separately determined in an experiment lasting
98 1/2 hours.

Permeability determinations are shown for
two samples, run at the same time. One is a virgin
sample, which has passed through the magnetic trans-
formation temperature only during the preparation
of the sample. The heating and cooling of this
sample is designated as cycle 1. Only a small portion
of this sample was available, so that the sample tube
was but one-third filled. The other sample designated
cycle 3, has been heated and cooled, passing through
the Curie point region twice previously.

The heating cycle of the virgin sample reveals
downward deflections of the capacity difference at
39.2° and 44.7°. The third cycle heating curve shows
breaks in the permeability occuring at precisely the
same temperatures. Upon cooling the samples, the
virgin alloy broke upward slightly at 35.3° and an
additional upward break was noted at 30.7° C. The
cooling cycle for the cycle three alloy did not increase
at exactly the same temperature as the cycle one alloy
though. The more prominent upward sweep of permeability
occurs at 33° with a smaller break at 28° C.

For cycle one, the temperature hysteresis for the two magnetic breaks amounts to 9.4° and 8.5° C. With the cycle three sample, the hysteresis was about 12° and 11° C. for the magnetic transformations.

The thermal expansion results as shown by the graph indicate that the change of slope reaches a maximum at about 38° C. for the heating cycle of the fast run, and 33° C. for the cooling cycle.

The slower determination of the thermal expansion indicates two points of inflection. A break is observed at 37.7° followed by a small jump at 40.2° C. Upon cooling the same sample, 38.0° C. and 35.4° C. appear to be the temperatures for the transformations. Hysteresis values of 2.2° and 2.3° C. are thus indicated for the alloy when the cooling was slowly carried out.

The thermoelectric potential for the heating cycle shows definite points of inflection at 38.7° and 43.2° C. The cooling curve for the same sample shows inflections at 41.2° and 37.2° C. Hysteresis of 2.0° and 1.5° C. is thus indicated.

The thermogalvanic action shows dips in the heating curve, the maximum change of slope occurring at 38°, with a corresponding rise showing at 38.5° C.

The thermogalvanic potentials given by this experiment
form the clearest curve given by this effect.

The results of the experiments with manganese-
arsenic alloys can be summarized in the following manner:

i.   The magnetic transformation is not simple but
     occurs with two breaks in all except the MnAs
     sample. The heating cycle of a virgin alloy
     sample and a sample passed through the
     magnetic transformation twice agrees very well;
     the cooling cycle of the sample passing
     through the magnetic transformation for the
     third time was at a slightly lower temperature
     than the sample heated through the Curie
     region for the first time. Temperature
     hysteresis was observed for all samples, the
     thermal lag varying from 8.5° C. up to more
     than 20° C.

ii. The magnitude of the capacitance difference was
     nearly constant with the three samples.

iii. The volume of the samples, as evidenced by
     the density changes exhibits fluctuations
     similar to those of the phosphides with the
     exception that the density changes of inflec-
     tion or breaks occur only approximately at

the magnetic transformation temperature; the
temperature difference between the magnetic
and density transition may be as great as
several degrees.

iv. Thermoelectric potential changes quite
sharply at transition temperatures closely
approximating the magnetic transformation
temperature. In general, the thermoelectric
instability observed with the phosphides
was not to be noted with the arsenides.

v. Thermogalvanic potentials exhibit changes in
the region of the transformation points,
though difficult to interpret because of
their extreme irreversibility.

DISCUSSION

Compound Formation: The results of the
permeability changes for the manganese phosphorus alloys
(Figures 3, 4, 5 and 6) show that the changes of permeabil-
ity become much sharper as the manganese-phosphorus ratio
approaches one. The magnitude of the permeability effect
also approaches a maximum at this point. This would seem
to provide evidence that in the range of materials studied
the ferromagnetism was due to the compound of empirical
ratio MnP, and that the behavior noted with the samples of
ratio greater or less than one phosphorus atom per mangan-
ese atom was due to MnP diluted with phosphorus or mangan-
ese, respectively. It is evident that the addition of a
diluent would tend to decrease the noted effect in
measuring the relative permeability.

