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MAGNETIC PROPERTIES OF HEUSLER ALLOYS

BY

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UNIVERSITY OF ILLINOIS
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MAGNETIC PROPERTIES OF HEUSLER ALLOYS

BY EDWARD B. STEPHENSON, FORMERLY ASSISTANT IN PHYSICS

CONTENTS

I. Introduction.................................................. 3
II. Historical Review.......................................... 3
III. Test Pieces.................................................. 8
IV. Tests.......................................................... 13
V. Thermal Analysis........................................... 16
VI. Discussion of Cooling Curves.............................. 22
VII. Photo-micrography......................................... 23
VIII. Summary.................................................... 26

Appendix.......................................................... 29
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MAGNETIC PROPERTIES OF HEUSLER ALLOYS

I. INTRODUCTION

The Heusler alloys, so named in honor of their discoverer, are composed of copper, manganese and aluminum, and are remarkable for the fact that, in certain proportions, they are ferromagnetic, although the component metals are not ferro-magnetic.

The following investigation of the properties of these alloys is a contribution of data on the ultimate nature of magnetism. If the permeability of a magnetic substance could be increased, and also the hysteresis losses be decreased, it would evidently be of the greatest importance to electro-technics; hence an investigation on the ultimate nature of magnetism has a commercial importance as well as a theoretical value.

The methods of thermal analysis and photo-micrography have been used in an attempt to find relations between the magnetic and the other physical properties of the alloys. These methods have been described in considerable detail, inasmuch as they will probably be of value in the study of the whole subject of alloys, and especially in the study of steels and brasses. Thermal analysis accompanying a chemical analysis gives an insight into the nature of an alloy not possible to the latter alone, and photo-micrography is an excellent method of studying the crystalline structure on which numbers of physical properties so largely depend.

II. HISTORICAL REVIEW

In 1901, Dr. Heusler reported\(^1\) that he had accidentally discovered that certain manganese alloys were magnetic. While turning a certain alloy in a lathe, he had noticed that the turnings adhered to the tool. This discovery led to a general investigation of the magnetic properties of manganese alloys.

\(^*\) The thanks of the writer are due to Dr. A. P. Carman for aid and facilities, and to Dr. Chas. T. Knipp for his constant advice and kind supervision of the work.

\(^1\) Verh. d. deut. Phys. Gesel. v. 5, p. 219, 1903.
Later, it was found by Dr. Heusler, W. Stark and E. Haupt\(^1\) that a copper-manganese alloy itself was not magnetic, but, when mixed with zinc, arsenic, antimony, bismuth, or boron, it was more or less magnetic; and when aluminum was added, a good ferromagnetic alloy was obtained. In general, the properties of any given piece varied radically with the previous heat treatment, but the most magnetic alloy was formed when the manganese and aluminum were in the proportion of their atomic weights, i.e., manganese, 25%, aluminum 12.5% and copper 62.5%.

From this fact and also from the values of the molecular susceptibilities of certain salts, as given by G. Wiedmann\(^2\), Liebknecht and Wills\(^3\), and others, Dr. Heusler considered the case analogous to a salt solution in which the combination of manganese and aluminum in atomic proportions was the salt, and the copper the solvent.

The discovery of these alloys did not attract much attention in England until 1904, when R. N. Hadfield exhibited a sample at the meeting of the British Association, and soon afterwards Flemming and Hadfield\(^4\) published the results of their investigation. In their experiments, they had made two rings which gave B and H curves similar to those of cast iron, with a maximum value for the permeability of 28 to 30 for $B = 1500$. They considered the magnetic properties to be due to molecular grouping and not as characteristic of the elements in themselves.

Andrew Gray\(^5\) made a further investigation with two rods which he tested at low fields only. His specimens were fairly magnetic and improved slightly upon heating to temperatures below 400°C, but quenching from that temperature almost destroyed their magnetism. Neither vigorous tapping nor immersion in liquid air had much effect. The critical temperature was found to be about 350°C. Several quenchings produced a change in structure and, when viewed under the microscope, showed large nodules imbedded in a granular matrix.

Ross\(^6\) working at the University of Glasgow on some speci-

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\(^1\)Verh. d. deut. Phys. Gesel. v. 5, p. 224, 1903.
\(^2\)Lehre von Elektrizität v 3, p. 928.
\(^3\)Ber. d. deut. chem. Gesel., v. 33, p. 448, 1900.
mens containing 25% manganese, 12.5% aluminum, a trace of lead, and the remainder copper, found large variations due to different thermal treatments. Prolonged heating below 100°C had little effect, but distinct improvement was shown upon heating to 160°C, and a gradual deterioration on heating further to 220°C. Testing while immersed in liquid air showed a temporary improvement which was lost on returning to room temperature. Mr. Ross quenched his specimens at 50°C intervals between 400°C and 750°C and then tested them, (1) as quenched, (2) in liquid air, (3) back at room temperature. The effect of quenching shows clearly in the permeability which gradually decreased to 550°C, dropped to a minimum of about half value at 615°C, and then rose to approximately the original value at 650°C and above.

The magnetostriction was carefully measured by Austin\textsuperscript{1} and found to give, for his particular specimen, a value $\frac{d\lambda}{l} = 11 \times 10^{-7}$ for a field of 400 c.g.s. units, which is about one-third that for cast iron. The curves showing the relation of the magnetostriction to the field strength had the same general form as the magnetization curves, though rising more slowly.

Guthe and Austin\textsuperscript{2} found expansion curves similar to the magnetization curves and a numerical value about one-half that for soft iron. In general, the softer samples gave the greater expansion.

McLennan\textsuperscript{3} found the continuous shortening, especially in strong fields, observed by Austin\textsuperscript{4}, and marked effects due to the heat treatment and the difference in lengths of time after casting. The maximum elongation was observed in specimens having the manganese and aluminum in the proportion of their atomic weights. The permeability of some rings was found to vary greatly with the quenching temperature and was much greater when they were quenched from near their melting point than from a red heat.

Guthe and Austin\textsuperscript{5} also tested their samples for Young's modulus and found it very large, although no exact results could be determined on account of flaws in the material.

Bidwell has shown, for iron and nickel, that there is a

\textsuperscript{1}Ber. d. deut. Ges., v. 6, p. 211, 1904.
\textsuperscript{3}Phys. Rev., v. 24, p. 449, 1907.
\textsuperscript{4}ibid.
\textsuperscript{5}ibid.
change in the thermo-electric power proportional to the magnetic expansion corrected for mechanical stress, but Guthe and Austin found no such effect for the Heusler alloys, even for a temperature difference of $100^\circ$ C. Mendenhall reported in a private letter to them that he could find no evidence of the Kerr effect.

Hill\textsuperscript{1} tried heating to various temperatures and found the effect reversible up to about $375^\circ$ C., but at $500^\circ$ C., irreversible.

In a discussion of the theory, Hill suggests that manganese may really be a magnetic substance under the proper conditions, as a consideration of the atomic susceptibilities and molecular magnetism of certain substances would indicate.

