THE MAGNETIC SUSCEPTIBILITY OF DILUTE COPPER-IRON ALLOYS

by Thomas W. Raudorf
THE MAGNETIC SUSCEPTIBILITY OF
DILUTE COPPER-IRON ALLOYS AT LOW TEMPERATURE

by

Thomas W. Raudorf

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of
the requirements for the degree of Master of
Science.

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ABSTRACT

The temperature dependence of the magnetic susceptibility of dilute copper-iron alloys has been investigated in the liquid helium temperature range. The samples studied had the following concentrations: 0.011, 0.055, and 0.122 at.% Fe. The susceptibility of the least concentrated (0.011 at.% Fe) copper-iron specimen obeyed a Curie-Weiss law and gave a value of the magnetic moment of iron in copper of $3.46 \pm 0.16$ Bohr magnetons and a Curie temperature of $-21.1^0 K$. The temperature variation of the susceptibility of the two more concentrated copper-iron alloys indicated antiferromagnetic ordering between the iron atoms. A Néel temperature of $2.8^0 K$ was found for the sample containing 0.055 at.% Fe. The Néel temperature for the most concentrated (0.122 at.% Fe) alloy occurred above the liquid helium temperature range. Using the data of Bitter et al. (1941) this temperature was estimated to be about $5^0 K$. Curie temperatures of $-17.1^0 K$ and $-12.8^0 K$ were calculated for the 0.055 at.% Fe alloy and the 0.122 at.% Fe alloy, respectively, using the previously determined value of $3.46 \pm 0.16$ Bohr magnetons for the magnetic moment of iron dissolved in copper. The value of the s-d exchange integral $J_{s-d}$ for iron in copper was calculated from the concentration dependence of the Néel temperature, as described by Owen et al. (1956) yielding a value of $-1.4$ ev. A value of $J_{s-d} = -0.66$ ev. also obtained by modifying the simple molecular field expression for the Curie temperature as will be subsequently shown. Finally qualitative agreement between the high temperature susceptibility data of Hoeve (1965) and the above low temperature data could be obtained by assuming a temperature dependent magnetic moment of the Hoeve form in the Curie-Weiss expression for the susceptibility.
CHAPTER I
INTRODUCTION

The behaviour of the magnetic susceptibility of dilute copper-iron alloys at various temperatures has been the subject of a number of investigations. Table 1-1 on the next page summarizes the findings of previous researchers giving the concentration of the alloys studied, their heat treatment, temperature range of measurement, values of the Curie θ and effective magneton numbers. It can be seen that while there is some agreement in the high temperature data (i.e., above 200ºK), at low temperature (i.e., less than 200ºK) agreement is lacking.

All investigators found that in the region above 200ºK dilute copper-iron samples obeyed a Curie-Weiss law with an effective magneton number varying between 4.23 and 4.9. The Curie θ value, however, ranged from -200ºK (Bitter et al. 1941) to +122ºK (Knappwost 1954).

Berghout (1961) showed that when iron exists out of solution in a copper-iron alloy, deviations appear in the Curie-Weiss law along with an increase in the Curie θ. For example Scheil et al. (1959) solution annealed their samples at 1070ºC for only five hours and they reported deviations in the Curie-Weiss law at approximately 150ºK, and a large positive Curie θ. On the other hand, Bitter et al. (1941) and Hoeve (1965) gave their samples solution anneals for periods from twenty-four hours to five days. Their susceptibility measurements yielded negative Curie θ's at room temperature and above. Thus it seems that high temperature susceptibility data (>200ºK) yielding positive Curie θ's are purely the result of iron out of solution. For this reason the results of Bitter et al., Hedgcock, Berghout, and Hoeve appear to be preferable to those obtained by Knappwost and by Scheil et al.

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<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>CONCENTRATION RANGE</th>
<th>TEMPERATURE RANGE</th>
<th>HEAT TREATMENT</th>
<th>CURIE θ</th>
<th>$P_{\text{Eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitter et al. (1941)</td>
<td>0.009 to 0.8 at.% Fe</td>
<td>14-1298°C K</td>
<td>1000°C anneal for 5 days + 24 hour anneal at 1050°C + quench</td>
<td>0 to -16°C K (low temp. data)</td>
<td>2 to 6.9 (low temp. data)</td>
</tr>
<tr>
<td>Knappwost, A. (1954)</td>
<td>1.3 and 0.5 vt.% Fe</td>
<td>80-290°C K</td>
<td>1000°C anneal + quench</td>
<td>+122°C K</td>
<td>4.7</td>
</tr>
<tr>
<td>Hedgcock, F.T. (1956)</td>
<td>0.016 and 0.005 at.% Fe</td>
<td>4.2-20°C K</td>
<td>Single Cu-Fe crystals</td>
<td>Curie-Weiss law not followed</td>
<td>Curie-Weiss law not followed</td>
</tr>
<tr>
<td>Scheil et al. (1959)</td>
<td>0.57 to 2.16 at.% Fe</td>
<td>90-300°C K</td>
<td>1070°C anneal for 5 hours + quench</td>
<td>+18 to +112°C K</td>
<td>4.9</td>
</tr>
<tr>
<td>Berghout, C. (1961)</td>
<td>0.11 to 0.82 vt.% Fe</td>
<td>20-350°C K</td>
<td>1000°C anneal + quench</td>
<td>$\sim$-10°C K</td>
<td>4.9</td>
</tr>
<tr>
<td>Hoeve, H.G. (1965)</td>
<td>0.0058 to 0.38 at.% Fe</td>
<td>300-800°C K</td>
<td>1000°C for 24 hours or 575°C for one week + quench</td>
<td>$\sim$-130°C K</td>
<td>4.23</td>
</tr>
</tbody>
</table>
deal of discrepancy between the results of the various investigators. Bitter et al. found Curie θ's between -160°K and 0°K as the iron concentration in their samples was increased. The magneton numbers seemed to vary with concentration also, with values of 2 to 6.9 being reported. Berghout (1961) found a value of 4.9 for the magneton number and a Curie θ of ~ -10°K for all his alloys. Both Knoppwost and Scheil et al. found deviations in the Curie-Weiss law at about 150°K, but, as discussed previously for high temperature data, these low temperature deviations were probably due to iron out of solution. Hedgcock, measuring magnetic susceptibility from 20°K to 4.2°K, found large deviations in the Curie-Weiss law. These deviations were not at all similar to those observed by Scheil et al., and considering the dilution of the alloys, iron out of solution can probably be discarded as the cause.

Therefore, with regard to the magnetic susceptibility of copper-iron at low temperature, the following situation exists. Bitter et al. (1941) reported a concentration dependent magnetic moment; Berghout (1961) arrived at a value of 4.9 Bohr magnetons for his alloys, regardless of concentration; Hedgcock (1956) could not calculate a moment because of the large deviations from the Curie-Weiss law observed in the temperature range studied.

Bitter et al. found a concentration-dependent Curie θ that is negative; Berghout found a more or less concentration-independent Curie θ of approximately -10°K; Hedgcock could not arrive at a θ because of the great deviations of the susceptibility from a Curie-Weiss law over his temperature range.

The lack of agreement in the low temperature magnetic susceptibility data suggests that a further study of the susceptibility of dilute copper-iron specimens, in the liquid helium temperature region might be instructive.

Recent theoretical work (e.g., Nagaoka 1965, Schrieffer and Wolff 1966, Yosida 1966) predicts a temperature-dependent magnetic moment at low tempera-
tures. Hoeve (1965) in his dissertation postulated a slight temperature dependence of the magnetic moment; however, since low temperature measurements were not made, evidence is lacking in the liquid helium temperature range for such a temperature dependent magnetic moment. Measurements of the low temperature susceptibility would, therefore, also be of interest for comparison with recent theory.

Antiferromagnetic transitions have been found in some dilute alloys; for example from magnetic measurements Owen et al. (1957) found such transitions in copper-manganese, Collings and Hedgcock (1962) in magnesium-manganese and Collings et al. (1964) in zinc-manganese. All of these transitions were found to occur in the low temperature region, so that any similar magnetic transition in copper-iron would require measurements in the liquid helium temperature range. This magnetic ordering is believed to produce a so-called resistive maximum (see Silverstein 1966). White (1955) observed that the resistivity versus temperature curve of a copper-iron specimen of 0.056 wt.% Fe concentration, after going through a minimum, levelled off and became constant. If this levelling off (in White’s case this was 2–5°K) is a result of magnetic ordering, a study of magnetic susceptibility of copper-iron alloys in the liquid helium temperature range should confirm the presence of such ordering.
CHAPTER II
APPARATUS

2-1 Introduction

Most methods of determining paramagnetic or diamagnetic susceptibilities depend on measurement of the force which a specimen experiences in a non-uniform magnetic field. This force is given by

\[ F = \frac{1}{2} \int_{V} k H^2 dV \]  (2-1)

where \( k \) is the volume susceptibility and \( H \) is the applied magnetic field (Bates 1963).