The view that the behavior observed is due to
the compound of ratio MnP is given support in a discussion
by Nowotny (39, pp. 256-9). He shows that for a given
Curie temperature, a particular value of the Slater
critical ratio (interatomic distance/radius of energy
shell) is indicated. Then since the Curie temperature
remains constant with composition, the critical ratio
essentially must not be disturbed and the excess manganese
or phosphorus over that required for the compound formation
is merely filling holes in the lattice. That is, the
critical ratio remains constant, because it is due to a

particular bounding of electrons between the atoms involved in the compound and all excess materials are effectively inert.

When it is pointed out that the compound formed has an empirical ratio MnP (or MnAs), a lattice compound or macromolecule having one manganese atom per phosphorus atom is presumed present rather than the simple diatomic molecule. It was pointed out earlier (p. 29) that simple combination of trivalent manganese and phosphorus in solution did not produce the magnetic alloys.

The results of the magnetic transformations of the manganese-arsenic alloys (Figures 7, 8, 9) are not as simple as those for the phosphorus alloys. The temperature corresponding to the change of permeability is not as plainly the same for the alloys of different composition; some of the curves have double breaks and very considerable temperature hysteresis is shown by the measurements. In addition the transitions are much slower than those exhibited by the phosphorus alloys.

It is quite possible that the multiple breaks in the curves are due to the formation of more than one compound; that is, that the crystal is a mixture of two compounds.

The changes occuring at about 44° C. are common to all three curves. Since the transition is

most distinct for the alloy of composition Mn As, it
is supposed due to compound formation of that formula.

The compound described by Figure 7 has a
prominent break at 38°, followed by a smaller change in
permeability at 44°. It might be supposed that the
38° change is due to a compound richer in manganese, such
as the Mn_3As_2 described by Arrivaut (2), and by Shoen
(44). Shoen claims Mn_3As_2 is the most ferromagnetic of
the manganese-arsenic alloys.

The curve for the sample containing 1.34
arsenic atoms per manganese atom also has steps at
38° and 44°. If we are to explain the behavior as above,
then we must suppose a compound poorer in manganese and
one richer in manganese than MnAs having a magnetic
transformation point at 38°. However, such behavior is
in disagreement with the results of Nowotny (39, pp. 256-
9). Although he gives the same transformation tempera-
ture for MnP and Mn_2P, the transition temperatures for
other series of compounds of manganese and the group V-A
non-metals differ markedly. Application of the charts
given by Nowotny shows, for example, that the difference
between the Curie temperature of Mn_2N and MnN is about
250° and about a 200° difference in transition temperatures
is shown by Mn_2Sb and MnSb. In general, for the combination
between manganese and a given group V-A element, the

richer the compound is in manganese, the lower the transition temperature.

From the consideration of the data given by Nowotny (loc. cit.) we must suppose that the Curie temperature of Mn_3As_2 would be at least 100° lower than that of MnAs, and the transition temperature for a compound such as Mn_2As_3 would be 100° or more greater than that of MnAs. This would then suggest that the double changes in the curves of Figures 7 and 9 are not real but are due to non-equilibrium values associated with the slow changes of state involved. It should be noted that the permeability changes of the samples shown in Figures 7 and 9 were run simultaneously, and so the second transition shown may be a continuation of the first change, equilibrium not being achieved due to the slow changes involved. The temperature range from the beginning to the end of the transformation shown by Figure 8 agrees quite well with the range from the beginning of the first transition to the end of the second magnetic transformation region for the samples of Figures 7 and 9. This explanation would point out quite clearly the extremely slow transformations shown by the manganese-arsenic alloys, for the determinations of Figures 7 and 9 required 380 hours. The time from the beginning of the first transition to the end of the second transition (35.63^o to 44.73^o)

was 41 hours during the heating cycle, and 144 hours
(34.92° to 18.12°) for the cooling cycle.

