THE STRUCTURE AND MAGNETIC PROPERTIES
OF SOME TERNARY ALLOYS CONTAINING
MANGANESE AND BORON

by

MAX LYNN SWANSON

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department
of
METALLURGY

We accept this thesis as conforming to the
standard required from candidates for the
degree of MASTER OF SCIENCE.

Members of the Department of
Metallurgy.

THE UNIVERSITY OF BRITISH COLUMBIA

October, 1954.
ABSTRACT

Binary alloys of manganese and boron and ternary alloys of manganese and boron with aluminum, zinc, tin and indium were prepared. Their structures were determined from x-ray powder photographs, and their ferromagnetic properties were measured with a Sucksmith ring balance, using a powerful electromagnet. The orthorhombic phase MnB had a ferromagnetic Bohr magneton number of 1.73 per molecule and a Curie point of 309°C. Most of the ternary alloys were slightly ferromagnetic, but no strongly ferromagnetic single phase regions were found.

Paramagnetic measurements on Heusler alloys showed that they followed the Curie-Weiss law for the restricted range of temperature in which measurements could be made.
ACKNOWLEDGEMENTS

The author is grateful for assistance rendered by members of the staff of the Metallurgy department, especially his research director, Dr. H. Myers, and Mr. R. Butters.

The work was done with the help of funds provided by the Defense Research Board under Research Grant 281.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. MAGNETIC MEASUREMENTS</td>
<td>5</td>
</tr>
<tr>
<td>Theory</td>
<td></td>
</tr>
<tr>
<td>Apparatus</td>
<td>5</td>
</tr>
<tr>
<td>III. X-RAY MEASUREMENTS</td>
<td>9</td>
</tr>
<tr>
<td>IV. SUMMARY OF WORK DONE</td>
<td>10</td>
</tr>
<tr>
<td>V. PREPARATION OF ALLOYS</td>
<td>11</td>
</tr>
<tr>
<td>VI. RESULTS</td>
<td>13</td>
</tr>
<tr>
<td>1. Manganese-Boron alloys</td>
<td></td>
</tr>
<tr>
<td>2. Manganese-Aluminum-Boron alloys</td>
<td>21</td>
</tr>
<tr>
<td>3. Manganese-Zinc-Boron alloys</td>
<td>23</td>
</tr>
<tr>
<td>4. Manganese-Tin and Manganese-Tin-Boron alloys</td>
<td>27</td>
</tr>
<tr>
<td>5. Manganese-Indium and Manganese-Indium-Boron alloys</td>
<td>30</td>
</tr>
<tr>
<td>VII. PARAMAGNETIC MEASUREMENTS ON HEUSLER ALLOYS</td>
<td>31</td>
</tr>
<tr>
<td>VIII. DISCUSSION OF RESULTS AND CONCLUSIONS</td>
<td>38</td>
</tr>
<tr>
<td>IX. BIBLIOGRAPHY</td>
<td>41</td>
</tr>
</tbody>
</table>
# ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Illustration</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The ferromagnetic ring balance</td>
<td>7</td>
</tr>
<tr>
<td>2. Pole pieces producing a uniform field gradient</td>
<td>7</td>
</tr>
<tr>
<td>3. Ferromagnetic Curie point determination for MnB</td>
<td>17</td>
</tr>
<tr>
<td>4. Magnetic moment per unit mass divided by saturation moment, ( \sigma/\sigma_0 ) against absolute temperature divided by ferromagnetic Curie point, ( T/\Theta_F )</td>
<td>18</td>
</tr>
<tr>
<td>5. The determination of the saturation moment at absolute zero of MnB.</td>
<td>19</td>
</tr>
<tr>
<td>6. The paramagnetism of MnB</td>
<td>20</td>
</tr>
<tr>
<td>7. Manganese-aluminum-boron ternary diagram showing phases at room temperature</td>
<td>22</td>
</tr>
<tr>
<td>8. Manganese-zinc-boron ternary diagram showing phases at room temperature</td>
<td>25</td>
</tr>
<tr>
<td>9. Manganese-tin-boron ternary diagram showing phases at room temperature</td>
<td>29</td>
</tr>
<tr>
<td>10. The paramagnetism of Cu(_2)MnIn</td>
<td>34</td>
</tr>
<tr>
<td>11. The paramagnetism of Cu(_2)MnAl</td>
<td>35</td>
</tr>
<tr>
<td>12. The paramagnetism of Cu(_3)MnAl</td>
<td>36</td>
</tr>
<tr>
<td>13. The paramagnetism of Cu(_2)MnSn</td>
<td>37</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

It was assumed by Langevin that a paramagnetic substance consisted of non-interacting atoms or molecules, each having a permanent magnetic moment. If in a magnetic field these moments are distributed statistically, the magnetic susceptibility of the substance is:

\[ \chi = \frac{C}{T} \]  \hspace{1cm} (1)

where \( C \) is the Curie constant of the substance, and \( T \) is the absolute temperature. \( \chi \) is defined as the magnetic moment per unit mass, \( \sigma \), divided by the applied field, \( H \).

Weiss modified the Langevin theory by considering that interactions between atoms produced an internal field which was proportional to the magnetisation or magnetic moment per unit volume, \( I \). This field, \( NI \), is added to the external field to give the effective field:

\[ H_e = H + NI \]

\( N \) is the Weiss inter-molecular field constant. The Curie-Weiss law results from substituting this effective field for the applied field in equation (1):

\[ \chi = \frac{C}{T - \Theta} \]  \hspace{1cm} (2)
\( \Theta \) is the paramagnetic Curie point. For a gram molecular weight of substance,

\[
\Theta = \frac{Np \sigma_{OM}^2}{3RM} = \frac{Np CM}{M}
\]

where \( p \) is the density, \( \sigma_{OM} \) is the gram molecular saturation magnetic moment, \( R \) is the gas constant and \( M \) is the molecular weight.