The two main methods involving force measurement by a balance are the Gouy and Curie methods. The specimen is in the form of a thin rod in the Gouy method and the vertical force can be expressed by

\[ F_y = \frac{1}{2} kA \int \frac{V2}{y} \frac{d}{dy} (H^2) dy = \frac{1}{2} kA (H_2^2 - H_1^2) \]  (2-2)

The sample in the Curie method is considered to be a point mass with the vertical force being given by

\[ F_y = \frac{1}{2} kV \frac{d}{dy} (H^2_x) = kV H_x \frac{dH_x}{dy} \]  (2-3)

or if the mass susceptibility is used

\[ F_y = m \times H_x \frac{dH_x}{dy} \]  (2-4)

where \( x \) is the magnetic susceptibility per unit mass in emu/gm.

It is difficult to produce a large homogeneous copper-iron specimen as would be required by the Gouy method; the Curie method on the other hand, has the advantage that small samples may be used. Therefore it was this method that was chosen for the subsequently described investigations.

The difficulty of exact positioning of the sample in the Curie method was overcome by employing specially designed Feraday pole tips, as will be discussed.
later. These pole tips produce a nearly constant $H \frac{dH}{dy}$ over an extended distance in the $y$ direction (in this case 1.2 cm). Unfortunately $H$ still varies over the length of the sample so that the determination of the magnetic field dependence of the susceptibility will be somewhat imprecise.

To measure the susceptibility of an unknown specimen the variation of force versus magnet current is determined for both it and a specimen of known susceptibility. If both samples experience the same $H \frac{dH}{dy}$ (i.e., the same magnet current when hysteresis is compensated for) the unknown susceptibility can then be found as follows:

$$\frac{F_k}{F_s} = \frac{m_k \chi_k H \frac{dH}{dy}}{m_s \chi_s H \frac{dH}{dy}}$$  \hspace{1cm} (2-5)

where $F_s$ = force on unknown

$F_k$ = force on known specimen at same $H \frac{dH}{dy}$

$m_s$ = mass of the unknown

$m_k$ = mass of known specimen

$\chi_s$ = susceptibility of unknown

$\chi_k$ = susceptibility of known

and

$$\chi_s = \frac{\chi_k F_s}{m_k}$$ \hspace{1cm} (2-6)

For a specimen that is paramagnetic or diamagnetic a plot of $\chi$ versus field will show a straight line of zero slope. If domains of a ferromagnetic substance are present, the magnetic susceptibility will show a field dependence. The contribution to the susceptibility from such domains can be separated from the field independent part, as shown in Chapter III. While great metallurgical effort was made to prevent such domains from forming, there still
existed a ferromagnetic susceptibility component in the copper-iron samples presently studied.

2-2 The Servo-Balance

To overcome damping difficulties in metallic samples at low temperatures, it is essential to have a sensitive but extremely rigid balance system. To do this an electrodynamic balance in a feedback loop, similar to that described by Hedgcock and Muir (1960), was used. This particular system "...as well as possessing the ability to overcome eddy current damping has a quick response, high gain to ensure minimum movement of the sample in the magnetic field and sufficient power amplification to ensure stability of the system when large transient effects are present."

The electrical components of the servo-system are shown schematically in Figure 2-1. When a slight movement of the balance arm occurs due to a force on the sample, the movement of light on the photoconductive cell causes an imbalance in the Wheatstone bridge. The error signal is fed to a D.C. amplifier through a stabilizing network and finally to the balance coil in a direction which opposes the original motion. The feedback current so produced creates a voltage across two decade resistors in series with the coil. This voltage is measured by means of a strip chart recorder, thus providing a determination of the feedback current. The strip chart recorder does not, therefore, read the force on a sample but a voltage which is directly proportional to this force. The susceptibility is still given by Equation (2-6) but instead of \( F_s/F_k \), the ratio of \( d_s/d_k \) is used (\( d_s, d_k \) being the recorder deflection due to the unknown and known specimen, respectively).

The circuit for measuring this voltage was identical to that of Hedgcock and Muir, and is shown in Figure 2-1. The zero suppression unit was incorpor-
Figure 2-1. Filter and zero suppression circuit (top) and servo-system (bottom).
ated to make it possible to back off to a new zero. The decade resistors enable the sensitivity to be changed, and the low pass filter eliminates any excessive noise since all that is of interest is the d.c. feedback signal.

To minimize noise it was found necessary to use a d.c. source for the photocell illumination lamp and to shield the photocells from any stray a.c. light (i.e., fluorescent lamps for room lighting). Also the isolation of the servo-system from any mechanical vibration was found to be essential. In spite of an extremely heavy shock mount, precise measurements could only be made during the evening when vibration due to movement in the building and outside traffic was at a minimum.

2-3 Steady State Analysis

A servo-system will be linear and independent of the gain of the amplifier if \( C/2KB \ll 1 \) where \( C \) is the natural restoring force on the balance arm, \( K \) is the force constant of the balance coil and magnet assembly, and \( B \) is the gain of the detector and amplifier in milliamperes per degree. For a more complete discussion see Hedgcock and Muir (1960).

Using the measured values of \( C = 5 \) dynes per degree, \( K = 13.5 \) dynes per milliamperc and \( B = 2330 \) milliamperc per degree gives a value of \( C/2KB = 7.96 \times 10^{-5} \) which is sufficiently small to assure the linearity of the system.

Due to the eddy currents induced in the sample by a change of field the servo-system must be able to compensate for surge forces of the order of one gram. The feedback current needed to compensate for this is 74 milliamperes, which in turn results in a 0.00056 cm sample movement. Using presently obtainable values of \( K \) and \( dH/dy \), this would correspond to an error in the susceptibility of less than 0.01%.
2-4 Stability of the Servo-System

As Hedgcock and Muir point out, "The stability of operation of a servo system is determined by the gain versus frequency characteristic of the control elements with feedback disconnected." Bode in his book (1945) shows that if a logarithmic plot of the open loop voltage gain versus frequency crosses the frequency axis with a slope of 6 dB per octave for two octaves on either side of the crossing point, the system is stable and slightly underdamped.

When such a plot is made (see Figure 2-2) for the above servo-system, it is seen that the frequency response curve crosses the frequency axis with a slope of 12 dB per octave. An R-C stabilizing network is, therefore, introduced into the circuit with a rising frequency response of 6 dB per octave. Following the same stability calculation as Hedgcock and Muir, it is found that the stabilizing capacitor required is 0.59 microfarads and the stabilizing resistor required is 15 kilo-ohms.

2-5 The Pole Tips and Magnet

As mentioned in Section 2-1, constant force (i.e., constant $H \, \text{d}H/\text{dy}$) or Fereday pole tips are desirable for the Curie method of susceptibility measurement. The pole tips were designed by the method of electrical analogy (Malavard 1947), and were similar to those described by Garber et al. (1960). The constant force region was approximately 1.2 cm in the y direction, as shown in the sketch below. Figure 2-3 shows the variation of force with displacement along y. This was found by suspending a small germanium sample at various positions between the pole tips. The displacement was then plotted against recorder deflection which is directly proportional to the force on the germanium. In the indicated region of constant $H \, \text{d}H/\text{dy}$ the maximum variation is only 2.7%.
Figure 2-2. Open loop response of amplifier and balance.
Figure 2-3. Determination of constant force region.
The magnet used was the fifteen inch Harvey Wells H S 1365 B model. Due to the space requirements of the double dewar cryostat system, a gap of 38 mm was necessary between the pole tips. With this gap a maximum field of 21 kilogauss could be produced. In the center of the constant force region a maximum field of 17.6 kilogauss was generated. Slight hysteresis of the pole tips did influence the field below 12 kilogauss, and this could readily be detected by the servo-system. The direction of the magnet current was chosen to keep the magnet cyclic with respect to its hysteresis loop, and all measurements were taken above 12 kilogauss so as to eliminate this difficulty. Figure 2-4 shows the field variation with magnet current.

2-6 The Low Temperature Cryostat

For low temperature work a standard double dewar helium cryostat was designed. The major problem was to achieve minimum pole tip separation by size reduction of the dewar system. Two suitable double dewar sets were, however, constructed by H.S. Martin and Son, that would fit a pole tip gap of thirty-five millimeters, leaving a seventeen millimeter diameter working space.

Figure 2-5 shows a detailed diagram of the cryostat system. A is the connection for the evacuation of the balance case and stainless steel sample tube E. B is the connection to the helium pumping system and C and D are the actual helium and nitrogen dewars, respectively. F doubles as the connection to the manometer and as the opening for the helium transfer tube. G is a styrofoam radiation shield and is placed between the helium level and the
Figure 2-4. Variation of magnetic field with magnet current at centre of constant force region.
Figure 2-5: The Cryostat

Scale: 1 cm = 1 inch

Components:
- BALANCE
- COIL
- BELLOWS
- UNION
- UNION
- UNION
- UNION

Annotations:
- A
- B
- C
- D
- E
- F
- G
top of the liquid nitrogen level. This shield decreased the lowest attainable temperature to 1.24°K, while without it a temperature of 1.40°K was the lowest obtainable limit.

2-7 The Pumping System

A Stokes 149H-10 Microvac helium pump was connected to the cryostat at B of Figure 2-5 via a 3-inch 30-foot pumping line. The absolute vacuum achieve at the end of this line was of the order of thirty microns, which was almost exactly that achieved directly above the pump with the line valved off. However, the pumping rate right above the pump was about twice that at the end of the thirty-foot line.