By comparison, the determination of Figure 8
required 306 hours to traverse the range from 38.37° to
47.37° with the heating cycle and 191 hours for cooling
from 36.98° to 0°.

Of particular interest is the fact that the
beginning of transitions for the determinations of Figures
7, 8, and 9 are at very nearly the same temperature for
the heating and cooling cycles. It appears then that the
extremely long times allowed for the magnetic transforma-
tions of the arsenic alloys were not sufficient, for the
transitions are extremely slow.

A factor of importance in explaining the differ-
ences of behavior of the phosphorus and arsenic alloys is
the magnetic energy. Fortunately we have some evidence
relating to this viewpoint. Bates (3, pp. 686-9)
determined the specific heat-temperature curve for MnAs
and found a rather large peak in the curve at the magnetic
transformation point. He obtained a value of 1.79
calories per gram for the magnetic energy of transforma-
tion. Whitmore (54) similarly investigated the phosphide
MnP and found a very small peak in the specific heat
curve. Whitmore did not determine the absolute values
of the specific heat and hence no estimate of the energy
of magnetization was made. However, it is quite evident

from his curve that the energy of magnetization for the
phosphide is much smaller than for the arsenide, perhaps
by as much as an order of magnitude. The specific heat
determinations thus indicate a considerable difference
in behavior. Bitter (12, pp. 14-22) develops a relation
between magnetic energy and magnetic hysteresis. Although
the parallel between magnetic hysteresis and temperature
hysteresis has not been developed, it seems evident from
comparison with other ferromagnetic materials that some
parallel in behavior should be noted.

In looking for the reason for the observed
difference between the phosphide and arsenide, the
differences in the atom size, electronegativity and the
crystal structure must be considered.

According to Pauling (41, p. 165) the diff-
erence between the covalent radii of arsenic and phosphorus
is quite small. He gives the values $P = 1.10$ Å. and
$As = 1.21$ Å. If the difference in behavior is due to
the atom size and hence to mobility of the atom in the
crystal for movements for changing of bonding, etc., the
size must be extremely critical. Antimony with a
covalent radius of 1.41 Å should then show a rather con-
siderable temperature hysteresis, and on the other hand
nitrogen with a covalent radius of 0.70 should show
extremely small thermal hysteresis. Unfortunately there

are no data on this point.

In a similar manner, the electronegativity of the elements is very close. Pauling (41, p.64) gives values of 2.1 for the phosphorus and 2.0 for arsenic.

The evidence upon the crystal structure of the phosphides and arsenides of manganese is somewhat confused but does give some promise of explaining some of the behavior noted.

Gottfried and Schlossberger (23, pp. 263-4) report a crystallographic investigation involving the materials MnP and MnAs. The phosphide structure was determined by the X-ray powder patterns, the Laue photograph and the moving crystal photograph. From the results of the determinations, a rhombic pattern was assigned to the phosphide, very similar to the hexagonal NiAs structure but differing from it in that a zig-zag pattern of the elements is to be noted in the general picture.

Fylking reports that the powder photograph results for the MnAs sample were "fairly unsharp", and that MnAs tends toward the NiAs hexagonal type.

A report of the work of Oftedal (22, p. 765) with the substance MnAs, shows a structure of the hexagonal NiAs type. The antimonide is also shown to be of this symmetry. Only powder photographs were used.

The crystal structure data then shows a
significant difference between MnP and MnAs. The
phosphide is clearly of the rhombic symmetry of the
modified NiAs structure having zig-zag chains of mangan-
ese and phosphorus atoms, while the arsenide is either
border-line to this structure or of the hexagonal nickel
arsenide type of symmetry. There may then be sufficient
differences in the structure to account for the differ-
ences in the thermal hysteresis involved in ferromagnetic-
paramagnetic transitions.