If \( N \) and thus \( \Theta \) are positive, the substance is ferromagnetic, because, as can be shown, there may exist below \( T = \Theta \) a spontaneous magnetisation in the substance. This magnetisation increases as \( T \) decreases, approaching a maximum as \( T \) approaches zero. For \( T \) greater than \( \Theta \), equation (2) is true, and the substance is paramagnetic.

The spontaneous magnetisation of a body is directed differently in different regions, called domains. The resultant magnetisation is zero, because of the random distribution of the magnetic directions. Only a relatively small external field is required to line up the directions of magnetisation, and thus make the body ferromagnetic as a whole.

Experimental evidence (especially gyromagnetic ratio measurements) indicates that the magnetic moment for ferromagnetic substances is caused by electron spin. The moment of a spinning electron is one Bohr magneton, \( \mu_B = \frac{e\hbar}{2\mu_0} = 9.27 \times 10^{-21} \text{erg/gauss} \), where \( e \) and \( m \) are the charge and mass of the electron, and \( h \) is Planck's constant. A pair of electron spins can be directed only parallel or antiparallel. If interactions cause an excess of spin moments to point in one direction, spontaneous magnetisation exists.

The collective electron theory presents a model of the metallic state which is more realistic than that of Weiss. Outer electrons of atoms are thought of as shared collectively through the substance. Although
this model leads to satisfactory results for simple substances, such as nickel and its alloys with copper, the quantum mechanical problems involved in the study of more complex substances are too difficult to be solved.

Atomic interactions are mainly due to the outer electron shells. Heisenberg postulated that the exchange interaction energy between the same shells (i.e.: 3d shells of transition metals) of adjacent atoms could be positive, in which case the electrons line up with parallel spins, producing ferromagnetism. This postulate has had as yet no quantitative theoretical verification. Zener, on the contrary, postulated that the exchange energy between adjacent atomic 3d shells of transition metals was always negative, and that ferromagnetism was caused by coupling between 3d and 4s shell electrons of the same atom. The results of this assumption are not in good agreement with observed properties.

Using Heisenberg's postulate, Slater and Bethe have assumed the following variation of the exchange energy, \( J \), with the ratio of the internuclear distance, \( D \), to the 3d shell diameter, \( d \).

![Diagram showing variation of exchange energy with \( D/d \)](image)

It is seen from this curve that the exchange energy is positive and large enough to cause ferromagnetism for values of \( D/d \) slightly greater than 1.55 (e.g.: Fe, Co and Ni). Thus paramagnetic
manganese, with a ratio only slightly less than 1.55, could become ferromagnetic if its internuclear distance were increased so that D/d became greater than 1.55. This increase occurs for ferromagnetic manganese alloys and compounds:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu$_2$MnIn</th>
<th>Cu$_2$MnAl</th>
<th>Cu$_2$MnSn</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/d</td>
<td>2.98</td>
<td>2.84</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Previous work in the University of British Columbia Metallurgy department has shown that an ordered face-centered cubic ferromagnetic phase occurs in the ternary alloys of manganese and carbon with a metal (X) having high valency and a positive size factor with respect to manganese. Aluminum, zinc, tin and indium were used successfully in this capacity. The optimum composition for this phase is Mn$_3$XC; carbon occupies the body centered position.

This work suggests that similar alloys with the carbon replaced by boron or nitrogen may exist. In the work to be described, boron alloys with similar structures and magnetic properties to those containing carbon were sought. Little is known about binary boron alloys and none about the ternary alloys considered.
II. MAGNETIC MEASUREMENTS

Theory.

Magnetic measurements of the saturation magnetic moment per unit mass, \( \sigma \), and the susceptibility, \( \kappa \), were required. The principle for the determination of these quantities is the measurement of the force exerted on a specimen of mass \( m \) when placed in an inhomogeneous magnetic field. This force is:

\[
F = \sigma m \frac{\partial H}{\partial z} = \kappa m H \frac{\partial H}{\partial z}
\]

The method used was based on a comparison of the specimen having unknown \( \sigma \) and \( \kappa \) with a standard substance. If \( H \frac{\partial H}{\partial z} \) is kept constant while the force is being measured for the specimen and the standard, \( \sigma \) and \( \kappa \) can be determined without knowing the value of \( H \frac{\partial H}{\partial z} \), since

\[
\frac{F_1}{F_2} = \frac{\kappa_1 m_1}{\kappa_2 m_2}
\]

Apparatus: (a) The Magnet:

The magnetic field was produced by an electromagnet of the Weiss type, built by R. Shier and G. Kidson while in this department. A maximum field of 21,500 gauss could be attained. To produce a constant vertical field gradient, the pole pieces were shaped as shown in figure 2.

(b) The Ferromagnetic Balance:

The force exerted on a ferromagnetic specimen placed in the region of constant field gradient was measured using a Sucksmith ring
balance (Figure 1). The deflection of a light beam reflected from mirrors suitably attached to the beryllium copper ring was proportional to the force distorting the ring. A molybdenum rod was used to connect the ring to a platinum iridium collar, into which a cylindrical platinum iridium specimen box could be placed. A very convenient specimen size of only thirty milligrams was normally needed. Pure iron was used as a standard.

(c) The Paramagnetic Apparatus:

The paramagnetic apparatus differed from the ferromagnetic apparatus only in the following particulars:

(i) the balance was similar but more sensitive.
(ii) the molybdenum rod was replaced by a silica tube.
(iii) the specimen was either machined into a ring shape or carried in a carbon capsule. It was attached by means of a wire clamp placed in a groove at the bottom of the silica tube (see sketch).

![Silica tube, specimen, clamp, thermocouple diagram]

A specimen size of only 100 mg. was adequate. Allowance was made for specimen carrier deflections. Nickel was used for calibration.