Defining “atomic susceptibility” as the mean susceptibility of the space containing one gram atom of substance in 1000 cc., Meyer\textsuperscript{2} gives the following arrangement of elements in the order of their atomic susceptibilities: Ho, Er, Gd, Mn, Fe, Sa, Co, Yt, Nd, Ni, Pr. Liebknecht and Wills\textsuperscript{3} give the following list of magnetic susceptibilities for certain salts:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper nitrate</td>
<td>.00163</td>
</tr>
<tr>
<td>Ferric nitrate</td>
<td>.01352</td>
</tr>
<tr>
<td>Ferrous sulphate</td>
<td>.01272</td>
</tr>
<tr>
<td>Manganic nitrate</td>
<td>.01536</td>
</tr>
<tr>
<td>Manganese sulphate</td>
<td>.01514</td>
</tr>
</tbody>
</table>

Yager and Myer\textsuperscript{4} give the following values for the molecular magnetism of certain elements:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$I_m \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>$2 \times 2.5 \text{ c.g.s.}$</td>
</tr>
<tr>
<td>Cobalt</td>
<td>$4 \times 2.5 \text{ c.g.s.}$</td>
</tr>
<tr>
<td>Iron</td>
<td>$5 \times 2.5 \text{ c.g.s.}$</td>
</tr>
<tr>
<td>Manganese</td>
<td>$6 \times 2.5 \text{ c.g.s.}$</td>
</tr>
</tbody>
</table>

McLennan and Wright\textsuperscript{5} studied the susceptibilities of several salts of the metals, copper, manganese and aluminum, and found approximately the same values given above with the additional value of $-0.00018$ for $\text{Al}_2(\text{SO}_4)_3$ and $+0.00002$ for $\text{Al} (\text{NO}_3)_3$. When

\textsuperscript{1}Phys. Rev. v. 21, p. 335, 1905.
\textsuperscript{2}Ann. d. Phys., v. 68, p. 325, 1899.
\textsuperscript{3}' ' v. 1, p. 173, 1900.
\textsuperscript{4}Wiener Ber., v. 106, pp. 534, 623, 1897; v. 107, p. 5, 1898.
\textsuperscript{5}Phys. Rev., v. 24, p. 276, 1907.
combined in the proportions of the Heusler alloys, the susceptibilities followed the simple additive law and changed but little with concentration.

Hill\(^1\) suggests that there is a simple explanation of many of the phenomena of the Heusler alloys in the allotropic theory of Osmond. Thus iron shows the allotropic forms:

- Alpha—soft, magnetic and stable below 700–780°C.
- Beta—hard, non-magnetic and stable between 750°C. and 860°C.
- Gamma—soft, non-magnetic and stable above 860°C.

In passing from one form to another, there is a transformation point, e.g., the common recalcement point in iron.

Nickel has only two known allotropic forms:

- Alpha—magnetic and stable below 340°C to 360°C.
- Beta—non-magnetic and stable above 360°C.

The transformation point can be depressed by alloying with another metal and the amount of depression is proportional to the amount of the substance added. Thus it is possible that the form of manganese stable at ordinary temperatures is non-magnetic, but that the alloying produces another allotropic form that is magnetic.

Zahn and Schmidt\(^3\) studied the Hall effect and allied phenomena, chiefly the thermo-magnetic effect of Nernst and Ettingshausen,\(^4\) for the Heusler alloys and their individual constituents. They found the following values for the coefficient $R$ of the Hall effect and for the coefficient $Q$ of the thermo-magnetic effect.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$R \times 10^5$</th>
<th>$Q \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heusler alloy</td>
<td>+ 1300</td>
<td>- 500(^*)</td>
</tr>
<tr>
<td>Manganese</td>
<td>- 93</td>
<td>- 15</td>
</tr>
<tr>
<td>Aluminum</td>
<td>- 40</td>
<td>+ 20</td>
</tr>
<tr>
<td>Copper</td>
<td>- 50</td>
<td>+ 80</td>
</tr>
<tr>
<td>Lead</td>
<td>+ 9</td>
<td>+ 5</td>
</tr>
<tr>
<td>Iron</td>
<td>+ 1080</td>
<td>+ 1050</td>
</tr>
</tbody>
</table>

It is evident that the values of $R$ and $Q$ are not additive for the

\(^1\)Phys. Rev. V. 24, p. 276, 1907.
\(^3\)Verh. d. deut. Phys. Ges., v. 9, p. 93, 1907.
\(^*\)The values for the alloy are average and approximate. The iron is inserted for comparison.
Heusler alloys, and comparison with iron shows no certain relation of sign or magnitude. The temperature coefficients of $R$ and $Q$ were found to be $+0.003$ and $-0.006$, respectively. Four other allied effects were detected, but not with enough certainty for quantitative measurement.

Recently, Knowlton\(^1\) has succeeded in making specimens of especially good and uniform mechanical properties. He did not find any simple relation between composition and magnetic properties, and suggests that the copper has a much larger influence than is usually attributed to it. He made a study of the structure by means of photo-micrographs. Three distinct types of crystals were evident: (1) bright ones, unaffected by the etching fluid (HCl and FeCl\(_3\)); (2) dark ones, deeply etched, and (3) yellowish ones of the nature of a matrix. Crystals of the first type were evidently the magnetic ones, as no specimen from which these were absent was magnetic, and the value of $I$ could be estimated with a fair degree of approximation from the area of these crystals. He found, also, no evidence of recalescence, and that the critical point for one specimen was $0^\circ\text{C.}$ and for the others about $200^\circ\text{C.}$

### III. Test Pieces

1. *Preparation.*—Considerable time was spent in preliminary experiments with small quantities of copper, manganese and aluminum in order to learn the best method of alloying and casting. The test pieces were finally prepared in the following manner.

The materials were all tested qualitatively for iron, cobalt and nickel and found quite free from these, although they showed some carbon. Each combination of the metals was weighed out in a given proportion so as to make a total of about two pounds, melted in a brass furnace at the University foundry, and cast in fine sand molds. The melting crucible was a new clay-graphite one. The manganese and copper were put in first, and when they were thoroughly fused the aluminum was put in, a flux added, the mixture stirred with a well seasoned hard wood stick, and then quickly poured into vertical molds. Two rods, each 45 cm. long and 1.1 cm. in diameter, were poured from each melt

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and allowed to cool slowly in the molds.

The ends of the rods, which were enlarged in the casting, were cut off and the whole length dressed down on an emery wheel to the form of a very prolate ellipsoid. The specimens were tested magnetically as cast, and again after grinding, and the grinding was shown to have had no effect upon them. Twelve samples, about 35 cm. long and 1 cm. in diameter, were thus prepared. None of the specimens could be satisfactorily worked and those with the larger per cent of manganese and aluminum were especially hard and brittle.