The pressure regulation was done by means of a bypass valve (Figure 2-6). It was found possible to keep the pressure variation to less than that corresponding to a temperature change of 0.01°K (5 mm at 4.2°K or 0.2 mm at 1.5°K) by hand adjustment of this valve. A 0.02°K change in temperature corresponded, for the samples studied, to a change of approximately 1/5 of a division of the recorder strip. Thus, if a great deal of time was taken for a sample to come to equilibrium with the helium bath, a field run would not be reproducible until such equilibrium was reached. In fact, after three or four minutes every run was reproducible, providing the pressure was kept within the limits noted above. This demonstrates that the temperature of the sample and helium bath came to equilibrium rapidly, and that the vapour pressure method of temperature determination is accurate.

Thermal contact was effected by introducing helium exchange gas into the balance case and stainless steel sample tube. This was done by evacuating the balance case to less than 10^-5 mm first, then transferring the liquid helium into the storage dewar, and finally introducing the exchange gas into the
Figure 2-6. Helium pumping and manometer systems.
balance case to a pressure of one or two millimeters.

Great care had to be taken in evacuating the balance case long enough to ensure no outgassing during a temperature run occurred. Outgassing will appear as noise on the recorder strip and can actually shift the zero position of the pen if it is sufficiently violent. The amount of helium exchange gas (1-2 mm) will introduce an insignificant diamagnetic correction of \( \sim 10^{-14} \) emu/gm to the total susceptibility. This, of course, is much too small to affect any measurement.

2-8 Operating Procedure

After the entire system was aligned with the vertical, the sample was hung from one side of the microbalance by a thin copper-beryllium wire. Even though this wire was only 0.002 inches thick, it was extremely strong. It gave a paramagnetic contribution to the susceptibility of only \( 10^{-10} \) emu/gm which could be neglected in all but one set of measurements in this work. Also the thermal conductivity is small being 0.00001 cal/sec which ensured the heat input to the sample from this source may be neglected.

When the microbalance with the sample attached was observed to swing freely the servo-system was engaged as follows. The photocell illumination lamp and the photocell holder were adjusted to ensure the light spot from the mirror fell equally on the two photocells. A quick measurement of the resistance of the photocells was then made, and the two variable resistors which complete the Wheatstone bridge were adjusted to make the bridge arms equal. The Wheatstone bridge energizing battery was switched on, and the current adjusted so that the one-half watt power rating of the photocells was not exceeded.

The stabilization resistor and capacitor were then checked to make sure
correct values (see section 2-4) were used, and then, starting with low gain (50 or 100), the amplifier was switched on. At this point, the output being monitored by an oscilloscope, it could be seen if the servo-system was operating satisfactorily. If everything was normal, the gain was then increased to its full value of 1000.

With the servo-system operating, the balance case was pumped out by a diffusion pump for a few hours. This ensured maximum stability of operation of the servo-system and reduced the effects of outgassing of the balance case when actual measurements were taken. Before the cryostat was cooled, a field run was made at room-temperature for comparison purposes (more completely described in Chapter III). Liquid nitrogen was then introduced into the nitrogen dewar. After 20 or 30 minutes when both dewars had reached equilibrium temperature, the liquid helium was transferred. Then, in order to ensure thermal contact, low pressure (1-2 mm) helium exchange gas was admitted into the balance case and stainless steel sample tube.

The measurements were made by sweeping the field in current steps of 5 amperes, and noting down the current on the recorder strip itself. When this was done, the pressure over the helium was then reduced, the sample given enough time to come to thermal equilibrium, and another field run performed.

After the field run at lowest temperature ($\sim 1.5^0K$), the pressure over the liquid helium was of the order of 1 mm. Helium gas was used to bring the pressure back up to atmospheric pressure. The liquid helium which remained was boiled off by blowing room temperature helium gas into the dewar. Afterwards the remaining gas in the helium dewar was removed by either blowing dry air directly in the dewar, or by pumping it out with the helium pump then admitting dry air. The reason for such care in removing the helium was that it diffuses quickly through glass at room temperature, thus "softening" the dewar as soon as the liquid nitrogen boiled off.
CHAPTER III
MAGNETIC SUSCEPTIBILITY MEASUREMENT

3-1 Determination of $X$

As mentioned in Chapter II the force on a particle in a magnetic field is given by

$$ F = mX \frac{dH}{dy} \quad (3-1) $$

Unless, however, $H \frac{dH}{dy}$ and $F$ are accurately known, the direct use of this formula in susceptibility measurements will not result in precise determinations. In the last chapter it was shown that by using a sample of known susceptibility, such as germanium, accurate values could be obtained by the use of the formula

$$ X_s = \frac{m_m}{m_s} X_{ge} \frac{d_s}{d_{ge}} \quad (3-2) $$

$X_s$, $X_{ge}$ are the susceptibility values of the sample to be measured and germanium respectively; $m_s$, $m_{ge}$ are the respective masses and $d_s$, $d_{ge}$ are the recorder deflections. The recorder deflection is proportional to the d.c. current in the balance coil and hence to the force experienced by the specimen. As $H$ is varied both $d_s$ and $d_{ge}$ also vary, thus any field dependence can be seen from a simple $X$ versus $H$ plot.

The above method of susceptibility determination was used to obtain room temperature values of $X$ for various copper-iron alloys. At low temperatures for a particular magnet current the relative susceptibility (i.e., $X_T/X_{RT}$) is simply the ratio of the recorder deflections at temperature $T$ and at room temperature.

$$ \frac{d_T}{d_{RT}} = \frac{m X_T \frac{dH}{dy}}{m X_{RT} \frac{dH}{dy}} = \frac{X_T}{X_{RT}} \quad (3-3) $$
Using Equation (3-2), these relative susceptibilities can be converted into absolute ones by multiplying them by the room temperature value obtained with the aid of the germanium data.

The accuracy of the above method is determined by the precision to which a recorder division can be read. Positioning was not too critical because the constant force region is 1.2 cm long in the y direction. Thus the reading of the recorder deflections will introduce the main error. All actual measurements were estimated to a tenth of a division, but in practice, 0.25 div. is really the limit. An average deflection of say 50 div. can, therefore, be stated with an accuracy of 0.84%. This means relative susceptibilities can be stated with a possible error of 1.68% and absolute susceptibilities with an uncertainty of twice this figure. As an example, the susceptibility at full field and 4.2⁰K of specimen I of Table 3-1 is 0.0234 x 10⁻⁶ emu/gm. This figure, in view of the above, is really 0.0234 ±0.0008 x 10⁻⁶ emu/gm.

3-2 Heat Treatment of Samples

The phase diagrams of Figure 3-1 show that if a copper sample is rapidly quenched from the melting point of copper, up to 4.5 at.% Fe can be put into a supersaturated solution. The iron will go into a substitutional solution rather than an interstitial one since both iron and copper atoms are roughly the same size. At the lowest temperature shown on the phase diagrams (550⁰C) up to 0.14 at.% Fe will dissolve in copper. C. Berghout (1961) pointed out that according to G. Tamman and W. Oelsn (1930), up to 0.14 at.% Fe will still dissolve in copper at temperatures well below 550⁰C. Thus if a copper sample, containing this amount or less of iron, is subjected to a high temperature homogenizing anneal over a number of hours followed by a rapid quench, virtually all the iron should be put into substitutional solution. Table 3-1 shows the
Figure 3-1. Phase diagrams of the copper-iron system from Metals Handbook (1960).
samples investigated in this work, the amount of iron nominally present, the amount found in solution from susceptibility measurements (see Chapter IV) and the heat treatments used. The heat treatment used would not reduce any iron oxide present to free iron.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NOMINAL AT.% Fe</th>
<th>HEAT TREATMENT APPLIED</th>
<th>ACTUAL AMOUNT IN SOLUTION AS DETERMINED FROM ROOM TEMPERATURE SUSCEPTIBILITIES (see Chapter IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.01</td>
<td>233-hour anneal at 1000°C and quench</td>
<td>0.011 at.% Fe</td>
</tr>
<tr>
<td>II</td>
<td>0.05</td>
<td>289-hour anneal at 1000°C and quench</td>
<td>0.055</td>
</tr>
<tr>
<td>III</td>
<td>0.10</td>
<td>90-hour anneal at 995°C and quench</td>
<td>0.122</td>
</tr>
<tr>
<td>IV</td>
<td>0.05</td>
<td>90-hour anneal at 1000°C and quench--iron not in solution</td>
<td></td>
</tr>
</tbody>
</table>

Even though the nominal iron concentration was below 0.14 at.% in all cases, and homogenizing anneals as long as 289 hours were applied, not all the iron could be put into solution. In the liquid helium temperature range, field dependence of the susceptibilities was noticed in all cases, thereby indicating the presence of iron out of solution. The iron not in solution could exist in two forms: (i) precipitated iron, referring to agglomerations of iron atoms large enough to exhibit ferromagnetic domain behaviour; (ii) superparamagnetic iron or agglomerations of iron atoms not big enough to have domain properties but exhibiting a large magnetic moment (see Figure 3-2).