Some sizes for the ring balance are:

Ring diameter = 6 cm.

Ferromagnetic ring: 3 mm. by 0.3 mm. thick; spiral springs: 0.3 mm. thick.

Paramagnetic ring: 3 mm. by 0.1 mm. thick; spiral springs: 0.1 mm. thick.
Balance Mirrors  

Microscope  

Beryllium Copper Ring  

Oil Damping  

Molybdenum rod  

Flat Spiral Springs  

Specimen Box  

Figure 1: The ferromagnetic ring balance

Figure 2: Pole pieces producing a uniform field gradient.
(d) High and Low Temperature Apparatus:

For low temperature magnetic measurements the specimen was suspended just above liquid oxygen in a Dewar flask. A copper-constantan thermocouple in conjunction with a potentiometer, a standard cell and a galvanometer was used to measure the temperature.

High temperature measurements were made in a specially constructed water cooled furnace. A platinum-platinum rhodium thermocouple was used.

The ring balances and high and low temperature apparatus were built by H. Myers and R. Butters of this department.
III. X-RAY MEASUREMENTS

A Philip's x-ray machine and Straumanis type powder cameras were used to take photographs of samples of all the alloys. The resulting Debye-Scherrer powder patterns were measured. Film shrinkage effects were eliminated by referring all distances to that distance known to correspond to a Bragg angle of 90°.

The films were indexed by using the ratios of the sin²θ values of the lines; the equation for sin²θ in the cubic system is:

\[
\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)
\]

where θ is the Bragg angle, λ is the wave length of the x-radiation, a is the parameter of the unit cell, and h, k, l are the indices of the reflecting plane. Parameters were calculated from the same equation, and plotted against the Taylor-Sinclair function to eliminate the error caused by absorption of x-rays by the specimen.
IV. SUMMARY OF WORK DONE.

The following alloy systems were investigated:

1. Mn - B
2. Mn - Al - B
3. Mn - Zn - B
4. Mn - Sn - B
5. Mn - In - B

Other binary alloys were made to aid in identification of phases. Magnetic measurements were made on ferromagnetic alloys, MnB in particular.

Paramagnetic measurements were also made for some Heusler alloys.
V. PREPARATION OF ALLOYS

Two methods of preparation were used:

(1) Induction Melting:

The alloy components were heated in alumina crucibles under argon at atmospheric pressure by induced eddy currents. The melts were chill cast into a brass mould if possible. The resulting ingots were homogenized in evacuated silica tubes or under an argon atmosphere. Samples were mounted in lucite and examined microscopically.

(2) Sintering:

Because of the difficulty in melting by induction alloys containing zinc or a large proportion of boron, they were prepared by sintering intimately ground mixtures of their components. The mixtures were heated in evacuated silica tubes containing very little free volume. The following alloys were sintered:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sinter Components</th>
<th>Temperature (°C)</th>
<th>Time (hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnB</td>
<td>Mn;B</td>
<td>950 - 1050</td>
<td>72</td>
</tr>
<tr>
<td>MnAl₂B</td>
<td>MnAl₂;B</td>
<td>900</td>
<td>72</td>
</tr>
<tr>
<td>Mn₆Al₃B₁₁</td>
<td>MnAl₂;Mn;B</td>
<td>900</td>
<td>72</td>
</tr>
<tr>
<td>All Mn-Zn-B</td>
<td>Mn;Zn;B</td>
<td>900</td>
<td>72</td>
</tr>
<tr>
<td>MnSnB</td>
<td>MnSn;B</td>
<td>600</td>
<td>75</td>
</tr>
<tr>
<td>MnInB</td>
<td>MnIn;B</td>
<td>1000</td>
<td>48</td>
</tr>
</tbody>
</table>
The materials used in the preparation of the alloys were:

Manganese: 99.9% purity, donated by the Electromanganese Corporation of America.

Aluminum: 99.99% purity, donated by the Aluminum Company of Canada.

Zinc: dust; 98% purity (major impurity being oxygen)

Tin: 99.99% purity

Indium: 99.99% purity, donated by the Consolidated Mining and Smelting Company of Canada.

Copper: 100.0% purity

Boron: 'pure amorphous' and 99.2% purity.
VI. RESULTS

1. Manganese-Boron Alloys:

Previous Work: Heusler\(^6\) (1904), Jassoneix\(^7\) (1906) and Wedekind\(^8\) (1907) first investigated manganese-boron alloys. They reported that only MnB was ferromagnetic.

H. Forestier and M. Graff\(^9\) (1936) found the Curie point of MnB to be about 300°C. R. Hocart and M. Fallot\(^10\) (1936) evaluated the moment of the manganese atom in MnB at 9.65 (± 5%) Weiss magnetons; they discovered the structure to be orthorhombic with eight MnB per unit cell and with parameters \(a = 2.95\), \(b = 11.5\), \(c = 4.10\)\(\text{Å}\).

R. Kiessling\(^11\) (1950) found four manganese-boron phases:

- \(\text{MnB}\): orthorhombic: \(a = 5.560\), \(b = 2.977\), \(c = 4.145\)\(\text{Å}\) with 4 MnB per cell.
- \(\text{Mn}_3\text{B}_4\): orthorhombic: \(a = 3.032\), \(b = 12.86\), \(c = 2.960\)\(\text{Å}\) with 2 \(\text{Mn}_3\text{B}_4\) per cell.
- \(\text{Mn}_2\text{B}\): tetragonal: \(a = 5.148\), \(c = 4.208\)\(\text{Å}\) with 4 \(\text{Mn}_2\text{B}\) per cell.
- \(\text{Mn}_4\text{B}_{13}\): orthorhombic: \(a = 14.53\), \(b = 7.29\), \(c = 4.21\)\(\text{Å}\) with 8 \(\text{Mn}_4\text{B}\) per cell.