The magnetometer method was chosen as being best adapted to all parts of the investigation. A diagram of the apparatus is shown in Fig. 1. The resistance of the magnetizing coil was so high that 110 volts gave only two amperes through it, so this source of current was used for most of the work, but when a very small current was desired, storage batteries could be cut in at the switch $S_1$. The current was led through a 0–5 ammeter, reading to hundredths, and through an extra compensating coil $C_2$ to a reversing switch $S_3$, then through two control resistances, $R_1$ and $R_2$, and by the switch $S_3$, either through the coil $C_1$ alone, or through it and the magnetizing coil, $MC$ in series. The extra compensating coil $C_2$ was made necessary by a small permanent field due to the wiring and the various instruments, and its position was located by trial. By means of the switch $S_3$, the magnetizing coil could be cut out and the coil $C_1$ used as a calibration coil, without change of position. Control magnets were used, so that
the field was about 0.275 c.g.s. The ammeter, switches, resistances, etc., were placed on a convenient table about two meters back of the magnetometer, while the magnetizing and compensating coils and the magnetometer were placed on a slideway about three meters long, clamped to a pier. The magnetizing coil was made one meter long with an average diameter of 9.2 cm., and was wound with two layers of No. 30 copper wire, on a copper water jacket with a water space of about 1 cm. For testing the specimens at higher temperatures, an electric furnace could be slipped inside the water jacket. The furnace consisted of a porcelain tube of 1.3 cm. inner diameter, on which was wound, bifilar, a nickel wire. The heating coil was covered with magnesite and placed inside a fire-clay tube which fitted closely inside the water jacket. The bifilar winding eliminated most of the field due to the heating current, and as soon as the coil reached about 350° C., the nickel lost its magnetic effect. For this arrangement of the magnetometer, the following formulas were used.

If $H_e$ is the earth's field as determined with the calibrating coil, then

$$H_e = \frac{2\pi n a^2 I}{10 r^3} \cot \psi \quad \text{............... (1)}$$

where $n =$ the number of turns, $a =$ the radius of the coil, $d =$ the distance of the coil from the magnetometer, $r = \sqrt{(d^2 + a^2)}$, $D =$ the distance of the scale from the mirror, $\cot \psi = \frac{2D}{d}$ def. In the magnetizing coil

$$H = \frac{4\pi n I}{10 l} \quad \text{............... (2)}$$

where $n =$ the total number of turns, $l =$ the length of the coil, and $I =$ the current in amperes.

On the assumption that the magnetic length is two-thirds the actual length,

$$I = \frac{3 (r^2 - \frac{l^2}{9}) H_e \tan \phi}{4 \pi a^2 l r} \quad \text{............... (3)}$$

where $I =$ the intensity of magnetization, $l =$ the length of the specimen, $2a =$ the diameter of the specimen, $r =$ the distance from the center of the specimen to the magnetometer, and $\tan \phi = \frac{\text{def.}}{2D}$
2. Composition.—The specimens were made up with the idea of testing some important points that had been developed in previous investigations; e. g., the effect of different percentages of manganese and aluminum, the effect of a little lead on the mechanical properties, and also the effect of a small amount of iron. Because there was considerable slag left in the crucible, it was believed that the percentage composition had changed somewhat in the process of melting, and so careful analyses of six specimens were made and the results are shown in Table 1.

TABLE 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Length (cm)</th>
<th>Diam. (cm)</th>
<th>Cu percent</th>
<th>Mn percent</th>
<th>Al percent</th>
<th>Pb percent</th>
<th>Fe percent</th>
<th>IM* percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.7</td>
<td>1.1</td>
<td>74.7</td>
<td>13.4</td>
<td>11.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>44.2</td>
<td>1.1</td>
<td>69.7</td>
<td>12.4</td>
<td>17.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>48.0</td>
<td>1.1</td>
<td>54.8</td>
<td>28.1</td>
<td>17.0</td>
<td>1.51</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>43.3</td>
<td>1.1</td>
<td>66.4</td>
<td>14.4</td>
<td>16.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>43.3</td>
<td>1.1</td>
<td>62.4</td>
<td>23.3</td>
<td></td>
<td></td>
<td>2.52</td>
<td></td>
</tr>
</tbody>
</table>

* IM is matter insoluble in HCl or HNO3.

The analyses showed a larger percentage of aluminum than was intended, probably because the aluminum was put in last, melted very quickly, and seemed to fuse readily with the molten mass which was immediately poured into the molds without the aluminum having had much time to oxidize. The series formed by No. 1, 2, 6, and 4 had increasing percentages of manganese and aluminum, No. 3 had 1.5% lead and No. 5 had 2.5% of iron.

When the specimens had been prepared as given above, they were tested by the magnetometric method. The water jacket furnished an excellent means of controlling the temperature, as the hydrant water remained quite constant at 18°C and this was the temperature of all the tests unless otherwise specified.

The data for the original test of a complete hysteresis cycle for No. 3 are given in Table 2 and shown graphically for the other specimens in Fig. 2 and 3. No curves are given for specimens 1 and 2, as they were so slightly magnetic as to be beyond the sensitiveness of the apparatus.

A study of the curves shows that No. 6 was the best of the series as it had the largest value of B with the least hysteresis, and Table 1 shows that it came nearest having the individual elements in the proportions of their atomic weights, i. e., copper 62.4%, manganese 23.4%, aluminum 14.2%.
TABLE 2
ORIGINAL TEST OF SPECIMEN NO. 3

<table>
<thead>
<tr>
<th>( l )</th>
<th>( H )</th>
<th>( B )</th>
<th>( M )</th>
<th>( I )</th>
<th>( H )</th>
<th>( B )</th>
<th>( M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>0.0</td>
<td>1220</td>
<td>...</td>
<td>-35</td>
<td>24.0</td>
<td>465</td>
<td>19.3</td>
</tr>
<tr>
<td>160</td>
<td>24.0</td>
<td>2030</td>
<td>84.6</td>
<td>91</td>
<td>34.4</td>
<td>1175</td>
<td>34.2</td>
</tr>
<tr>
<td>174</td>
<td>34.4</td>
<td>2220</td>
<td>64.6</td>
<td>167</td>
<td>51.6</td>
<td>2120</td>
<td>41.0</td>
</tr>
<tr>
<td>207</td>
<td>51.6</td>
<td>2540</td>
<td>51.2</td>
<td>216</td>
<td>68.8</td>
<td>2785</td>
<td>40.5</td>
</tr>
<tr>
<td>236</td>
<td>68.8</td>
<td>3030</td>
<td>44.1</td>
<td>188</td>
<td>51.6</td>
<td>2415</td>
<td>46.8</td>
</tr>
<tr>
<td>264</td>
<td>86.0</td>
<td>3400</td>
<td>39.5</td>
<td>153</td>
<td>34.4</td>
<td>1960</td>
<td>57.0</td>
</tr>
<tr>
<td>278</td>
<td>103.0</td>
<td>3595</td>
<td>34.9</td>
<td>132</td>
<td>24.0</td>
<td>1685</td>
<td>70.3</td>
</tr>
<tr>
<td>306</td>
<td>120.0</td>
<td>3960</td>
<td>33.0</td>
<td>62</td>
<td>0.0</td>
<td>778</td>
<td>...</td>
</tr>
<tr>
<td>375</td>
<td>137.4</td>
<td>4860</td>
<td>35.4</td>
<td>75</td>
<td>24.0</td>
<td>980</td>
<td>40.3</td>
</tr>
<tr>
<td>237</td>
<td>68.8</td>
<td>3040</td>
<td>44.2</td>
<td>132</td>
<td>34.4</td>
<td>1695</td>
<td>49.3</td>
</tr>
<tr>
<td>216</td>
<td>51.6</td>
<td>2760</td>
<td>51.5</td>
<td>195</td>
<td>51.6</td>
<td>2500</td>
<td>48.5</td>
</tr>
<tr>
<td>202</td>
<td>43.0</td>
<td>2580</td>
<td>60.0</td>
<td>229</td>
<td>68.8</td>
<td>2950</td>
<td>43.0</td>
</tr>
<tr>
<td>188</td>
<td>34.4</td>
<td>2395</td>
<td>61.6</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
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<td>24.0</td>
<td>2210</td>
<td>92.2</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>104</td>
<td>0.0</td>
<td>1305</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Fig. 2.
No. 3, with the lead in it, gave about three-fourths the value for $B$ that No. 6 did and had much greater hysteresis. No. 5, with the iron in it, gave about one-third the value for $B$ that No. 6 did, but had very little hysteresis. No. 4 which had a high percent of manganese is only slightly magnetic.