Sample IV of Table 3-1 nominally has the same iron content as Sample II, however most of the iron is in precipitated form. Its susceptibility was measured so the magnetic field dependence of $\chi$ could be compared with that of Sample II, the iron of which is mainly in solution. This is illustrated
Figure 3-2. a) Magnetic moment versus superparamagnetic particle diameter
b) Saturation of magnetic moment with field for 20 Å diameter superparamagnetic particle at 4.2°K.
graphically by Figure 4-2(b) and Figure 4-2(d) of Chapter IV showing $X$ versus $R^{-1}$ plots for the two samples. The slope of Figure 4-2(d) is so great that it is not possible to make an accurate estimate of $X$ due to the iron actually in solution. For example, the susceptibility of Sample II can be stated as $-0.0444 \pm 0.0004$ emu/gm from Figure 4-2(b) while that of Sample IV is $-0.045 \pm 0.005$ emu/gm as determined from Figure 4-2(d). For this reason, great metallurgical effort was made to ensure that a maximum amount of iron was put into substitutional solution in each sample. However, it was found almost impossible to put all of the iron into solid solution.

3-3 Ferromagnetic and Superparamagnetic Component of $X$

The susceptibility due to iron in solution is field independent; the contribution to $X$ from the precipitated iron is field dependent. For low iron concentrations the contribution to the susceptibility is equal to $c\sigma/H$ (Bates 1963), where $c$ is the number per unit mass of ferromagnetic particles, $\sigma$ their magnetic moment per unit mass, which depends on the geometry of the particle, and $H$ the magnetic field. Figure 3-3 illustrates the variation of $c\sigma$ with magnetic field.

The data of Berkowitz and Flanders (1960) can be used to obtain information about the superparamagnetic component of the susceptibility if present. These authors show that even when a sample of beta-brass containing 0.07 wt.% Fe has supposedly been homogenized, superparamagnetic particles with an average diameter of 20 Å still exist. Using their data, an average magnetic moment of $10^{-17}$ emu/gm, averaged over particle size, can be calculated for such a particle. For fields over 10 kilo-oersteds and temperatures in the liquid helium range $\mu H$, where $\mu$ is the above magnetic moment of the particle, is much greater than $kT$. The magnetic moment must then be expressed:

$$\sigma = NgB J_{B}(x)$$

(3-3)
Figure 3-3. Variation of $c\sigma$ with magnetic field.
where 

\[ x = \frac{gJ \beta H}{kT} = \frac{\mu H}{kT} \]

- \( N \) = number of particles per unit mass
- \( g \) = spectroscopic splitting factor
- \( \beta \) = Bohr magneton
- \( J \) = angular momentum quantum number

\[ B_J(x) = \text{Brillouin function} \]

Now in the limit \( \mu H \gg kT \), \( B_J(x) \) becomes constant. \( x_{\text{superpara.}} \) could then be expressed as

\[ x_{\text{superpara.}} = \frac{\text{constant}}{H} = \frac{K}{H} \quad (3-4) \]

3.4 The Ferromagnetic and Superparamagnetic Correction

The total susceptibility measured is the sum of the lattice contribution of the copper, the contribution of the iron in solution and that of the superparamagnetic and ferromagnetic components, or

\[ x_H = x_{Cu} + x_{Cu-Fe} + \frac{c0}{H} + \frac{Ng \beta JB_J(x)}{H} \quad (3-5) \]

- field independent ferromagnetic superparamagnetic component contribution contribution

If low temperatures (i.e., liquid helium range) and high fields (above 10 kilo-oersteds) are used, both \( c0 \) and \( B_J(x) \) saturate and become constant. \( x_H \) can then be written:

\[ x_H = x_{Cu} + x_{Cu-Fe} + \frac{c0 + Ng \beta JB_J(x)}{H} \quad (3-6) \]

\[ = x_{\infty} + \frac{A}{H} \]

A simple graph of \( x_H \) versus \( H^{-1} \) should yield a straight line with a slope of \( A \) and an intercept of \( x_{\infty} \), at \( H^{-1} \) equal to zero (Bates 1963). If the slope is small then this would be quite an accurate way of determining \( x_{\infty} \). However,
it is observed that the ferromagnetic and/or superparamagnetic component increases as the temperature is lowered. This will increase the slope of a $X$ versus $H^{-1}$ curve thus increasing the error in the intercept (or $X_\infty$) at low temperature. Therefore a method which eliminates the need for long extrapolations is desirable. A type of plot which avoids any extrapolation is, for example, that of magnetization $M$ (equal to $X_HH$) versus $H$, such as shown by Figure 3-4. The slope of such a curve will be $X_\infty$, and the intercept will be equal to the constant $A$ in Equation (3-6), i.e.,

$$X_H = X_\infty + \frac{A}{H} \quad (a)$$

$$HX_H = HX_\infty + A = M \quad (b)$$

$$\frac{dM}{dH} = X_\infty \quad (c)$$

The accuracy, with which $X_\infty$ can be determined from Equation (3-7c), depends on the precision of the magnetic field, on $X_H$ and on the precision of the slope measurement. While $H \, dH/dy$ is nearly constant in a 1.2 cm region between the magnet poles, it should be pointed out both $H$ and $dH/dy$ vary appreciably over the length of the sample. At maximum current the difference in field between top and bottom of the constant force region is 2.2 kilo-oersted (see Figure 2-4). Thus a specimen 8 mm in length will experience a difference in field of 1.76 kilo-oersted between the ends. This means that only an average field can be quoted for a sample, and a possible error in positioning of 2 mm will introduce 2.5% deviation in the average field value. Fortunately such an error would be systematic throughout a complete field run. A $XH$ versus $H$ plot, therefore, would in first approximation only be shifted parallel to itself leaving the slope, i.e., $X_\infty$ unchanged.

As previously discussed, the possible error in $X_H$ is ±3.3%. The possible error in field, as above, is 2.5%, therefore a maximum possible error in each
Figure 3-4. Plot of $\chi_H H$ versus $H$ for Sample II of Table 3-1 at 2.80°C.
individual $X_H$ determination is 5.8%; this is shown in Figure 3-4. Since the error in $H$ is a systematic error and will not show up in the slope measurements, the possible error in $X_\infty$ is again 3.3%. However, this maximum error in $X_\infty$ is highly unlikely to occur, since drawing the best straight line through experimental points is by definition an averaging process. Thus, it is more meaningful to quote a statistically probable error. This turns out to be 1.3% when six different points, each having a possible random error of 3.3%, are used.
CHAPTER IV
EXPERIMENTAL RESULTS

Figure 4-2 shows the room temperature susceptibility as a function of magnetic field for Samples I, II, III and IV of Table 3-1, respectively. It is interesting to note the much increased field dependence of the room temperature susceptibility of Sample IV (Figure 4-2(d)) relative to that of Sample II (Figure 4-2(b)), even though both samples nominally contain the same amount of iron. This illustrates the importance of the heat treatment applied to a sample, and the desirability of long high temperature homogenizing anneals.

In Chapter V the amount of iron actually in solution must be known for the calculation of magnetic moments. While no spectroscopic or chemical analysis was done, the number of iron atoms in solution still could be determined. Dilute copper-iron alloys follow a Curie-Weiss law at room temperature. Hoeve (1965) found the following temperature dependence of $X$ for temperatures close to $300^\circ K$ for all the copper-iron alloys he studied:

$$X = \frac{C}{T+150}$$

(4-1)

Now $C = \mu^2/3k$, thus Hoeve found a value of $\mu = 4.23$ Bohr magnetons for iron dissolved in copper at room temperature.

Using Hoeve's relation:

$$X = \frac{C}{T+150}$$

and his value of $\mu = 4.23$ Bohr magnetons, the number of iron atoms per gram can be calculated for the samples of Table 3-1 from the following equation:

$$N = \frac{X_\infty (T+150)^3 k}{\mu^2}$$

(4-2)

$X_\infty$ is taken from Figure 4-2. Hoeve's value of $\mu$ is substituted, thus the
values of $N$, or concentration in at.$\%$, can be calculated for Samples I, II and III of Table 3-1. These values are shown in the column at the extreme right of the aforementioned table and in the inset of Figure 4-1 which shows $\chi_\infty - \chi_{\text{cu}}$ plotted against $N$ at room temperature. This is seen to be a linear relation which is in agreement with the theoretical expression for the Curie constant, i.e., $C$ proportional to $N$.

Figures 4-3 to 4-5 are graphs of $(\chi_H - \chi_{\text{cu}})H$ versus $H$ for Samples I, II, and III of Table 3-1. $\chi_H$ is determined from recorder deflections by the method explained in Section 3-1 of Chapter III and $\chi_{\text{cu}}$ represents the field and temperature independent component due to the copper lattice. As can be seen $(\chi_H - \chi_{\text{cu}})H$ is a linear function of $H$ which is, according to equation 3-7, to be expected and the slope of this straight line is $\chi_\infty$. The $H = 0$ intercept of such a graph is merely the magnetization of the superparamagnetic and ferromagnetic iron inclusions in the sample, thus being of little interest in this work. Figure 4-3, corresponding to Sample I of Table 3-1, shows how the slope increases as the temperature is decreased. Figure 4-4, corresponding to Sample II of Table 3-1, shows first an increase in slope as the temperature is lowered, then a decrease, while Figure 4-5 corresponding to Sample III of Table 3-1 shows an essentially temperature-independent slope.