The behavior of the nitride alloys would provide
further interesting data. Oshsenfeld (40, pp. 360-76)
investigated some manganese-nitrogen alloys and found a
transformation temperature of about 500° C. and a cubic
crystal structure for the nitrides. His alloys were
quite poor in nitrogen. Since this behavior is so differ-
ent from that of the phosphide, arsenide, etc. interesting
results may be obtained from them. Since the Slater
critical ratio is decreasing in going from bismuth to
phosphorus in group V-A, it may well be that MnN is not
ferromagnetic.

Guillaud (25) determined the powder pattern of
MnAs at temperatures above and below that of the magnetic
transition and confirmed the NiAs structure for the
arsenide as given by Oftendal. It is the observation of

Guillaud that the arsenic-manganese distance becomes
shorter by about 0.02 Å for the transition from ferro-
magnetism to paramagnetism. He claims that the man-
ganese-manganese distance remains constant during the
transition.

The explanation given by Guillaud is that a
change in bonding of the manganese and arsenic atoms
occurs. In going to the paramagnetic state the 3d
shell is more completely filled and the magnetic moment
of the manganese is reduced or eliminated. Since Guill-
aud suggests the formation of more of a covalent bond as
the condition responsible for paramagnetism, then there
should be a corresponding change in the thermoelectric
action as the magnetic effect changes. Guillaud says
that since the manganese interatomic distance remains
constant any change in the Slater critical distance
ratio must be due to a change in the radius of the
energy shell.

Nowotny (39, p. 257) has calculated the Slater
critical ratio for the phosphide and arsenide and gives
the values of 3.03 for MnP and 3.18 for MnAs. Since the
critical ratio must be larger than 3.0 for ferromagnet-
ism, it is evident that only a very small change must be
made in the bonding of the phosphide in order to lose the
ferromagnetism, while the arsenide must be changed by
a larger amount. If this is true, then the temperature

hysteresis and slowness of the transition should be
greatly amplified in the antimonide and bismuthide,
where the ratios are respectively 3.26 and 3.40.

The slowness of the transition may be due to
the difference in diffusion of the metalloid atom
as it is being heated. Since the distance of movement
of the arsenic to change bonding sufficient for the
transition is much greater than for the phosphide, a
longer time must be required. Then too, the covalent
volume of arsenic is about one-third larger than that
of phosphorus.

Volume Effects: The volume of the phosphide
changes at a temperature coincident with the maximum
change in magnetic properties. Some of the changes
seem to be more of a change of slope than of a discon-
tinuous change in volume. The same is to be said of
the arsenic alloy systems, although the temperature of
the change did not occur exactly at the point of inflection
nor was the rate of change the same as that of the mag-
netic transformation.

If the view of Guillaud that the magnetic
transition is due to a lattice change is correct, then
the magnetic transition should occur at the same temp-
erature and at the same rate as that of the volume changes.

The possibility of a phase change at the trans-
ition temperature has not been ruled out. In fact the

crystal pattern data suggests the possibility of change between similar structures.

Slater (47, pp. 291-304) points out that phase changes as ordinarily considered have discontinuous changes of volume and entropy. In order to explain much experimental data, phase changes of the second order are recognized. In these changes, the volume and entropy change fairly rapidly but not discontinuously. The specific heat rises to a maximum (as noted by Bates, loc. cit.) and the changes are spread over several degrees rather than being discontinuous.

Slater mentions the ferromagnetic transition as a particular example of a second order transition. The magnetization falls gradually to zero, the specific heat shows a maximum although does not discontinuously change, and no crystal change is necessary for the transition. Crystal changes have been noted with some alloy systems, however, at the Curie temperature. The phase change requires no latent heat, although energy of the magnetic process may be shown.

The curves of the effects of this study follow quite well the noted ones for second order transitions as given by Mayer and Streeter (34, pp. 1019-21).

In a second order transition, the curve of density versus temperature will change in slope at a particular temperature, although the change may be sharp

enough to appear almost discontinuous. Since the transitions are slow, it is quite possible because of non-equilibrium at a preceding temperature to get the effect of a discontinuous change. Unavoidable small evaporation losses occur as a sample is held for a considerable period of time at a particular temperature. This may also give the effect of a discontinuous break. With this in mind, the change of slope as predicted by a phase transition of the second order would be seen to occur with all of the samples observed. Evaporation losses and non-equilibrium slow transitions may well explain behavior observed in Figures 3 and 7, where the change of the density during the heating and cooling cycles changed in opposite manner from that observed with other samples.