For the purpose of comparison a few other tests gave results as shown below.

Good Swedish iron, $H = 50$, $B = 12,000$ to $14,000$
Iron Wire, $H = 50$, $B = 7,500$
No. 6 alloy $H = 50$, $B = 3,600$

IV. Tests

1. Working Hypotheses.—It was thought that in some way somewhat analogous to that of iron, the manganese, or some compound of it, in the Heusler alloys, might have two or more allotropic forms, which the alloying rendered magnetic at ordinary temperatures. Also, if the alloys were the most magnetic when the components were in the proportions of their atomic weights, it seemed possible that some compound might be formed which was the magnetic substance.

2. Preliminary Tests.—To test the first hypothesis, specimen No. 4 was cut into six pieces about 8 cm. long, placed in an Heraeus electric furnace and slowly heated. At each 100° interval, the temperature was kept constant for at least fifteen minutes, and then one piece was taken out and quickly quenched in water.
The theory of quenching is that the substance remains in the molecular condition that it was in at the temperature from which it was quenched.

It was found that when quenched between 300°C and 400°C, the specimen was slightly magnetic; between 500°C and 650°C, non-magnetic; and above 700°C stronger than the original. These tests were simply qualitative, as the specimen was suspended by a thread and then placed between the poles of a horse-shoe magnet. The tests were repeated several times and were consistent. Quenching in the field of a Du Bois magnet of about 5,000 lines per square centimeter was also tried. It seemed to make no difference in the permanent magnetism, whether the pieces were quenched in the field or put in the field after being quenched.

Because the quenching in water cracked the specimens and made them very brittle, cooling in air was tried and found to produce the same result as quenching in water from a somewhat lower temperature.

3. Effect of Quenching on Magnetic Properties.—For more careful tests, the strongly magnetic pieces, No. 3 and 6, were used. They were heated to the temperature shown, in the order of the
numbers of the curves, allowed to cool in air, and tested at 18°C. The results for No. 3 are shown graphically in Fig. 4, and the results for No. 6 are plotted in Fig. 5. In order to simplify the figures, the upper fourth only of the hysteresis curve is plotted from the data for the complete cycle.

![Graph of hysteresis curves for different quenching temperatures.](image)

**Fig. 5.**

A study of the curves makes several generalizations possible. It is quite evident in both figures that when the specimen is heated to temperatures between 600°C. and 700°C. and allowed to cool in air, B is reduced to about 15% of its former value. On heating to still higher temperatures, B regains its former value and when quenched from within 100°C of the melting point of the specimen, gives the highest value obtained. No. 3 has a lower value of B but a larger hysteresis and retentivity than No. 6. The retentivity increases in about the same proportion as B. To show the effect of quenching in another way, the values of permeability M, for H = 50, are plotted against quenching temperatures in Fig. 6.

Both curves show minimum values between 600°C. and 700°C. and larger values for the higher temperatures. The values of M around 250°C. are low. This is the temperature at which it
has always been noticed that the beneficial effects of baking are lost.

After the above series of tests of heating to a given temperature and cooling in air, specimen No. 3 was heated to several high temperatures and quenched in water. As mentioned above, the effect was much the same as cooling in air, although in the latter process there would undoubtedly be time for a limited transformation, thus making the effective air quenching temperature somewhat lower than that actually read.

Quenching No. 3 in water after heating for 20 minutes at 870°C gave the highest value ever observed for B. For H = 69, B = 4,500, M = 65 and for H = 52, B = 4,300, M = 83.2.

These data seem to emphasize the point that the alloy is in its most magnetic state in the molecular condition existing near its melting point.

V. THERMAL ANALYSIS

It is evident that there is something peculiar about the condition of the alloy between the temperatures of 600°C and 700°C, and in the hope of throwing some light on this and on the hypothesis that a chemical compound might be formed, a limited thermal analy-
sis was undertaken. The general method of thermal analysis consists in heating the substance above its melting point, allowing it to cool under constant conditions, and taking time and temperature readings at regular intervals. From the form of the curve obtained, it may be possible to draw conclusions regarding the composition and molecular arrangement of the substance.

The particular method and some of the apparatus was that used by Clement and Egy in the calibration of their thermocouples.

A cross-section of the electric furnace used by them is shown in Fig. 7. It has the heating coil on the inside of the furnace.

FIG. 7.

The coil of heavy nickel wire was wound on a sectional wooden core and plastered over with magnesite mixed with glue. When this had hardened, the core was removed and the coil put inside two cylinders of magnesite, the intervening spaces being filled with calcined magnesia. A large barrel of water with two iron grids for electrodes, the upper one being movable, was used as a control resistance for the furnace. The furnace would carry a maximum current of about 30 amperes on 110 volts.

The specimen for which a cooling curve was to be made was put in a graphite crucible and covered with powdered charcoal to give a reducing atmosphere. The crucible was made from a

1University of Illinois Engineering Experiment Station Bulletin No. 36.
graphite rod turned to the required size in a lathe, and fitted rather closely inside the furnace.

The thermocouple was enclosed in a quartz tube of 2 mm. internal diameter, the wires being insulated from each other by mica strips. This tube passed through holes in the lids of the furnace and crucible and was pushed down to within 2 cm. of the bottom of the crucible when the charge was melted.

The e. m. f. of the couple was balanced against that of a Weston standard cell by means of an Otto Wolff potentiometer arranged to be direct reading. This is shown diagrammatically in

![Diagram](image.png)

Fig. 8. The dials of the potentiometer were set on the numbers corresponding to the e. m. f. of the standard cell and the auxiliary resistance in series with the battery and potentiometer adjusted for a balance. This balance was sensitive to 1 ohm in 20,000 ohms.