Only MnB was ferromagnetic.
Results: The results are tabulated:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat Treatment</th>
<th>Phases at Room Temperature</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnB</td>
<td>chill cast; homogenized</td>
<td>MnB; Mn_2B</td>
<td>strong (\sigma_0 = 147); (\theta_F = 309^\circ C)</td>
</tr>
<tr>
<td></td>
<td>sintered</td>
<td>MnB</td>
<td></td>
</tr>
<tr>
<td>Mn_{54}B_{46}</td>
<td>homogenized 50 hrs. at 1000°C.</td>
<td>MnB; Mn_2B</td>
<td>(\sigma_0 = 100)</td>
</tr>
<tr>
<td>Mn_{58}B_{42}</td>
<td>homogenized 50 hrs. at 1000°C.</td>
<td>Mn_2B; MnB</td>
<td>(\sigma_0 = 50)</td>
</tr>
<tr>
<td>Mn_2B</td>
<td>homogenized 50 hrs. at 1000°C.</td>
<td>Mn_2B; Mn_4B; (\alpha - \text{Mn})</td>
<td>None</td>
</tr>
<tr>
<td>Mn_3B</td>
<td>chill cast</td>
<td>Mn_2B; Mn_4B; (\alpha - \text{Mn})</td>
<td>None</td>
</tr>
<tr>
<td>Mn_4B</td>
<td>homogenized 50 hrs. at 1000°C.</td>
<td>Mn_4B; (\alpha - \text{Mn})</td>
<td>None</td>
</tr>
</tbody>
</table>

The phases MnB, Mn_2B and Mn_4B had the same structures and parameters as those found by Kiessling. The \(\alpha - \text{manganese}\) phase seemed to be almost as stable as the Mn_2B and Mn_4B phases, since it occurred in the alloys Mn_2B, Mn_3B and Mn_4B even after homogenization. It is possible that impurities in the boron stabilized the \(\alpha - \text{Mn}\) phase.

The sintered alloy MnB was single phase, but the induction melted MnB, which was only slightly off composition, had a little Mn_2B phase present. Thus the range of composition for the single phase, MnB, is narrow.

Magnetic Properties:

The magnetic properties of the MnB phase were investigated for two different specimens:

(1) For the first specimen, the magnetic moment per unit mass, \(\sigma\), was 136 ergs per gram per oersted at 20°C. (measured using a field of 16,000 gauss). If \(\sigma\) is plotted against absolute temperature
squared, $T^2$, at low temperatures, a straight line results, which when extrapolated to absolute zero gives the saturation moment, $\sigma_0$. Such a line was plotted for the MnB specimen, using temperatures down to 140°C; the resulting value of $\sigma_0$ was 147.

The ferromagnetic Bohr magneton number for a molecule of a substance having gram molecular weight $M$ is $P_B = \frac{M \sigma_0}{5585}$. For the MnB, $P_B = \frac{65.75 \times 147}{5585} = 1.73 \mu_B$ per MnB molecule, or per manganese atom. For purposes of comparison, this is almost identical with the value for pure cobalt: $P_B = 1.72$.

The ferromagnetic Curie point, $\Theta_F$, of MnB was determined by plotting $\sigma^2$ against $T$ (Figure 3). This plot produces a straight line near the Curie point, which was found to be 309°C.

Also, $\sigma / \sigma_0$ was plotted against $T / \Theta_F$ (Figure 4). As this curve is generally structure sensitive, the plot for MnB differed from that for nickel.

(2) For the second specimen the results were:

$\sigma = 132$

$\sigma_0 = 143$ (Figure 5); $P_B = 1.68$

$\Theta_F = 304°C$.

This specimen probably had a small amount of a second phase present.

Paramagnetic measurements were made on this MnB specimen. The paramagnetism followed the Curie-Weiss law (Figure 6):

$$\chi = \frac{C}{T - \Theta}$$
The values calculated for the constants were: \( C = 1.48 \times 10^{-2} \) per gram and the paramagnetic Curie point, \( \Theta = 305^\circ C \). This value agrees well with the ferromagnetic Curie point of 304°C. The paramagnetic Bohr magneton number, \( P_B = 2.828 \sqrt{CM} \) per molecule. For MnB, \( P_B = 2.79 \) per molecule. The ratio between this value and the ferromagnetic Bohr magneton number, 1.68, is of the usual order of magnitude.
Figure 3: Ferromagnetic Curie point determination for MnB (first specimen):

Magnetic moment per unit mass, $\sigma$, and moment squared, $\sigma^2$, against temperature, $T$. 
Figure 4: Magnetic moment per unit mass divided by saturation moment, $\sigma/\sigma_s$, against absolute temperature divided by ferromagnetic Curie point, $T/\Theta_F$. 
Figure 5: The determination of the saturation moment at absolute zero of MnB (second specimen):
Magnetic moment per unit mass, $\sigma$, against absolute temperature squared, $T^2$. 
Figure 6: The paramagnetism of MnB (second specimen):

The inverse of susceptibility, $1/\chi$ ($\chi$ is measured in ergs per gram per oersted), against temperature, $T$. 
2. Manganese-Aluminum-Boron-Alloys

Previous Work: No previous work has been done on Mn-Al-B alloys. The phase diagram of the Mn-Al system is well known.

Results:

All alloys were homogenized for 50 hrs. at 800 to 1000°C.

The main phases occurring were β-manganese, MnB, Mn₂B, and the body-centered cubic $\delta$ phase of the manganese-aluminum system (Figure 7). The Mn₂B phase had slightly larger parameters than it had in the binary alloys. The alloy MnAl₂ was made in order to obtain the $\delta$ phase.