Figures 4-6 to 4-8 are the actual graphs of $\chi^{-1}_\infty$ versus temperature for the three samples. Figure 4-6 shows an essentially linear or Curie-Weiss temperature dependence of $\chi^{-1}_\infty$ for Sample I of Table 3-1, while Figure 4-7 shows that $\chi^{-1}_\infty$ goes through an actual minimum for Sample II of Table 3-1. Figure 4-8 shows $\chi^{-1}_\infty$ is nearly an independent function of temperature for Sample III of Table 3-1, which has the highest iron concentration of the three samples.

The values of $\chi_\infty$ obtained by the above method were checked with values
derived from the conventional technique for obtaining $\chi_\infty$ as outlined in Section 3-4 and found to be in agreement within the experimental error. The experimental error in the conventional technique being much larger than in the present method.

The accuracy of the slope values determined from the graphs on pages 36 to 39 was checked by the method of least squares for several cases. For example at $T = 1.30^\circ K$ Figure 4-3 shows a graph of slope $0.120 \times 10^{-6}$ emu/gm; by the method of least squares the slope obtained is $0.122 \times 10^{-6}$ emu/gm, the percentage difference being 1.64%. Similarly for Figure 4-4(b) at $T = 3.40^\circ K$ the corresponding values are $0.588 \times 10^{-6}$ emu/gm and $0.595 \times 10^{-6}$ emu/gm, the percentage difference being 1.17%. For Figure 4-5 at $T = 2.02^\circ K$ the corresponding values are $1.60 \times 10^{-6}$ emu/gm and $1.60 \times 10^{-6}$ emu/gm with no percentage difference.
Figure 4-1. Room temperature susceptibility versus number of magnetic atoms per unit mass as determined from the data of Hoeve (1965).
Figure 4.2: Room temperature susceptibilities versus inverse magnetic field for samples I, II, III and IV of Table 3.1 from top to bottom, respectively.

\[ \chi \times 10^6 \text{emu/gm} \]

- (a) \( \chi = 0.010 \text{ emu/gm} \)
- (b) \( \chi = 0.044 \text{ emu/gm} \)
- (c) \( \chi = 0.077 \text{ emu/gm} \)

\[ H' \times 10^3 \text{(oersted)}^{-1} \]

- 0.02
- 0.04
- 0.06
- 0.08

- 0.10
- 0.14

3.36%

3.56%
Figure 4-3. Graph of $(x_H - x_{cu})H$ versus $H$ for Sample I of Table 3-1.
Figure 4-4(a). $(x_H - x_{cu})H$ versus $H$ for Sample II of Table 3-1.
Figure 4-4(b). \((X_H - X_{cu})H\) versus \(H\) for Sample II of Table 3-1.
Figure 4-4(b). $(X_{H}-X_{Cu})H$ versus $H$ for Sample II of Table 3-1.
Figure 4-5. $(X_H - X_{Cu})_H$ versus $H$ for Sample III of Table 3-1.
Figure 4-6. Graph of $x^{-1}_\infty$ versus $T$ for Sample I of Table 3-1.

Probable errors: $x^{-1}_\infty = \pm 1.3\%$

$T = \pm 0.01^\circ K$
Figure 4-7. Graph of $X_\infty^{-1}$ versus $T$ for Sample II of Table 3-1.

Probable errors: $X_\infty^{-1} = \pm 1.3$

$T = \pm 0.01^\circ K$
Figure 4-8. Graph of $\chi^{-1}_{\infty}$ versus $T$ for sample III of Table 3-1.
CHAPTER V
INTERPRETATION OF RESULTS

5-1 Review of Experimental Results

An interpretation of the experimental results presented in Chapter IV must account for the variation with temperature of the susceptibility of all samples measured. In order to see how such an interpretation can be arrived at, the important features of the temperature dependence of \( \chi^{-1} \) of each specimen will subsequently be discussed in more detail.

Figure 4-6 depicting \( \chi^{-1} \) versus \( T \) for Sample I shows a linear temperature dependence of \( \chi^{-1} \). Extrapolation of this dependence reveals that \( \chi^{-1} \) is not zero at \( T=0 \), but assumes a positive value. It should also be noted that the slope of the straight line is positive, indicating \( \chi \) increases with decreasing temperature. Figure 5-1(a) shows this linear behaviour along with a higher temperature point taken from a measurement of Bitter et al. (1941) on a copper-iron specimen of 0.009 at.% Fe-concentration. The result of a measurement of C. Hurd (1966) on a sample of 0.0106 at.% Fe is also shown. It can be seen from Figure 5-1(a) that the linear temperature dependence of the inverse susceptibility of Sample I does not, then, appreciably change above the liquid helium temperature range.

Figure 4-7, showing \( \chi^{-1} \) versus \( T \) for Sample II displays an entirely different behaviour. The graph is no longer a straight line and \( \chi^{-1} \) goes through a minimum at approximately 2.8\( ^{\circ} \)K. Referring to Figure 5-1(b), measurements of Bitter et al. on a sample of 0.069 at.% iron concentration in copper, indicate that above 4.2\( ^{\circ} \)K a linear temperature dependence of \( \chi^{-1} \) similar to that of Sample I would be observed.

Figure 4-8, depicting \( \chi^{-1} \) versus \( T \) for Sample III, shows that in the liquid helium temperature range \( \chi \) is essentially temperature independent.
Figure 5-1. Extension of $\chi^{-1}$ versus $T$ curves of Chapter IV.
In Figure 5-1(c) the points of Figure 4-8 are plotted, as well as the susceptibility measurements of Bitter et al. on a sample containing a factor 1.07 more iron than the specimen investigated in this work. Again, it appears that at higher temperatures a linear temperature dependence of $\chi^{-1}$ also exists for Sample III. However, as the temperature is lowered, this linear dependence discontinues at some temperature above 4.2°K. The susceptibility then becomes independent of temperature as shown in Figure 4-8.

5-2 Review of Theoretical Work

At this point, an explanation of the experimental data of Section 5-1 will not yet be attempted. Instead, a discussion of current theories concerning the behaviour of magnetic atoms in a non-magnetic matrix will be undertaken in order that a complete picture may be later presented.

(i) The Curie or Curie-Weiss Law

The Curie law is given by $\chi = C/T$. This means that if the inverse susceptibility is plotted versus temperature, a straight line of slope $1/C$ passing through the origin will result. The constant $C$ is given by $\frac{N\mu^2}{k}$ where:

$$\mu = g\beta \sqrt{J(J+1)}$$

(5-1)
as found in any textbook (e.g., Kittel 1956) on solid-state physics. $N$ is the number of magnetic atoms; $\mu$ the magnetic moment of each atom; $k$ the Boltzmann constant; $g$ the spectroscopic splitting factor; $\beta$ the Bohr magneton and $J$ the angular momentum quantum number. If the orbital angular momentum is quenched then $\mu = g\beta \sqrt{S(S+1)}$, where $S$ is the spin of the atom.

The Curie-Weiss law is a generalization of the Curie law, taking into account the possibility of an internal field in the specimen. This law is written $\chi = C/T^\theta$. $\theta$ is a constant and, as before, $C$ is the Curie
constant. If the inverse susceptibility is plotted versus temperature, the result is again a straight line of slope $1/C$. However, upon extrapolation, the $X^{-1} = 0$ intercept is given by $\Theta$ unequal zero. The simple molecular field expression for $\Theta$ is:

$$\Theta = \frac{2zJ}{3k} S(S+1)$$  \hspace{1cm} (5-2)

where $z$ is the number of nearest neighbour atoms; $J$ the direct exchange integral; $k$ the Boltzmann constant and $S$ the spin of the impurity atom. A positive or negative $\Theta$ determines whether the sign of $J$ is positive or negative, indicating either a ferromagnetic or antiferromagnetic interaction respectively.

### (ii) Hoeve's Modification of the Curie Law

In his study of the magnetic behaviour of dilute magnetic systems Hoeve (1965) found that a strict Curie or Curie-Weiss law was not observed. Rather a temperature dependence of the susceptibility as shown in Figure 5-2 was found. Since other investigators (e.g., Bitter et al. (1941); Kaufmann et al. (1945)) obtained similar results, Hoeve concluded that an analysis in terms of the Curie-Weiss law was wrong, and that instead a Curie law with a temperature dependent magnetic moment should be used. This seemed to be quite reasonable since for the alloys in question large negative Curie $\Theta$'s were observed at high temperatures and smaller ones at lower temperatures. This is consistent with Figure 5-2, as can be seen if tangents are taken at points in different sections of the curve. Hoeve found that by using the empirical formula:

$$P_{\text{eff}} = a + bT + cT^2$$  \hspace{1cm} (5-3)

where $P_{\text{eff}}$ is the magnetic moment in Bohr magnetons, $a$ is of the order of $3$, $b$ of $10^{-4}$ and $c$ of $10^{-6}$, he could explain the temperature dependence.
Figure 5-2. Product of solute concentration (c in at.%) and reciprocal atomic solute susceptibility vs temperature for a copper-iron sample of 0.0386 at.% iron concentration as plotted by Hoeve (1965).
of X for all his experimental results. This empirical temperature dependence of $P_{\text{eff}}$ is shown in Figure 5-3, where $P_{\text{eff}}$ is plotted versus $T$ for the case of copper-iron alloys.