Thermocouple readings were taken in microvolts (MV) and the figure in the last place was found from the galvanometer reading. The resistance in series with the galvanometer and the scale distance were so adjusted that a deflection of one scale division corresponded to one microvolt. It was thus possible to read to 1 MV at 10,000 MV.

The thermocouple used was made of platinum-platinum, 10% rhodium, and was carefully calibrated at the freezing points of three pure metals which are accurately known—zinc 419°C., silver 961.5°C. and copper 1084°C.

When time-temperature readings are taken on a pure substance as it cools from the liquid state, the temperature of the
substance falls with that of the furnace until the freezing point is reached. There it remains constant until all the substance is frozen and then quickly falls to that of the furnace again. It has been found experimentally that the freezing point is much more definitely marked than the melting point, and that it is much easier to keep conditions constant when cooling than when heating.

The calibration data for the couple used are given in Table 3.

The temperature was assumed to be a parabolic function of the e. m. f. as expressed by the equation

\[ T = a + bE - cE^2 \]

Table 3 gave three pairs of readings for \( T \) and \( E \), from which the three constants in the equation were determined and a temperature-microvolt curve calculated. For this couple the equation was

\[ T = 118.067 + 0.128478E - 2.40282 \times 10^{-6}E^2 \]

For small intervals MV are approximately equal to tenths of a

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<th>Copper Point</th>
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<th>Zinc Point</th>
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<td>Time</td>
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degree and it was thus possible to read to 0.1° at 1000°C., although the absolute value of the temperature was probably not closer than ± 1°.

The specimen of alloy to be tested was broken into small pieces, put into the crucible, covered with powdered charcoal, and heated in the furnace. It was kept above the melting point for
FIG. 11*. Specimen 1, twice recast, no further heat treatment. Etched with FeCl₃. Very slightly magnetic.

FIG. 12. Original specimen 1, heated for 1 hour at 880³ and quenched. Etched with FeCl₃. Non-magnetic.

FIG. 13. Same as in FIG. 12, repolished and etched with HNO₃. Blank pits are due to imperfect surface. Very slightly magnetic.

FIG. 14. Specimen 2, twice recast, no further heat treatment. Etched with FeCl₃.

FIG. 15. Specimen 2 heated for two hours at 415³ and quenched in water. Polished not etched. Very slightly magnetic.

FIG. 16. Specimen 2 heated for 3 hours at 575³ and quenched. Etched with FeCl₃. Very slightly magnetic.

* All temperatures Centigrade.
FIG. 17. Original specimen 3 heated for 1 hour at 345° and quenched. Polished but not etched. Strongly magnetic.

FIG. 18. Same as FIG. 17. Etched with HNO₃ and slightly repolished. Almost non-magnetic.

FIG. 19. Specimen 3 heated for 30 minutes at 466° and quenched. Etched with FeC₁₃. Only slightly magnetic.

FIG. 20. Specimen 3, twice recast; no further heat treatment. Etched with FeC₁₃. Strongly magnetic.

FIG. 21. Specimen 3 heated for 3 hours at 495° and quenched. Etched with FeC₁₃. Strongly magnetic.

FIG. 22. Specimen 3 heated for 3 hours at 495° and quenched. Etched with FeC₁₃. Strongly magnetic.
FIG. 23. Original specimen 5 heated for 2 hours at 620° and quenched. Etched with HNO₃. Slightly magnetic.

FIG. 24. Original specimen 6 heated for 2 hours at 880° and quenched. Etched with FeCl₃. Very slightly magnetic.

FIG. 25. Specimen 5, twice recast, no further heat treatment. Etched with FeCl₃. Slightly magnetic.

FIG. 26. Specimen 6, twice recast, no further heat treatment. Etched with FeCl₃. Strongly magnetic.

FIG. 27. Specimen 6 heated for 30 minutes at 470° and quenched. Etched with FeCl₃. Only slightly magnetic.

FIG. 28. Specimen 6 heated for 3 hours at 500° and quenched. Etched with FeCl₃. Strongly magnetic.
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### TABLE 4

**Cooling Curve Data for Specimen No. 3**

Readings Taken Every 20 Seconds

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<th>MV</th>
<th>Time</th>
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<td>2932</td>
<td>4:30</td>
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</table>
some time, to allow the pieces to fuse together, then the couple was pushed down into it, the heating current shut off, and readings of the potentiometer taken every 20 seconds. It took about two hours for the temperature to fall to 300°C.

When it was desired to pass very slowly through a point, the heating current was merely reduced, and, in order to keep it constant, the storage batteries were "floated on the line". The battery of forty cells was charged with a current of, say 16 amperes, while a current of 18 amperes was taken from it. This current would remain quite constant for several hours.

The cooling curve data for the six specimens are shown in Fig. 9 and Fig. 10, the curves in each figure being numbered to correspond with the specimen. Microvolts are plotted as ordinates and time as abscissas. The squares in the figure are centimeters and 1 mm. is equal to 10 sec. so the points are too close together to be shown in the figure.

VI. DISCUSSION OF COOLING CURVES

The upper parts of the cooling curves are plotted in Fig. 9 and the lower parts in Fig. 10. In the intervening region, the specimen cooled regularly with the furnace. The various curves show four characteristic regions, viz., (1) an almost straight line where the molten liquid is cooling with the furnace; (2) an abrupt change to an almost horizontal line, curves 1 and 2, Fig. 9, which indicates that a pure substance is freezing out of the solution; (3) a rounded portion with a quick drop to the temperature of the furnace which is given by the dotted line; (4) another abrupt change in slope in curves 3, 4 and 6, Fig. 10, which indicates a transformation, or recalescence point.

All the curves are those generally characteristic of solid solutions, but there are not enough data to draw any conclusions as to the formation of a compound. It was noticed that when an alloy was at the temperature represented by the bulge in its curve in Fig. 9, it was possible by pressing a rod into the crucible, to squeeze a liquid out of the semi-solid mass much as water can be pressed out of a sponge.

The data for each curve were taken at least twice and the freezing points found to be quite constant. The depressions of the freezing points are in the order of increasing percentages of
STEPHENSON—MAGNETIC PROPERTIES OF HEUSLER ALLOYS

manganese, except No. 5, which is high, possibly on account of the 2.5% of iron in it, and No. 3, which is low, due to the 1.5% of lead in it.

Curve 4, Fig. 10, has an exceptional transformation point. The test piece for it was made of the small pieces of No. 4 used in the preliminary quenching tests above. When the specimen had cooled to about 595°C, a pronounced change evidently took place, for there was a distinctly audible cracking, and on examination, the charge was found to be very loose in the crucible and the contraction had crushed the quartz tube containing the thermocouple.