The results were as follows:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat Treatment</th>
<th>Phases at Room Temperature</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₆Al₃B</td>
<td></td>
<td>$\beta$ -Mn; cubic</td>
<td>slight</td>
</tr>
<tr>
<td>Mn₄.₅Al₄.₅B</td>
<td></td>
<td>$\delta$</td>
<td>$\sigma = 15.7; \theta_F = 310°C$</td>
</tr>
<tr>
<td>Mn₃Al₅B</td>
<td>as-cast homogenized</td>
<td>MnB</td>
<td>slight</td>
</tr>
<tr>
<td>Mn₃Al₂B</td>
<td></td>
<td>$\delta$; MnB</td>
<td>$\sigma = 43.9; \theta_F = 310°C$</td>
</tr>
<tr>
<td>Mn₂Al₂B</td>
<td>as-cast</td>
<td>MnB</td>
<td>medium</td>
</tr>
<tr>
<td>MnAl₂B</td>
<td>as-cast or sintered</td>
<td>MnB</td>
<td>slight</td>
</tr>
<tr>
<td>Mn₄AlB</td>
<td>homogenized</td>
<td>$\beta$ -Mn; Mn₂B</td>
<td>none</td>
</tr>
<tr>
<td>Mn₃AlB</td>
<td></td>
<td>$\beta$ -Mn; Mn₂B</td>
<td>none</td>
</tr>
<tr>
<td>Mn₂.₅AlB</td>
<td>as-cast homogenized</td>
<td>MnB; $\beta$ -Mn</td>
<td>medium</td>
</tr>
<tr>
<td>Mn₂AlB</td>
<td></td>
<td>$\delta$; MnB</td>
<td>$\sigma = 55.9; \theta_F = 310°C$</td>
</tr>
<tr>
<td>Mn₁.₅AlB</td>
<td></td>
<td>$\delta$, MnB</td>
<td>$\sigma = 67.3$</td>
</tr>
<tr>
<td>MnAlB</td>
<td>as-cast homogenized</td>
<td>MnB</td>
<td>$\sigma = 66.0$</td>
</tr>
<tr>
<td>Mn₆Al₃B₁₁</td>
<td>sintered</td>
<td></td>
<td>$\sigma = 22.9; \theta_F = 71.2$</td>
</tr>
</tbody>
</table>
Figure 7: Manganese-Aluminum-Boron Ternary Diagram

Showing Phases at Room Temperature

□ denotes non-ferromagnetic alloy
○ denotes ferromagnetic alloy
Where no heat treatment is given in the Table, the alloys had the same structures before and after homogenization, and the magnetic measurements apply to the homogenized alloys.

It is seen that the alloys \( \text{Mn}_3\text{Al}_6\text{B} \), \( \text{MnAl}_2\text{B} \), \( \text{Mn}_2.5\text{AlB} \) and \( \text{MnAlB} \) are the only ones having unstable phases in the as-cast state. The important unstable phase is \( \text{MnB} \), which forms readily in alloys with high boron and low manganese content.

The ferromagnetism of the \( \text{Mn-Al-B} \) alloys prepared was largely due to the \( \text{MnB} \) phase.

3. **Manganese-Zinc-Boron-Alloys.**

**Previous Work:** No previous work has been done on \( \text{Mn-Zn-B} \) alloys.

For the \( \text{Mn-Zn} \) system, the phase diagram from zero to fifty weight percent zinc was studied by E. Potter and R. Huber\textsuperscript{13} (1949). Room temperature phases were \( \alpha - \text{Mn}; \beta - \text{Mn} \), and \( \alpha - \text{Zn} \). \( \alpha - \text{Zn} \) is face-centered cubic with four atoms per unit cell. It is formed by decomposition of \( \varepsilon \) (which is close packed hexagonal with two atoms per unit cell) only after very slow cooling to room temperature.

The phase diagram from fifty to one hundred weight percent zinc was studied by Schramm\textsuperscript{14} (1940).
Results:

The alloys were slightly ferromagnetic for a large range of composition.

The alloys and their properties are listed (Figure 8):

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phases at Room Temperature</th>
<th>Britteness</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₁₁Zn₇B₂</td>
<td>50% $\alpha$ - Mn; 45% $\Theta$</td>
<td>malleable</td>
<td>medium</td>
</tr>
<tr>
<td>Mn₆Zn₁₀B₂</td>
<td>60% $\alpha$ - Mn; 30% $\Theta$</td>
<td>malleable</td>
<td>slight</td>
</tr>
<tr>
<td>Mn₆ZnB</td>
<td>75% $\beta$ - Mn; 25% Mn₄B</td>
<td>brittle</td>
<td>none</td>
</tr>
<tr>
<td>Mn₃ZnB</td>
<td>75% Mn₄B</td>
<td>slightly brittle</td>
<td>slight</td>
</tr>
<tr>
<td>Mn₂ZnB</td>
<td>50% $\alpha$ - Mn; 50% Mn₄B</td>
<td>brittle</td>
<td>very slight</td>
</tr>
<tr>
<td>Mn₁₅ZnB</td>
<td>50% $\alpha$ - Mn; 25% Mn₄B; 25% $\Theta$</td>
<td>brittle</td>
<td>medium</td>
</tr>
<tr>
<td>MnZnB</td>
<td>50% $\gamma$</td>
<td>brittle</td>
<td>$\sigma = 56$, $\sigma_0 = 64$; remanent</td>
</tr>
<tr>
<td>Mn₁₅ZnB</td>
<td>60% Zn; 30% $\Omega$</td>
<td>malleable</td>
<td>none</td>
</tr>
<tr>
<td>Mn₁₀Zn₃B₇</td>
<td>75% Mn₄B</td>
<td>brittle</td>
<td>medium</td>
</tr>
<tr>
<td>Mn₉ZnB₈</td>
<td>80% $\phi$</td>
<td>brittle</td>
<td>$\sigma = 104$; remanent</td>
</tr>
<tr>
<td>Mn₆Zn₂B₁₀</td>
<td>70% $\phi$; 30% $\Omega$</td>
<td>brittle</td>
<td>strong; remanent</td>
</tr>
</tbody>
</table>

Only the first two listed alloys required annealing after filing to produce good X-ray photographs.