The thermal expansion changes are thus indications of long-range, slow changes in the alloy. It is not required that magnetic and expansion changes occur at the same rate, since they are associated phenomena, rather than being different aspects of a single effect.

The bonding change conception of Guillaud appears correct, if we modify it to consider the change in bonding as long-range effects in macromolecules, considering the bonding change as being a resonant or average result.

The volume change of MnAs was also studied by

Smits, Gerding and Vermast (48). They observed discontinuous changes in volume, with a temperature hysteresis of several degrees. They said their materials were not pure and that the use of more pure samples might reduce or eliminate the thermal lag of volume change.

Guillaud (25) made a dilatometric study of MnAs and noted apparently discontinuous changes of volume at temperatures of 45° on heating and 34° on cooling. Since the details of his experiments are lacking, it is hard to correlate it with experiments of this investigation.

An important difference between the results of this investigation and those of Guillaud and of Smits, Gerding and Vermast is that we have been able to completely or very nearly eliminate the temperature hysteresis of the volume effects. The volume expansion, as well as the other effects, are very slow and considerable time must be given for the transitions.

Néel has developed a theory for the dilation of ferromagnetic substances in the neighborhood of the transition temperature. Based on the action of near neighbors and elastic energy, he was able to calculate curves of the coefficient of dilation as a function of temperature. The general curves show a change of slope just as with the thermal expansion curves of this investigation, although a sharp peak and break in the coefficient

of expansion is also generally shown. Agreement with
experiment for iron and nickel is good, although some
experiments do not show the predicted peak and break
of the volume effect, but merely a change in slope as
observed in this investigation. The work of Néel fits
into the general idea of second order phase changes as
developed for ferromagnetic substances.

Thermoelectric Action: The changes in thermo-
electric action fluctuate in the region of the diffuse
change in magnetic properties. Since the supposed
long-range changes in distances are so slow, the conduc-
tion electrons responsible for thermoelectric action
indicate merely a transition in the substance. Bates (5)
was able to get sharp changes of thermoelectric power,
but he presumably heated his samples much faster than in
this investigation. The thermoelectric experiments of
Bates differed in two respects from those of this investi-
gation. Bates apparently made no effort to attain the
very slow equilibrium, since no mention is made of the
elapsed time of this experiments. Bates specific heat
determinations (3, p. 685), for example, were made in
three to five hours. Secondly, Bates kept his two
thermoelectric junctions one or two degrees different
in temperature, rather than holding one junction at a
constant temperature. Since the transformation region
is diffuse, both thermoelectric junctions will be in the

magnetic transformation region during much of the transition.

Thermogalvanic Action: The thermogalvanic action would give valuable information regarding the energy and entropy of the process if it were more reproducible. Again the instability of the effect is generally noted to follow the magnetic transformations, but no general or quantitative statements can be made for such an irreversible cell.

SUMMARY

Experimental: Ferromagnetic alloys of the systems Mn-P and Mn-As have been prepared by a new method, which has been found to produce a more general series of substances in a purer form and by a safer method.

A description of the construction and operation of apparatus for the obtaining of thermal expansion, thermoelectric power and thermogalvanic potential as related to magnetic properties is given. A new type of electronic magnetometer, employing the properties of a tuned inductance, is described.

Results were obtained of the above phenomena for four alloys of manganese and phosphorus, ranging from $MnP_{0.9}$ to $MnP_{1.4}$, and three alloys of the manganese arsenic system, composition of which ranges from $MnAs_{0.9}$ to $MnAs_{1.3}$. Fluctuations of all of the observed properties were shown in the region where the magnetic transformation takes place. The phosphorus alloys transform to a paramagnetic state at a temperature of 18° with little or no temperature hysteresis. The arsenic alloy transformation takes place at about 44° C. and is characterized by exceedingly slow transitions.