(iii) Spin Compensation of the Localized Moment

Kondo (1964) found a logarithmic singularity in the scattering of a conduction electron by an impurity spin in third order perturbation theory. Since then there has been a great deal of theoretical work on the exchange interaction between conduction electrons and localized spins of impurity atoms. Nagaoka (1965) using the Kondo model showed that perturbation theory breaks down at a critical temperature given by:

$$T_c = 1.14 \frac{D}{\pi^2 \nu}$$

(5-4)

where $D$ is a bandwidth about the Fermi surface with a constant density of states, $k$ the Boltzmann constant, $J$ the s-d exchange integral, and $\nu$ the unperturbed single particle conduction electron density of states at the Fermi level. Below this critical temperature a quasi-bound state was believed to appear around the localized spin if the s-d exchange interaction is antiferromagnetic. Yosida and Okiji (1965), furthermore, confirmed Nagaoka's calculation and asserted that below this critical temperature the localized moment would disappear if the exchange interaction between conduction electrons and impurity spin is antiferromagnetic. Yosida (1966), extending the above calculations, showed that the s-d exchange interaction itself is responsible for the creation of this quasi-bound state, provided the interaction is antiferromagnetic. Schrieffer and Wolff (1966) demonstrated the equivalence of the Anderson (1961) and the Kondo (1964) Hamiltonians describing localized moments in metals. They also predicted that at a critical temperature a spin condensation will take place around
the localized moment since the Anderson model demands an antiferromagnetic exchange interaction between conduction and d-electrons (Anderson and Clogston (1961)).

Scalapino (1966), also using the Anderson model, derived the following expression for the susceptibility of a localized spin in a free electron gas:

\[ \chi \sim \chi_p + \frac{\mu^2}{kT} \left[ 1 + \frac{N(0)J}{1 - N(0)J \ln \frac{kT}{W}} \right] \]  

(5-5)

where \( \chi_p \) is the susceptibility due to the free electrons and is temperature independent, \( N(0) \) is the unperturbed single-particle conduction-electron density of states over a bandwidth \( W \), and \( W \) is an effective bandwidth about the Fermi energy. This clearly shows that at temperatures greater than \( W/k \exp (1/N(0)J) \) a Curie law is followed, but at or below \( T_c = W/k \exp (1/N(0)J) \) the Curie law breaks down since \( J \) is negative. This expression is very similar to that derived by Nagaoka, Yosida, and others for the breakdown point of perturbation theory and the creation of the quasi-bound state around the impurity spin.

The foregoing, therefore, leads one to suspect that in the absence of impurity-impurity interactions, the susceptibility of a system of localized moments would follow a Curie law until the breakdown temperature \( T_c \) is reached. Below this temperature the localized magnetic moment would be reduced to that of the metallic host lattice and the free electron gas.

(iv) Magnetic Ordering

In the theories so far discussed any impurity-impurity interaction was considered to be negligible. This assumption, however, does not seem to be justified in all cases.

Yosida (1957) showed that magnetic impurities in a non-magnetic matrix could interact via the conduction electrons by a process similar to the Ruderman-Kittel (1954) interaction. Marshall (1960), Klein (1963, 1964)
Figure 5-3. Variation of $P_{\text{eff}}$ with temperature as calculated by Hoeve (Hoeve 1965) for iron in copper.
and Brout (1959) showed that magnetic atoms, even in very dilute alloys, are subject to effective molecular fields. Also Abrikosov and Gor'kov (1962), using Yosida's model, could show how a small amount of magnetic impurity in a non-magnetic matrix can exhibit ferromagnetic behaviour. C.J. Thompson (1966) extended the s-d exchange model and found that it was possible for dilute magnetic systems to exhibit ferromagnetic or antiferromagnetic properties, depending on whether J, the exchange integral, was positive or negative.

Magnetic interactions can also affect the temperature dependence of the electrical resistivity of dilute magnetic systems. For example, the resistance minimum observed in dilute magnetic alloys is preceded at lower temperatures by a maximum (see White 1955). As Hoeve (1965) mentioned, the maxima are probably due to cooperative magnetic interactions between the transition metal solute atoms. Silverstein (1966) explained this phenomena more quantitatively by redistribution among the Zeeman levels of the magnetic ions caused by effective molecular fields as the temperature is lowered. This would cause a suppression of the spin disorder scattering, and coupled with the Kondo log T term, a local maximum would appear. Harrison and Klein (1966) made an estimate that even one part per million of magnetic impurity in a noble metal host would cause the appearance of such a maximum at low enough temperature. Thus, any susceptibility study of greater concentrations of magnetic impurities than one part per million, should take impurity-impurity interactions into account.

Experimentally a dilute magnetic system, in which impurity-impurity interactions take place, would behave according to the sketch below. As is shown, a Curie-Weiss law would be followed by the susceptibility. A positive Curie θ would be indicative of a ferromagnetic impurity-impurity
interaction, and a negative Curie $\Theta$ would signify an antiferromagnetic impurity-impurity interaction. The Curie-Weiss law would be followed until a critical temperature (not to be confused with the spin condensation critical temperature) called $T_c$ for ferromagnetic, and $T_N$ for antiferromagnetic ordering, was reached. Below this temperature, a magnetic ordering of the impurity atoms would take place and the magnetic susceptibility would behave as shown in the sketch.

![Sketch showing the Curie-Weiss law with: (a) antiferromagnetic ordering (b) ferromagnetic ordering between the magnetic atoms](image)

Antiferromagnetic transitions have been found in copper-manganese alloys by Owen et al. (1957); in zinc-manganese by Collings et al. (1964) and in magnesium-manganese by Collings and Hedgcock (1962).

5-3 Suitability of the Above Theories for the Copper-Iron System

In the following, the various theories will be examined as to their applicability to the experimental results discussed in Section 5-1.

(i) The Curie or Curie-Weiss Law

Only Sample I exhibits a linear dependence of the inverse susceptibility on temperature. Sample II shows an actual minimum when $X^{-1}$ is plotted versus $T$ in the liquid helium temperature range. Sample III shows no dependence of $X^{-1}$ on temperature in this range. The behaviour of the susceptibility of Sample I can, therefore, be explained by a simple Curie or Curie-Weiss law, while that of the other two samples cannot. Since the inverse susceptibility of Sample I does have a linear dependence on temperature,
but upon extrapolation does not pass through zero at zero temperature, a Curie-Weiss rather than a Curie law must be assumed.

(ii) Curie Law with Temperature Dependent $\mu$

The temperature dependence of the magnetic moment assumed by Hoeve is extremely slight as obvious from equation 5-3. Even if a temperature dependence of $\mu$ one thousand times greater than this occurred, it would make the Curie law deviate from a straight line by only 1.1% in the liquid helium temperature range. In view of the 1.3% probable error in the experimental results of this work, such a slight temperature dependence could not be detected. Neither could such a small temperature dependence cause $\chi^{-1}$ to equal zero when $T$ equals zero. A negative Curie $\Theta$ must, therefore, be assumed and it must be concluded that Sample I actually follows a Curie-Weiss law in the temperature range of measurement.

The temperature dependent magnetic moment of the Hoeve type cannot explain the actual minimum of the inverse susceptibility observed for Sample II, or the temperature independent susceptibility of Sample III.

(iii) Spin Compensation of the Localized Moment

The quenching of the local moment of an impurity atom is a concentration independent effect. As a matter of fact, concentration does not enter into the formula for $T_c$ (equation 5-4). Hence, if this theory is employed an identical $T_c$ should result for all samples studied. Considering the susceptibility of Sample I, the fact that it follows a Curie-Weiss law means, in view of Scalapino's formula (equation 5-5), that all temperatures in the liquid helium range are very large relative to $T_c$. While perhaps the spin condensation effect could explain the minimum in the $\chi^{-1}$ versus $T$ graph in the case of Sample II, it could not explain why no similar
but upon extrapolation does not pass through zero at zero temperature, a Curie-Weiss rather than a Curie law must be assumed.

**(ii) Curie Law with Temperature Dependent μ**

The temperature dependence of the magnetic moment assumed by Hoeve is extremely slight as obvious from equation 5-3. Even if a temperature dependence of μ one thousand times greater than this occurred, it would make the Curie law deviate from a straight line by only 1.1% in the liquid helium temperature range. In view of the 1.3% probable error in the experimental results of this work, such a slight temperature dependence could not be detected. Neither could such a small temperature dependence cause $X^{-1}$ to equal zero when $T$ equals zero. A negative Curie $θ$ must, therefore, be assumed and it must be concluded that Sample I actually follows a Curie-Weiss law in the temperature range of measurement.

The temperature dependent magnetic moment of the Hoeve type cannot explain the actual minimum of the inverse susceptibility observed for Sample II, or the temperature independent susceptibility of Sample III.