Phases occurring were:

1. $\beta$ - Mn and Mn₄B: These phases are well known.

2. Body-centered cubic $\alpha$ - Mn type: This phase was similar to $\alpha$ - Mn, and had parameters $a_0 = 8.888$ Å for Mn₁₁Zn₇B₂ and $a_0 = 9.169$ Å for Mn₂ZnB. It was slightly tetragonal for the Mn₉ZnB₁₀ alloy.

3. $\Theta$, a cubic structure, probably ordered face-centered cubic: Its parameter was 3.913 Å for Mn₁₁Zn₇B₂. $\Theta$ was probably ferromagnetic only
Figure 8: Manganese-zinc-boron ternary diagram showing phases at room temperature.

- □ denotes non-ferromagnetic alloy
- ○ denotes ferromagnetic alloy
in the ordered state, since most of the ferromagnetism of Mn$_{11}$Zn$_7$B$_2$
was lost by filing.

(4) The pure zinc phase listed for the alloy Mn$_{0.5}$ZnB:
This is possibly not pure zinc, but a phase with the same structure
and parameters. (Such phases occurred for the Mn-Sn-B and Mn-In-B
systems).

(5) \(\Omega\), a non-magnetic phase of unknown structure
occurring in the alloys Mn$_{0.5}$ZnB and Mn$_3$Zn$_2$B$_{10}$.

(6) The \(\phi\) and \(\lambda\) phases, which were strongly ferromagnetic:
The \(\phi\) phase was almost as magnetic as MnB. It occurred in the alloys
Mn$_3$ZnB$_{10}$ and Mn$_3$Zn$_2$B$_{10}$, which were prepared to demonstrate that zinc
would not replace manganese to any appreciable extent in MnB. The \(\lambda\)
phase was present in the alloys Mn$_{1.5}$ZnB and MnZnB. Both \(\phi\) and \(\lambda\)
had complicated structures.

Previous Work: The manganese-tin system has been investigated by Potter\textsuperscript{15} (1931), Guillaud\textsuperscript{16} (1943), Nowotny and Schubert\textsuperscript{17} (1943) and Nial\textsuperscript{18} (1947).

Potter found for alloys annealed at 450 to 500°C:

\( \text{Mn}_4\text{Sn} \) was weakly ferromagnetic with \( \vartheta_F = 150°C \).
\( \text{Mn}_2\text{Sn} \) was strongly ferromagnetic with \( \vartheta_F = 0°C \).
\( \text{MnSn} \) was not ferromagnetic.

Nowotny and Schubert reported the following structures:

\( \text{Mn}_4\text{Sn}_3 \) : cph. with \( 2a = 5.65, c = 4.506\AA, \frac{c}{a} = 1.595 \)
\( \text{Mn}_2\text{Sn} \) : \( a = 4.392 - 4.370, c = 5.457 - 5.475\AA, \)
\( \frac{c}{a} = 1.242 - 1.250; \) crystallographically like the \( \text{NiAs} \) type.
\( \text{MnSn}_2 \) : tetragonal with \( a = 6.64\AA, c = 5.43\AA, \frac{c}{a} = 0.817. \)

Nial found the same phases with almost the same parameters except that \( \text{Mn}_4\text{Sn}_3 \) had \( a = 5.66\AA \)

Results: A. The following Mn-Sn alloys were melted:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phases at Room Temperature</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSn</td>
<td>75% MnSn(_2); 25% Mn(_2)Sn</td>
<td>medium at low temp.</td>
</tr>
<tr>
<td>Mn(_2)Sn</td>
<td>90% Mn(_2)Sn</td>
<td>medium at low temp.</td>
</tr>
<tr>
<td>Mn(_4)Sn</td>
<td>90% Mn(_{11})Sn(_3)</td>
<td>medium at low temp.</td>
</tr>
</tbody>
</table>

The phases MnSn\(_2\), Mn\(_2\)Sn and Mn\(_{11}\)Sn\(_3\) had the same parameters as found by Nial.
B. Mn-Sn-B alloys prepared were (Figure 9):

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phases at Room Temp.</th>
<th>Britteness</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn}_2\text{SnB}$</td>
<td>80% $\beta$ - Mn</td>
<td>brittle</td>
<td>none</td>
</tr>
<tr>
<td>$\text{Mn}_6\text{SnB}$</td>
<td>75% $\text{Mn}_{11}\text{Sn}_3$</td>
<td>brittle</td>
<td>medium at low temp.</td>
</tr>
<tr>
<td>$\text{Mn}_3\text{SnB}$</td>
<td>75% $\text{Mn}_2\text{Sn}$</td>
<td>brittle</td>
<td>medium at low temp.</td>
</tr>
<tr>
<td>$\text{MnSnB}$</td>
<td>80% $\Theta$; 20% $\text{MnSn}_2$</td>
<td>malleable</td>
<td>$\sigma = 33.8$; remanent</td>
</tr>
<tr>
<td>$\text{Mn}_2\text{Sn}_2\text{B}_2$</td>
<td>80% $\text{Mn}_2\text{Sn}$</td>
<td>brittle</td>
<td>medium at low temp.</td>
</tr>
<tr>
<td>$\text{Mn}_2\text{Sn}_2\text{B}_5$</td>
<td>50% $\text{Mn}_2\text{B}$; 30% $\text{Mn}_2\text{Sn}$ (possibly unstable)</td>
<td>brittle</td>
<td>medium at low temp.</td>
</tr>
<tr>
<td>$\text{Mn}<em>3\text{Sn}</em>{14}\text{B}_3$</td>
<td>70% Sn; 20% $\text{MnSn}_2$</td>
<td>malleable</td>
<td>slight at low temp.</td>
</tr>
</tbody>
</table>

The $\beta$ - Mn phase of $\text{Mn}_2\text{SnB}$ had parameter, $a_0 = 6.488\AA$.