The phosphide alloys were at least as ferro-magnetic as the arsenic alloys tested, in contradiction to the early results of Wedekind (51, pp. 624-32).

A sample of a rhenium antimonide was found to be non-ferromagnetic at 0° C.

Discussion of Results: It has been demonstrated that the ferromagnetic substance present in the alloys studied is a compound of empirical formula MnP or MnAs, diluted with excess manganese, phosphorus or arsenic as the case may be.

Qualitatively the magnetic transformation may be explained as follows:

At the temperatures of the transformation region, a diffuse movement of the metalloid-manganese bond takes place, bonding the metalloid into the 3d shell of the manganese more closely so as to reduce or eliminate the magnetic moment due to unshared 3d electrons. Since the magnetic moment due to the shield-ed electrons is lost or the Slater critical ratio is sufficiently disturbed, the substance is no longer ferromagnetic.

The phosphide critical ratio is very near the borderline of paramagnetism and so the rapid, easy transformation of the phosphide is achieved. The arsenide critical ratio is not as near the borderline

of ferromagnetism and so the transition is much slower. Since the movement of the atoms involved must be somewhat diffusional, the slightly larger size of the arsenic atom will contribute to the slowness of transfer.

The long-range changes in lattice dimensions, following Slater's concept of second order phase change (47, pp. 291-304) should take place without change in crystal structure, as was noted by Guillaud (25). There is no latent heat to the phase change but energy of the magnetization may be involved. The results of Bates (3) and Whitmore (54) indicate that a much larger energy of the magnetic transformation is shown by MnAs than MnP. The magnetic energy is predicted by the Weiss theory of ferromagnetism.

The temperature hysteresis noted by previous workers with MnAs (Bates; Guillaud; Smits; Gerding; and Vermast, etc. loc. cit.) has been almost or completely eliminated in this study. The changes occuring in the arsenide are extremely slow, and a false thermal hysteresis can be noted if the determinations are made so rapidly that equilibrium is not reached.

The anomalous action of the thermoelectric potential is presumed due to the changing conditions involving conduction electrons of the material during the transition. The thermogalvanic action is likewise

associated with the changing conditions but is so irregular as to defy interpretation.

Conclusions: The ferromagnetism of the manganese-phosphorus and manganese-arsenic alloys follows quite well the behavior predicted by the Heisenberg molecular field concept of ferromagnetism. The critical size ratios predicted by Slater, et. al. for the positive exchange effect in the Heisenberg theory have been very helpful in explaining the behavior of the alloys. However, the effect is probably a long-range effect. The general behavior of the alloys is explained by the following:

i. The ferromagnetism of the alloys is due to compounds of empirical formula MnP or MnAs diluted with excess metal or metalloid. The change to paramagnetism is caused by the compound bonding into the 3d shell of manganese, thus decreasing or removing the magnetic moment of the manganese.

ii. The transformation is due to a second order phase transition, probably taking place without a change in crystal structure, but involving changes in the lattice dimensions in a diffuse non-discontinuous manner.

iii. The magnetic transitions of the phosphide
is much more rapid than that of the arsenide
because the critical ratio is much nearer the
paramagnetic borderline conditions and so
the bonding must be changed much less for the
transition; the smaller size of the phosphor-
us atom makes diffusion easier.

iv. The thermal expansion undergoes a change of
slope as predicted by the change in lattice
dimensions and in general agrees with the
theoretical dilation curves of Néel.

v. Thermoelectric action and thermogalvanic
potentials reflect a transitory change involv-
ing the conduction electrons. The lack of a
definite change in thermoelelectric potential
rules out the ferromagnetic action as being
due solely to conduction electrons.

vi. The temperature hysteresis observed by
previous workers with MnAs was almost completely
removed by making very slow changes of tempera-
ture; the MnAs transitions are very slow and
magnetic equilibrium must not have been reach-
ed in some earlier studies where heating or
cooling cycles were completed in a few hours.

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