**(iii) Spin Compensation of the Localized Moment**

The quenching of the local moment of an impurity atom is a concentration independent effect. As a matter of fact, concentration does not enter into the formula for $T_c$ (equation 5-4). Hence, if this theory is employed an identical $T_c$ should result for all samples studied. Considering the susceptibility of Sample I, the fact that it follows a Curie-Weiss law means, in view of Scalapino's formula (equation 5-5), that all temperatures in the liquid helium range are very large relative to $T_c$. While perhaps the spin condensation effect could explain the minimum in the $X^{-1}$ versus $T$ graph in the case of Sample II, it could not explain why no similar
minimum is seen for Sample I. Spin condensation may also explain the behaviour of Sample III if this sample were considered alone. However, a $T_c$ of $\sim 5^\circ$K would be required here, which contradicts the value of $T_c$ of $2.8^\circ$K for Sample II, and that of $T_c < 1.4^\circ$K for Sample I. Also the behaviour of the magnetic susceptibility of Sample I demands an essentially temperature independent magnetic moment. For Sample II, $\mu^2$ would have to vary as $T^x$ where $x > 1$ and for Sample III, $\mu^2$ must be strictly proportional to $T$. Such behaviour of $\mu$ would require a dependence on iron concentration. It can be seen from equation 5-1 that $\mu$ has no such dependence.

Harrison and Klein (1966) made an actual estimate of $T_c$, using values pertaining to the copper-iron system, and came to a temperature of the order of $10^{-4}$K. Therefore, it seems that spin condensation of conduction electrons around the localized moment must be discarded as a cause for the deviations from the Curie or Curie-Weiss law of the susceptibility of Samples II and III.

(iv) Magnetic Ordering

The theory of magnetic ordering will explain the experimental observations for all three cases. Sample I is found to follow a Curie-Weiss law with a large negative $\theta$. If impurity-impurity interactions are assumed to be the cause of the negative $\theta$, it can be concluded that these interactions are antiferromagnetic in nature. If the temperature were decreased, or the iron concentration increased, one would expect an antiferromagnetic transition to occur. The transition temperature should be concentration dependent and increase with increasing iron concentration.

Figure 5-1(b) indicates that Sample II follows a Curie-Weiss law above the liquid helium temperature range; an experimental value of the
Néel temperature $T_N = 2.8^\circ K$ can then be assumed in the light of the above. Figure 5-1(c) shows that Sample III also follows a Curie-Weiss law at higher temperatures. A value of $T_N$ is in this case a bit more difficult to deduce, since the transition takes place above $4.2^\circ K$, but a value of 5 to $6^\circ K$ can be estimated when the data of Bitter et al. is taken into account.

It seems that magnetic interactions between impurity atoms are then responsible for the temperature dependence of the inverse susceptibility of all three samples studied. An interpretation of the experimental data of Chapter IV should, therefore, take these interactions into account.

5-4 Interpretation of Experimental Results

As stated in Section 5-3, an analysis of the experimental results of Chapter IV will be attempted in terms of the Curie-Weiss law and impurity-impurity interactions.

(i) Analysis of Results

The data of Figure 4-6, showing $X^{-1}$ plotted versus $T$, obeys a Curie-Weiss law. The temperature dependence of $X$ can then be described by:

$$X = \frac{2.67 \times 10^{-6}}{T + 21} \text{ emu/gm}.$$  (5-6)

The Curie constant is $2.67 \pm 0.13 \times 10^{-6}$ emu/gm $^\circ K$ and the Curie $\Theta$ is $21 \pm 1^\circ K$. Since $C = N\mu^2/3k$, $\mu$ or $P_{\text{eff}}$, the magnetic moment in Bohr magnetons, can be calculated. Using $N = 1.09 \times 10^{18}$, from the inset of Figure 4-1, a value of $P_{\text{eff}}$ equal to $3.46 \pm 0.16$ is found for iron in the liquid helium temperature range. For an $S$ state ion this corresponds to either a spin of $S = 1$, where $P_{\text{eff}} = 2.9$ or $S = 3/2$ where $P_{\text{eff}} = 3.9$.

Figure 4-7 showing $X^{-1}$ plotted versus temperature for sample II can be interpreted as exhibiting an antiferromagnetic transition with a Néel
point at $2.8^\circ$K. The Curie $\Theta$ can be calculated from the Curie-Weiss law if $C$, the Curie constant and the magnetic susceptibility at a given temperature above the Néel point are known. The Curie constant may be calculated if the magnetic moment $\mu$ determined for Sample I is substituted in $C = N\mu^2/3k$. Experimental values of $\chi$ can be used as long as $T > 2.8^\circ$K. Thus $\Theta$ is found equal to $-17^\circ$ to $-15^\circ$K.

Figure 5-1(c), a graph of $\chi^{-1}$ versus $T$ for Sample III, can also be interpreted as showing an antiferromagnetic transition. Since there is no minimum as is the case for Sample II, the Néel point cannot be determined. A range of temperature for $T_N$ can be estimated, however, viz., $4^\circ$K $\leq T_N \leq 6^\circ$K. As was done for Sample II, a Curie $\Theta$ can be calculated. In this case, $-11.8 \pm 0.8^\circ$K $\leq \Theta \leq -13.8 \pm 0.8^\circ$K.

Figure 5-4 shows these and other investigators' $\Theta$ values plotted versus iron concentration. Figure 5-5 shows both $\Theta$ and $T_N$ plotted against concentration for the three samples studied in this work.

(ii) Simple Molecular Field Theory

It can be observed from Figures 5-4 and 5-5 that as the iron concentration increases, the absolute value of $\Theta$ decreases linearly. Also $T_N$ increases linearly with iron concentration, but not as quickly as the absolute value of $\Theta$ decreases. This indicates that along with the antiferromagnetic interaction there exists a ferromagnetic interaction, the relative strength of which increases with iron concentration. The above experimental results are qualitatively consistent with a simple molecular field model as will now be shown.

Following Owen et al. (1957) the iron ions are divided into two sublattices A and B, such that interactions among the iron ions gives both ferromagnetic coupling A-A and B-B, and antiferromagnetic coupling A-B.
Figure 5-4. Variation of Curie $\theta$ with iron concentration.
Figure 5-5. The Curie $\Theta$ and $T_N$ (Néel point) versus iron concentration.
The magnetization of A can be written:

\[ M_A = \frac{C}{2T} (H + \mu M_A - \gamma M_B) \]  \hspace{1cm} (5-7a)

and that of B

\[ M_B = \frac{C}{2T} (H + \mu M_B - \gamma M_A) \]  \hspace{1cm} (5-7b)

H being the applied field and \( \mu \) and \( \gamma \) the ferromagnetic and antiferromagnetic coupling parameters, respectively. \( X \) is given by:

\[ X = \frac{M_A + M_B}{H} \]  \hspace{1cm} (5-8)

or solving in terms of \( C, T, \) and the coupling parameters:

\[ X = \frac{C}{T - \Theta} \quad \text{where} \quad \Theta = \frac{C}{2} (\mu - \gamma) \]  \hspace{1cm} (5-9)

Putting \( H = 0 \) in the expressions for \( M_A \) and \( M_B \) and solving for values of \( T \) at which \( M_A, M_B \) are non-zero it is found:

\[ T_N = \frac{C}{2} (\mu + \gamma) \]  \hspace{1cm} (5-10A)

Combining this expression with that for \( \Theta \), the following relations can be derived for \( \mu \) and \( \gamma \):

\[ |\mu| = |T + \Theta| / C \]

\[ |\gamma| = |T_N - \Theta| / C \]  \hspace{1cm} (5-11)

For \( \Theta < 0 \), \( |T_N + \Theta| < |T_N - \Theta| \) thus \( \mu < \gamma \), that is the antiferromagnetic coupling between ions on different sublattices is greater than the ferromagnetic coupling between ions on the same sublattice. When \( \Theta = 0 \), then

\[ |\mu| = |\gamma| \] and when \( \Theta > 0 \), \( |\mu| > |\gamma| \). The case where \( \Theta = 0 \) is interesting because

\[ |\mu| = |\gamma| \] which means \( M_A = M_B \) and \( M_A + M_B = CH/T \) or \( X = C/T \), in other words at a particular concentration, a copper-iron sample will seem to obey a Curie law until antiferromagnetic ordering sets in.
(iii) Estimates of the s-d Exchange Integral

In dilute magnetic alloys, such as the ones studied, the predominant form of impurity-impurity interaction will be via the conduction electrons. Values of $J_{s-d}$, the s-d exchange integral, therefore, are of great interest. The Curie $\Theta$, however, is related to $J$, the direct exchange integral, by equation 5-2, i.e.,

$$\Theta = \frac{2zJS(S+1)}{2k}$$  (5-2)

Again $z$ is the number of nearest neighbors; $J$, the direct exchange integral; $S$, the spin of the atom; and $k$, the Boltzmann constant. Clearly in order to obtain an estimate of $J_{s-d}$, this equation will have to be somewhat modified.

In dilute magnetic alloys, the nearest magnetic neighbor atoms are a few lattice spacings away. Allowance for this has to be made, therefore, in the value of $z$ used. The most simple way to do this is to multiply $z$, the actual number of nearest neighbors (magnetic or nonmagnetic) by $c$, the ratio of magnetic atoms to nonmagnetic atoms.