The $\Theta$ phase was body-centered tetragonal with the same parameters as pure tin: $a = 5.831$, $c = 3.181\AA$.

This phase was the only ferromagnetic phase found, other than the binary Mn - Sn phases. It was strongly remanent.
Figure 9: Manganese-tin-boron ternary diagram showing phases at room temperature.

- □ denotes non-ferromagnetic alloy
- ○ denotes ferromagnetic alloy
5. Manganese-Indium and Manganese-Indium-Boron Alloys.

Previous Work: Zwicker\(^1\) (1951) found room temperature phases for the Mn-In system to be \(\alpha\) - Mn, Mn\(_3\)In and indium; Mn\(_3\)In had a \(\gamma\) - brass structure. Shirokoff's\(^2\) results agreed with these, except that the alloy Mn\(_2\)In had a \(\beta\) - Mn structure. No ferromagnetic phases were found. Goeddel and Yost\(^3\) (1951), however, reported ferromagnetism from 3 to 55 weight percent manganese.

Results: A. Mn-In alloys prepared were:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phases at Room Temp.</th>
<th>Brittleness</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(_9)In</td>
<td>(\beta) - Mn</td>
<td>very brittle</td>
<td>none</td>
</tr>
<tr>
<td>Mn(_3)In</td>
<td>(\gamma)</td>
<td>brittle</td>
<td>none</td>
</tr>
<tr>
<td>MnIn</td>
<td>(\gamma); In</td>
<td>very malleable</td>
<td>none</td>
</tr>
</tbody>
</table>

The \(\gamma\) phase was that previously reported. These results agree with those of Shirokoff.

B. Mn-In-B alloys prepared were:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phases at Room Temp.</th>
<th>Brittleness</th>
<th>Ferromagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(_6)InB</td>
<td>50% (\gamma); 40% Mn(_2)B</td>
<td>brittle</td>
<td>none</td>
</tr>
<tr>
<td>Mn(_3)InB</td>
<td>60% Mn(_2)B; 30% In</td>
<td>malleable</td>
<td>none</td>
</tr>
<tr>
<td>MnInB</td>
<td>90% (\theta)</td>
<td>malleable</td>
<td>medium</td>
</tr>
</tbody>
</table>

\(\beta\) - Mn could be retained in Mn\(_6\)InB by quenching. The ferromagnetic \(\theta\) phase had the same structure and almost the same parameters as indium, which is face-centered tetragonal with \(a = 4.594\text{Å}\) and \(c = 4.951\text{Å}\).

This phase corresponds to the \(\theta\) phase of the Mn-Sn-B system.
VII. PARAMAGNETIC MEASUREMENTS ON HEUSLER ALLOYS.

Procedure: Single phase Heusler alloys were prepared by induction melting and were homogenized. Powders were annealed and rapidly quenched to retain the ordered single phase.

Results: The following alloys were prepared:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Annealing Temp. (°C)</th>
<th>Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂MnIn</td>
<td>530</td>
<td>6.2084</td>
</tr>
<tr>
<td>Cu₂MnAl</td>
<td>800</td>
<td>5.9502</td>
</tr>
<tr>
<td>Cu₂₀.₉₇Mn₀.₀₈₂Al</td>
<td>850</td>
<td>5.9167</td>
</tr>
<tr>
<td>Cu₂MnSn</td>
<td>680</td>
<td>6.1654</td>
</tr>
<tr>
<td>Cu₁₁Mn₆Sn₃</td>
<td>640</td>
<td></td>
</tr>
</tbody>
</table>

Paramagnetic measurements were made on the first four listed alloys while they were cooling from temperatures near their melting points. The inverse of the susceptibility, $\frac{1}{x}$, was plotted against temperature, $T$, giving the following results:

1. The curve (Figure 10) for Cu₂MnIn was slightly convex toward the temperature axis. This behaviour is common for ferromagnetic phases. The Curie-Weiss law was used for a straight line drawn through the high temperature points to calculate: $C = 1.41 \times 10^{-2}$ per gram and $\Theta = 328°C$. (The ferromagnetic Curie point is 233°C). The paramagnetic Bohr magneton number was calculated to be $5.78\mu_B$ per molecule. This value compares favourably with the ferromagnetic value, $P_B = 4.4\mu_B$ per manganese atom.
2. The curves (Figures 11 and 12) for Cu$_2$MnAl and Cu$_3$MnAl were similar. Both had straight line sections for a range of 200°C above the Curie point, and thus obeyed the Curie-Weiss law for this range. The calculated constants were:

\[ \text{Cu}_2\text{MnAl} : \quad C = 4.96 \times 10^{-3} \text{ per gram; } \]
\[ \Theta = 283^\circ\text{C}. \]
\[ \sim \text{Cu}_3\text{MnAl} : \quad C = 4.85 \times 10^{-3} \text{ per gram; } \]
\[ \Theta = 175^\circ\text{C}. \]

The ferromagnetic Curie point, \( \Theta_F \), of Cu$_2$MnAl is 330°C. As \( \Theta_F \) is generally almost the same as the paramagnetic Curie point, \( \Theta \), these two values conflict. However, when Cu$_2$MnAl was cooled rapidly, the curve was depressed toward the temperature axis, and \( \Theta \) was raised to 350°C (± 10°C), which is about the expected value. The difference between the two curves for Cu$_2$MnAl was probably caused by a loss of order in the more slowly cooled alloy. No such difference occurred for Cu$_3$MnAl.