Curves 1, 2 and 5 do not show any transformation points, but curves 3 and 6 do, and this point is at the same temperature, 615°C., from which these specimens were non-magnetic on quenching. It is evident then that at this temperature and for specimens of the approximate composition of No. 3 and 6, there is a molecular rearrangement accompanied by an evolution of heat, and that when kept in this state by quenching, the alloy is non-magnetic, but if it is allowed to cool slowly to room temperature, it goes over into a magnetic form.

VII. PHOTO-MICROGRAPHY

Since it is generally agreed that the magnetism of substances is due to their molecular arrangement and since even superficial examination of these alloys showed changes in crystalline structure with the heat treatment, a study by means of photo-micrography was carried out. This method has not been very generally used and specific directions are hard to find, so it will be described here somewhat in detail. A general account of the art of photo-micrography will be found in the Appendix.

The apparatus consisted of a Leitz “New Universal Photomicrographic Apparatus” fitted with an incandescent gas lamp, a microscope with a wide tube, and an opaque vertical illuminator. The magnification could be adjusted to any desired ratio by a suitable combination of eye-piece, objective and length of camera bellows. The magnification at which the accompanying photographs were taken was determined exactly by taking a photograph of a standard grating and counting the number of lines per cm. in the picture.

It is necessary that the specimen should have a plane surface
and a high polish in order to give a flat field for the microscope. This was accomplished by fixing the pieces in a block of wood and grinding them on a series of rapidly rotating disks covered with emery paper of increasing fineness and then grinding by hand on a glass plate charged with emery. Emery sufficiently fine for this purpose was obtained by shaking "flour" emery in water and decanting the liquid with the particles in suspension after allowing it to settle for various lengths of time from one minute to twenty-four hours. This grinding gives a plane surface but covered with very fine scratches.

To remove the scratches the specimen must be polished. Great care is necessary not to destroy the plane surface or make more scratches by a little grit or dirt getting on the polisher. First, a felt wheel charged with "Tripoli" was used, then a cotton buffer, and finally the process was finished by hand by rubbing on a linen cloth stretched over a glass plate and charged with jeweler's rouge. This process might be much simplified and hastened by using a good mechanical grinder and polisher, but the final work by hand, though rather tedious, seems to give the finest surfaces. Excessive polishing should be avoided because the rapidly rotating polisher seems to cause the metal to flow over a thin surface layer entirely obscuring the structure.

To bring out the structure clearly, it is usually necessary to "etch" the specimen, i.e., to use a reagent that will attack some parts more than others. The particular etching fluid must be determined by the composition of the substance studied. For the Heusler alloys, a dilute solution of nitric acid or a strong solution of ferric chloride with possibly a little hydrochloric acid added, was used to bring out the various points.

In taking the pictures, artificial light diffused by a ground glass screen was used in preference to daylight because of its greater constancy and ease of control. Stopping down the light and using a longer exposure gave more detail and sharper contrast. The focusing was accurately done with a lens and a fine adjustment.

The plates used were Standard "Orthonon", which are orthochromatic and non-halation. Because of the double film, the plates were developed slowly and until almost black, and left in the hypo and washed about twice as long as ordinary plates.
A printing paper with a glossy enameled surface was used to bring out the contrast in the structure. This glossy paper usually requires a special non-abrasion developer.

**PHOTO-MICROGRAPHS OF THE HEUSLER ALLOYS**

A large number of photographs were taken under various conditions and a few, which are all of a constant magnification of 50 diameters, are given in Fig. 11 to Fig. 28. The "original" specimens are pieces of those first cast and whose composition is given in Table 1. The others were made from the original ones of the same number by melting and recasting twice. This produced more homogeneous alloys with better mechanical properties. There was some slag formed at each melting, so the composition is probably not quite the same as the original, but they did not differ much, as the slag was of approximately the same composition as the specimen and was magnetic.

After a specimen had been heated and quenched, it was ground off for at least 2 mm. below the surface and care was taken to keep it from heating too much during the grinding.

The magnetic testing for this part of the work was done qualitatively by suspending the specimen by a thread in the field of a large permanent magnet. Slightly magnetic means that the specimen would orient itself with the field and possibly turn through an angle of 90° as the magnet was rotated. Strongly magnetic means that the specimen could be lifted by the magnet.

Some of the photographs show the three types of crystals described by Knowlton1, but no such simple relation as he found between the size of the white crystals and the magnetization could be determined. In fact there seemed to be no essential difference between specimens 3 and 6 when quenched from the temperature that made them non-magnetic and when taken in their originally strongly magnetic condition. Also it would be difficult to distinguish between Fig. 11 and Fig. 22, although the former is of specimen 1 which was almost non-magnetic and the latter is of specimen 3 which was strongly magnetic.

The photographs of specimen 2 show a peculiar arrangement of long slender crystals pointing towards the center of the specimen where the crystals are smaller and more regular. The recast specimens all show much smaller crystals than the original ones, but none of them shows the pronounced effects due to quenching or annealing that were expected.

VIII. SUMMARY

The results of this investigation may be summarized as follows:

(1) The best specimen had the manganese and aluminum in the proportion of their respective atomic weights. It gave a maximum value of $B = 4000$ and $M = 57$ for $H = 70$, but had not reached saturation.

(2) Heating to various temperatures, cooling in air and testing at room temperature gave, for $H = 50$, a practically constant value for the permeability from room temperature to $300^\circ$, a rapid drop between $300^\circ$ and $600^\circ$ to about one sixth its former value, and beyond $700^\circ$ a rapid rise to better than the original value at $900^\circ$. This series of changes was reversible for at least three times.

(3) The largest values of $B$ and $M$ were obtained when the specimen was quenched in water from near its melting point.

(4) A series of cooling curves gave melting points between $910^\circ$ and $970^\circ$C., and curves characteristic of solid solutions.

The curves for the two magnetic specimens showed transformation points, with evolution of heat, at $615^\circ$C. Specimens quenched from this temperature are non-magnetic when tested at room temperature.

(5) It seems evident that there is an allotropic form of the alloy or at least of the magnetic constituent of the alloy, which has a non-magnetic molecular arrangement at about $600^\circ$C.

(6) A series of photo-micrographs showed differences in the crystalline structure due to previous history, but no simple relation could be established between the magnetization and the presence of certain crystals.
APPENDIX
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PHOTO-MICROGRAPHY

The possibility of taking a photograph through a microscope was demonstrated as early as 1840, but only within the last two decades has it been possible to obtain satisfactory apparatus at moderate cost or to find books from which one could acquire a knowledge of the technique in a reasonable time. Even yet in this country photo-micrography is not so well understood or so fully applied as its advantages would warrant if better known.

It is the purpose here to give a few fundamental principles and essential points in the selection and use of the apparatus with some general methods of attack in the solution of the problems involved. Incidentally, it is well to distinguish a photo-micrograph, which is a photograph of a microscopic object, from a micro-photograph, which is a microscopic photograph of a large object.