Hence, when $c$ approaches zero, $\Theta$ will also go to zero. The Curie $\Theta$ upon introduction of iron atoms into the lattice of a pure copper sample thus will at first be zero. The specimen then will follow a simple Curie law. As the concentration $c$ increases an antiferromagnetic interaction occurs between the iron atoms, producing a negative Curie $\Theta$. At a given impurity concentration a further increase of $c$ will induce a ferromagnetic interaction between the iron atoms. If the strength of the ferromagnetic interaction increases more rapidly with concentration than the antiferromagnetic interaction, the two will just balance at a certain value of $c$, producing a maximum in the magnitude of $\Theta$ at this point. Beyond this value of $c$, as pointed out in Section 5-4 (ii), the absolute value of $\Theta$ will decrease as the ferromagnetic coupling becomes dominant over the antiferromagnetic coupling. The
dependence of $\Theta$ on $c$ is qualitatively shown in the sketch. For an estimate of the value of the s-d exchange integral, $J_{s-d}$, the section of the $\Theta$ versus $c$ curve where the ferromagnetic interaction is negligible, can only be considered. On the sketch this is the section which lies between $|\Theta| = 0$ and $|\Theta| = \text{maximum}$.

Sketch showing concentration dependence of both the ferromagnetic and antiferromagnetic couplings and the Curie $\Theta$.

Assuming that $\Theta \approx 2zcJ_{s-d}S(S+1)/3k$ in this section, and using the $\Theta$ value obtained for the sample of least concentration, one finds $J = -0.66$ ev.

In view of the drastic modification of formula 5-2 and the assumptions concerning the concentration dependence of $\Theta$, this value can only be considered to be the result of an order of magnitude calculation.

Another expression for $J_{s-d}$ has been derived by Owen et al. (1956). This is:

$$T_N = \frac{J_{s-d}^2S(S+1)}{2kE_F \left( \frac{100}{T} \right)}$$

(5-12)

$E_F$ being the Fermi energy of copper, $f$ the iron content in atomic percent, $S$ the spin of the atom, and $T_N$ the Neél point. Upon substitution of experimental values, $J_{s-d} = -1.4$ ev. This may be somewhat high, because Owen et al. made the assumption that the entire conduction band is polarized. This is an assumption which has not been found to be justified, since the conduction electrons are polarized near the impurity only (Yosida 1957).

These two values of $J_{s-d}$ for copper-iron do not compare favourably with the estimate of $J_{s-d} = -0.15$ ev. made by Kondo (1964) from electron
transport phenomena. They are in fair agreement, however, with values published by Collings and Hedgcock (1962) for magnesium-manganese, and Collings et al. (1964) for zinc-manganese. The difference in the various values of $J_{s-d}$ for copper-iron can only be attributed to the failure of the theory to give an exact expression for $J$ in terms of measurable quantities.

(iv) Temperature Dependence of $\mu$

An iron atom has a basic electron configuration of $3d^64s^2$. Assuming that the two $4s$ electrons join the conduction band and that the orbital angular momentum is quenched, an effective magneton number of 4.9 would be expected. This indeed has been observed at room temperature and above (e.g., see Scheil 1959 or Bitter et al. 1941). The experimental value obtained in this work of $p_{\text{eff}} = 3.46$ is much lower than the expected 4.9. Other authors, notably Hurd (1966) who found $p_{\text{eff}} = 3.68$, and Daybell and Steyert (1967) who found $p_{\text{eff}} = 3.2$, arrived at similar results. Obviously there does exist a temperature variation of the magnetic moment as proposed by Hoeve. This temperature dependence of $\mu$ can qualitatively be explained by the Anderson (1961) model as was pointed out by Hoeve (1965).

In order to explain a temperature dependent magnetic moment using the Anderson model, either the d-state (spin up) or the virtual d-state (spin down) must lie near the Fermi level, as shown by Hedgcock and Mathur (1962). If the virtual state lies just above the Fermi level, at a temperature $kT$, the thermal tail of the distribution function will depopulate the spin state at $E$ and populate the anti-parallel state at $-E+U$ as illustrated in the sketch below. This will result in a movement of the d-states toward the Fermi level and a net decrease in the magnetic moment. This effect is contrary to the observed result for the copper-iron case. It can, however, be assumed that the d-state itself lies at the Fermi level with the virtual d-state a distance
Sketch showing a) virtual state of spin down at Fermi level and b) d-state of spin up at Fermi level. The d-state and the virtual d-state being separated by energy difference U.

If U is assumed very large compared to kT, then the virtual d-state will be empty at all temperatures in question. On the other hand, the population of the spin-up d-state will vary with temperature as the thermal tail of the distribution function increases; this will augment the number of spin-up electrons, thereby increasing the magnetic moment.

(v) Temperature Dependent μ in a Curie-Weiss Law

As pointed out above, a slight temperature dependence of μ must be assumed in order to account for the difference between the high temperature and low temperature magnetic moment. Hoeve (1965) did this in his dissertation, but he assumed that no Curie θ existed. Since in this work a Curie θ cannot be discarded, the Hoeve theory should be generalized to include a θ value. This may be done as follows:

\[ \chi = \frac{C}{T^2 \Theta} = \frac{N \mu^2}{3k(T^2 \Theta)} \]  \hspace{1cm} (5-13)

Now from simple molecular field theory

\[ \mu = g \beta \sqrt{S(S+1)} \]  \hspace{1cm} (5-1)

and

\[ \Theta = \frac{2 \pi J}{3k} S(S+1) \]  \hspace{1cm} (5-2)
Assuming a linear temperature dependence of $\mu$

$$\mu = (a + bT)B$$  \hspace{1cm} (5-14)

$$\chi = \frac{N g^2 e^2 s(s+1)}{3k \left( T + \frac{2J}{3k} (a+bT) \right)} = \frac{N g^2 (a+bT)^2}{3k \left( T + \frac{2J}{3k} (a+bT) \right)}$$  \hspace{1cm} (5-15)

and

$$\chi^{-1} = \frac{3k}{N g^2} \left[ \frac{1}{\frac{a^2}{T} + 2ab + b^2} \pm \frac{2J}{3k g^2} \right]$$  \hspace{1cm} (5-16)

Figure 5-6 shows the actual curves that would result if equation 5-16 were used to predict the temperature variation of the susceptibility of Sample I. 'a' was chosen such that $\mu = 3.4$ Bohr magnetons at $T=0$; $N$ is the number of magnetic atoms/gm; $J$ is Kondo's value for the s-d exchange integral for copper-iron; and 'b' was given various temperature dependences ranging from ten to one thousand times that assumed by Hoeve. Such a Curie-Weiss law with a temperature dependent $\mu$ will, therefore, explain the difference between the values of $\mu$ at room temperature and above, and the values determined at low temperature. It also will, at least qualitatively, account for a temperature dependent Curie $\Theta$ which is a result of a temperature dependent $\mu$.

5-5 Summary

An apparatus to measure the magnetic susceptibility of dilute metallic alloys at low temperature was constructed. Four copper-iron specimens of various concentrations and heat treatments were measured in the liquid helium temperature range. Three samples had most of their iron in solution, the iron in the other sample being present mainly in precipitated form. The three copper-iron samples with the iron in solution were found to have iron concentrations of 0.011 at.%, 0.055 at.% and 0.122 at.%, respectively, as calculated from room temperature susceptibility data.
Figure 5-6. Demonstration of how a temperature-dependent $\mu$ affects a $X^{-1}$ vs $T$ curve.
The sample with 0.011 at.% iron content followed a Curie-Weiss law in the liquid helium temperature range. It was found to have a Curie Θ of -21 ± 10 K and a Curie constant corresponding to a $\text{P}_{\text{eff}}$ of 3.46 ± 0.16. No temperature dependence of $\text{P}_{\text{eff}}$ outside of the probable experimental error was observed.

The other two samples of 0.055 at.% and 0.122 at.% iron content displayed antiferromagnetic transitions with Néel temperatures of 2.8 K and ~5 K, respectively. The Curie Θ for both specimens was calculated using the value of $\text{P}_{\text{eff}}$ from the sample of 0.011 at.% iron content. For the samples of 0.055 and 0.122 at.% iron content, Θ is -17 ± 10 K and -12.8 ± 20 K, respectively.

The Curie Θ's and the Néel temperatures were found to exhibit a linear concentration dependence. Although all the Θ's were negative, upon extrapolation of this dependence, a transition from negative to positive Θ values was predicted. Also values of $J_{S-d}$, the exchange integral, were estimated from the concentration dependence of Θ and the Néel point. $J_{S-d}$, as deduced from the Curie Θ values, was found to be of the order of -0.66 ev. while $J_{S-d}$ as deduced from the Néel point temperatures, was approximately -1.4 ev. These two values of $J_{S-d}$ were compared with the value from transport phenomena with little agreement being found.

The value of $\text{P}_{\text{eff}}$ found in the liquid helium temperature range was compared with that found at room temperature by other authors. An explanation of the smaller $\text{P}_{\text{eff}}$ found at liquid helium temperatures was given in terms of the Anderson model of decoupled d-states.

Finally, in view of the definite Curie Θ found in this work and by others, a temperature dependent $\mu$ of the Hoeve type was substituted in a Curie-Weiss law rather than a Curie law. Such a generalization would explain both Hoeve's high temperature data and will be consistent with a small Curie Θ at low temperature.
BIBLIOGRAPHY