3. The curve (Figure 13) for Cu$_2$MnSn was a straight line from 400 to 600°C. The constants were:

\[ C = 3.92 \times 10^{-3} \text{ per gram. } \]
\[ \Theta = 219^\circ\text{C}. \]

The discrepancy between this value of \( \Theta \) and 340°C for \( \Theta_F \) is possibly caused by a loss of order in Cu$_2$MnSn while cooling.

At 390°C (± 5°C) the direction of the curve changed sharply, with \( \chi \) decreasing, indicating a rapid transformation to a non-ferromagnetic phase. The X-ray photograph verified this conclusion. This
result illustrates the use of magnetic measurements for phase boundary determinations.
Figure 10: The paramagnetism of Cu$_2$MnIn:

The inverse of susceptibility, $1/\chi$ ($\chi$ is measured in ergs per gram per oersted), against temperature, $T$ ($^\circ$C).
Figure 11: The paramagnetism of Cu₂MnAl:

The inverse of susceptibility, $1/\chi$ ($\chi$ is measured in ergs per gram per oersted), against temperature, T.
Figure 12: The paramagnetism of Cu$_3$MnAl:

The inverse of susceptibility, $1/X$ ($X$ is measured in ergs per gram per oersted), against temperature, $T$. 
Figure 13: The paramagnetism of Cu$_2$MnSn:

The inverse of susceptibility, $1/\chi$ ($\chi$ is measured in ergs per gram per oersted), against temperature, $T$. 
VIII. DISCUSSION OF RESULTS AND CONCLUSIONS

1. The saturation magnetic moment at absolute zero temperature for the purer specimen of MnB used was 147 ergs per gram per oersted. This result may be as much as two percent low, because of the possibility of a small amount of a second phase being present. The ferromagnetic Bohr magneton number was 1.73 \( \mu_B \) per MnB molecule (almost the same as the value for cobalt). This value is the same as that calculated for manganese when it forms \( d^2sp^3 \) octahedral bonds. Although octahedral bonds are not formed in MnB (which has the same orthorhombic structure as FeB), each manganese atom is surrounded by four atoms at 2.67\AA{} and two at 2.70\AA{}. Thus similar bonding probably occurs.

The ferromagnetic Curie point of MnB was 309°C, as compared with 1120°C for face-centered cubic cobalt. The paramagnetism of MnB followed the Curie-Weiss law closely; the paramagnetic Curie point was the same as the ferromagnetic one.

2. The ternary alloys investigated contained several ferromagnetic ternary phases. Some which merit further investigation are:

(1) The \( \Theta \) phases occurring in the alloys MnSnB and MnInB. These phases, besides having the same structures and parameters as tin and indium, had almost the same line intensities on the x-ray photographs. They were malleable, but retained their magnetism after cold working.
(2) The cubic \( \phi \) phase of the Mn-Zn-B system, occurring for alloys with boron content of ten atomic percent. This phase was apparently ferromagnetic only in the ordered state, and became disordered when cold worked.

(3) The phase, of unknown structure, occurring in the alloy \( \text{Mn}_6\text{Al}_3\text{B}_{11} \). This phase had a low Curie point, since the magnetic moment per unit mass was more than three times greater at absolute zero than at room temperature. It was the only Mn-Al-B phase found with a Curie point near room temperature.

The fact that there were no ferromagnetic phases like the ordered face-centered cubic \( \text{Mn}_3\text{XC} \) phases (where \( X \) is Al, Zn, Sn or In and carbon is in the body-centered position) can be explained in terms of size-factors. Hågg has found that, in general, interstitial binary compounds have simple structures only if the ratio of the atomic diameter of the small atom to that of the large atom is less than 0.59. Thus iron and nitrogen, with a ratio of 0.56, should form a simple structure; they actually do, since \( \text{Fe}_4\text{N} \) has the same structure as the \( \text{Mn}_3\text{XC} \) phases, with nitrogen in the body-centered position.

This structure is unstable for \( \text{Mn}_4\text{C} \), since the ratio for manganese and carbon is just at the critical value of 0.59. By replacing some of the manganese atoms with larger atoms, the average diameter of the metallic atoms is increased. Thus the ratio of the carbon diameter to the metal diameter can be lowered below 0.59, creating the simple face-centered cubic structure, by the addition of only a small amount of another metal, \( X \). Because the diameter of boron
is greater than that of carbon, the ratio for manganese and boron is increased to 0.67, and Mn₄B forms a complicated structure. Moreover, even if enough larger metal atoms are used to produce the composition, Mn₃XB, the ratio will still be greater than 0.59 and the simple face-centered cubic structure will be unstable.

The atomic diameters used for this discussion are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Mn</th>
<th>In</th>
<th>Sn</th>
<th>Zn</th>
<th>Al</th>
<th>N</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Diameter:</td>
<td>2.48</td>
<td>2.6</td>
<td>3.24</td>
<td>3.02</td>
<td>2.66</td>
<td>2.86</td>
<td>1.40</td>
<td>1.54</td>
<td>1.74</td>
</tr>
</tbody>
</table>

The effect of boron on the alloys investigated might also be explained in terms of its electrochemical properties. Boron often occurs in rows or sheets in its alloys, and thus has a strong tendency to bond with itself. Therefore, since the interstitial atoms in the Mn₃XC phases are as far separated from one another as possible, boron would not likely occupy such positions.

3. The results of the paramagnetic measurements on the Heusler alloys were inconclusive, because of the phase transformations and the loss of ordering at elevated temperatures. Most of the uncertainty was probably caused by the ordering effects.
15. H. Potter, Phil. Mag. (7), 12, 255.
17. H. Nowotny and K. Schubert, Naturwissenschaften 31, 582.