Photo-micrography may be applied in almost any case where the microscope is used and in some cases, as will be shown later, this art has extended the field of the microscope. As a record of the objects seen in a microscope, a photograph has advantages over the usual drawing, in that it tends to eliminate the personal bias and to give increased weight to the evidence presented. It saves much time when the necessary equipment and skill are once acquired, and it may be reproduced indefinitely in the positive print or the lantern slide. It is possible by the use of ultraviolet light to photograph objects that are invisible with ordinary light; by the proper choice of plates and color filters, the brilliant shading of colored objects may be correctly reproduced in monotone; because of the cumulative effect of the light on the sensitive plate, an object but dimly seen may be plainly photographed by prolonged exposure; while by the use of the cinematograph, moving pictures of a microscopic world may be had. Some application of photo-micrography is certain to be an advantage in almost any line of modern scientific work, and to the amateur photographer, it opens up new possibilities for the application of his highest skill.

APPARATUS

The apparatus necessary for photo-micrography depends upon the grade of work to be done, but it must include a microscope, a camera, a rigid support for them, properly prepared specimens,
some source of illumination with means of control, suitable plates, printing paper, developing and fixing solutions. Various home-made combinations may serve, in some instances, but for the best work, particularly at high powers, special apparatus will be more satisfactory because of the corrections of the optical system and the devices for accuracy and ease of adjustment that are so great a saving of time and patience.

Microscope.—A special microscope is not necessary, but the one used should have a wide tube for photographing without the ocular, a stable base, an adjustable stage, and the best possible lens equipment.

There are two properties of lenses that must be especially considered in photo-micrography. The spherical aberration is due to the fact that monochromatic light is unequally refracted in passing through a single spherical lens, being refracted more near the edge than it is near the axis, so that all the rays incident on the lens cannot meet exactly in the same focus. Chromatic aberration is due to the fact that the lens acts as a prism, resolving the white light into spectral colors which are unequally refracted, and thus the different colors cannot be brought to a focus at the same point. By a suitable combination of a bi-convex crown glass lens with a plano-concave flint glass (one with double the dispersive power) the chromatic aberration can be corrected for any two colors, but there is still a secondary spectrum left because the dispersion of the colors is not proportional in the two kinds of glass. Also the spherical aberration can be corrected for any one color, usually that of maximum visual intensity, but there remains under-correction for the red and over-correction for the violet. A lens of this type is called an achromatic lens. As is well known, the light that is most active photographically on the ordinary sensitive plate, the so-called "actinic" light, is that which is near and beyond the violet end of the spectrum, while the eye is more sensitive to the longer wave lengths in the yellow-green. Thus the ordinary achromatic lenses with corrections for spherical aberration in the region of maximum visual intensity and for chromatic aberration between the red and violet are not the best for photomicrography except under special conditions.

After an exhaustive investigation by Dr. Abbe, with the cooperation of the optical workshops of Zeiss and the German gov-
ernment, crown and flint glass were produced of such quality that, when combined with a fluorite lens and special eye-pieces, it was possible to correct the chromatic aberration of the objective for three colors, thus removing the secondary spectrum, and to correct the spherical aberration for two colors and therefore practically for all. These lenses are so well corrected over the whole visual and photographic range as to justify the name apochromatic. Besides their almost perfect achromatization, these apochromatic lenses have the advantage of utilizing the full theoretical aperture, and of permitting a great increase in magnification by the use of special high power oculars. These lenses are especially valuable for photo-micrography.

Camera.—The camera should have a stable base and a means by which the microscope may be firmly clamped to it. A very frequent cause of indistinctness in the negative is the vibration of the supporting table. This may at least be diminished by having the camera and microscope vibrate synchronously, and it may even then be necessary to work at some time when the whole building is quiet. Another important point to be observed is that the guides and grooves for the plate holder and ground glass slide should be accurately adjusted so that the plane of the photographic plate will lie exactly in that of the glass on which the object is focused. For the final adjustment, a clear glass and a focusing lens should be used instead of the ordinary ground glass. The extension of the camera determines the enlargement, but it is the microscope that determines the definition; the photograph may be merely of a convenient working size. The power of the objective used should be as low as is consistent with satisfactory definition, because this is the best working condition for the microscope, and the difficulties in the photographing increase rapidly with the magnification. To obtain the magnification of a given arrangement, the simplest method is the direct measurement of the enlarged image of a micrometer microscope ruled in thousandths of a centimeter, and an analogous method is applicable in determining the actual size of an object.

Illumination.—The use of artificial light for photo-micrography is almost universal because of its constancy and ease of control; and the choice between kerosene, gas, calcium, or electric light depends upon their availability and upon the particular work.
The yellow kerosene flame, though weak, may prove very satisfactory at low magnifications with ordinary achromatic lenses and ortho-chromatic plates without a color screen, while the arc light is far more intense, rich in actinic rays, and, in general, requires apochromatic lenses and color screens. Before making an exposure, it is necessary that the light be properly focused and centered, and the field properly illuminated. This involves centering the condenser, and then centering the light and focusing the condenser until a sharp image of the light source is projected through the condenser into the plane of the object. To secure uniform illumination, it is often necessary to introduce a bull’s eye condenser between the light source and the sub-stage condenser at such a point that the light will be at the principal focus of the bull’s eye, thus giving parallel light. When a ground glass is used to give diffused light or a colored glass for colored light, it may be placed between the bull’s eye and the condenser. The light from the microscope is then centered on the ground glass of the camera, and the circle of light should be uniformly illuminated and sharp around the edges. For instance, if there is a dim halo around the image, it may be due to a flooding of the objective with too much light, which should be reduced by means of the diaphragm in the condenser; or, on the other hand, it may be due to the use of an objective with too narrow an aperture.

Preparations.—It is assumed that the best specimens will be photographed, and the inherent difficulties of the process should not be increased by faulty technique in the preparation. In general, a flat field with clearly contrasted structure, is desirable. The depth of vision with which an object is seen in a microscope is the sum of two factors; the focal depth of the objective and the accommodation of the eye. This latter factor is absent in the photographic plate, so sharp definition is obtained only in the critical plane. No such composite image is possible as the microscopist often obtains visually by small alterations in the focus; hence the necessity for a flat field and a sharp focus.

Sensitive Plates.—As noted above, the ordinary plate is not sensitive to red and yellow light, but plates may now be obtained that are more or less sensitive to these colors and are variously called orthochromatic, isochromatic and panchromatic, depending upon their particular qualities. It is necessary that achromatic
lenses be especially corrected for photography and that orthochromatic plates and often a color screen be used with them. With apochromatic lenses, ordinary plates may be used although the plates that are sensitive over the wider range are better. The red-sensitive plates must be handled in deep ruby light or total darkness. Another important correction is that for halation—a blurring of the image due to light diffusely reflected from the back of the glass plate. The manufacturers correct this by giving the plate an extra coating of absorbent film. Any plate may be rendered non-halation by "backing". A coating of caramel, colored with lamp black, is recommended. It may be applied to the glass side of the plate with a stiff brush and removed with a wad of damp cotton before development. In general, the plate should be developed for contrast and detail with considerable density. Hydroquinone and metol are satisfactory developers.

Exposure.—The time of exposure depends on so many variables that exact directions can not be given, but the following rule will be found valuable: Secure as satisfactory an arrangement as possible before exposure, determine the time of exposure by trial, and then keep the conditions constant, or at least vary only one at a time so that the effect can be calculated. This rule applies to light source and distance, magnification, plates, developer, printing paper and time of development and printing. To determine the exposure by trial, withdraw the dark slide one cm. at a time at 10-sec. intervals thus obtaining a series of strips of known exposures. When developed for an average time, there is no difficulty in determining which is the best. The development of the plate gives much information in regard to the correctness of the exposure. Although, in special cases, a negative may be intensified or reduced, it is generally better to repeat the exposure until a satisfactory negative is obtained.

The Positive.—The positive print may be either on paper or on a lantern slide. If $3\frac{1}{2} \times 4\frac{1}{2}$ plates are used, they will be very convenient for printing slides by contact. Because the light shines through the lantern slide, thus giving the variations in shading with all the wealth of detail, it is really the best kind of a positive. For printing paper, a glossy surface especially sensitized for contrasted effects, is essential and the prints may then be burnished or squeegeed.
Color Photography.—The modern idea of color photography is not to reproduce in the negative or positive print the actual colors of the object, but to get in monotone the shading which we see in the colors. If one wishes to photograph a relatively weak color with increased contrast, the general rule is to use a plate but slightly sensitive to that color, and a screen cutting off the color of the preparation. Under these conditions, the object will photograph as though it were black. On the other hand, if it is desired to decrease the effect of a certain color or "hold it back", a light of the same color should be used and a plate sensitive to that color. Thus if a red flower were photographed with a red light and a red sensitive plate, the negative would be strongly affected, but the positive would be light.

The color screens may be made of a glass cell filled with various colored liquids of different densities, or they may be made of colored glass. Several of the dry plate manufacturers have a series of screens spectroscopically adjusted to work with certain plates.

Ultra-violet Light.—The use of ultra-violet light in photomicrography has been one of the most beautiful developments in this science. A short theoretical discussion will be necessary for the proper appreciation of this point. The resolving power of a lens, i.e., its property of showing two points close together as distinct and not fused into one, is, for central lighting, directly proportional to the numerical aperture and inversely proportional to the wave length of light used. The numerical aperture in turn is directly proportional to the index of refraction of the glass and the sine of half of the angle included between the lines drawn from the principal focus to the ends of a diameter of the lens. The numerical aperture for dry mountings in air must always be less than unity, and is limited in practice to 1.50 for the best oil immersion. Thus there is a practical mechanical limit to the resolving power of an objective with any of the kinds of glass now available for lenses. Now the resolving power might be increased by decreasing the wave length of the light used, but the eye is not sensitive much beyond the violet, and, too, ordinary lens glass is opaque to the short wave lengths. Fortunately, fused quartz is transparent to ultra-violet light and the photographic plate is sensitive to it. By making all the lenses of quartz glass and pro-
roducing the light by sparking between cadmium electrodes, the resolving power of a microscope may be doubled. The light from the cadmium spark has a wave length of 0.275 μ as compared with 0.589 μ for yellow sodium light, and is unusually monochromatic, thus eliminating the necessity of correcting for chromatic aberration. It is found also that many organic objects that are colorless under white light act as if they were colored under the ultra-violet. To render the object visible for selection and focusing, a uranium glass is used that fluoresces under the action of the ultra-violet light. The equipment for this work is rather expensive, on account of the extra apparatus necessary to produce the light, and the cost of the quartz lenses, which are monochromatic and not available for other work.

APPLICATIONS OF PHOTO-MICROGRAPHY.

Since the biologist has always made the largest use of the microscope, much of the technique of photo-micrography has been developed for his particular use and for the text-book written from his point of view, but there are other important fields of application of which two will be discussed by way of illustration.

Metallurgy.—Chemical analysis will give the percentage composition of a substance, but sometimes a wide difference in physical properties is found in substances having the same chemical composition. The application of the modern theory of solutions to solids has led to a remarkable development in our knowledge of alloys, and in this work thermal analysis and microscopic examination have been the chief aids to chemical analysis. It has been found that such physical properties as hardness, tensile strength or thermal conductivity are functions of the crystalline structure which may be seen in the microscope when the specimen is properly prepared. In the case of our best known alloy, steel, the physical properties of any given specimen are largely determined by the heat treatment, and the microscope shows that this treatment is accompanied by a definite change in structure. In the investigation described in this bulletin, an attempt was made to find a relation between the magnetic properties and the structure in the Heusler alloys, and although this was not established, there evidently is a relation between the structure and the heat treatment. When the structure associated with particular properties has once been established, a microscopical
examination is a rapid and convenient test for these properties, and the photograph is a good method of recording the data.

The technique for the study of metals differs in several points from that for transparent substances. Because the metals are opaque, it is necessary to use reflected light. With long focus objectives, the illumination may be from the side, but should be as nearly vertical as possible to prevent loss by reflection. For higher magnifications, some form of vertical illumination is used. It consists generally of a prism or glass plate inserted in the microscope tube above the objective, and set at such an angle that it reflects the light received through an aperture in the side of the tube down through the objective on to the specimen. A point to be noted is that the insertion of this illuminator increases the tube length and must be compensated for in the sliding sleeve as the lens system is corrected for a given length of tube, usually 170 mm. The common microscope objectives are corrected for the thickness of the cover-glass, and hence for work with dry mountings, it is necessary to have objectives without this correction, or with a device in the objective to compensate for it.

The application of photo-micrography to the study of the Heusler alloys has been given in detail on page 23 of this bulletin, and illustrates the general methods, though each alloy requires some special treatment. With alloys of better mechanical properties, the grinding and polishing are much simpler processes than those described. There seems to be no definite rule by which one can determine the best etching agent, and a large number of acids, bases or salts may have to be tried before a satisfactory one is found. Sometimes beautiful oxidation effects can be produced by heating, and indeed, it is difficult to prevent these effects at ordinary temperatures. If the specimens are to be preserved, they may be coated with a very thin transparent varnish.

Geology.—The microscope is in common use in geology, and a series of photo-micrographs gives an unsurpassed method of comparing a number of specimens. The size and shape of rock crystals not only furnish a means of recognizing the kinds of crystals, but may enable one to estimate the temperature at which they were formed and the rate of cooling, problems of particular importance to the dynamical geologist. Many speci-
men can be ground thin and viewed by transmitted light and others may be seen by side or vertical illumination. The use of polarized light brings out the anisotropic optical properties and shows the axial placing of the crystals. The color effects with polarized light are most beautiful. By a suitable combination of transmitted light, reflected light and dark ground illumination with long focus planar objectives, one may obtain photographs of minute fossils that show both the external form and a certain amount of internal structure.

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United States Experiment Station, State Laboratory of Natural History, Biological Experiment Station on Illinois River, State Water Survey, State Geological Survey.

Engineering Experiment Station. A department organized to investigate problems of importance to the engineering and manufacturing interests of the State.

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