The Magnetic Susceptibility of Pure Aluminum and Al-Mn Alloy.

by

Pei-Luen Li

M.Sc. Degree.

The temperature dependence of the magnetic susceptibility of pure aluminum (99.9999 + %) and Al-Mn (0.04 at.%) have been investigated using Faraday's method from 2°K to 300°K. In this temperature region, the susceptibility is independent of maqnetic field indicating the absence of any ferromagnetic impurities. From room temperature to 50°K, the susceptibility changes by 18% and exhibits a T^2 dependence which is the same slope for both the pure aluminum and the Al-Mn alloy. This T^2 dependence is an intrinsic property of the aluminum and can be interpreted in terms of the band structure of aluminum. The difference in susceptibility ($\Delta \chi = \chi_{alloy} - \chi_{pure}$) due to manganese is temperature independent to $\pm 0.04 \times 10^{-7}$ emu/gm from 50°K to 250°K. The present work does not confirm the presence of localized spin fluctuations in Al-Mn. However, the ratio of the enhancement factor to the width of the virtual bound states is in good agreement with that determined from resistivity measurements by Caplin and Rizzuto.

Department of Physics McGill University, Montreal. LI THE MAGNETIC SUSCEPTIBILITY OF PURE ALUMINUM AND AL-Mn ALLOY

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Pei-Luen Li

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Eaton Electronics Research Laboratory Department of Physics McGill University Montreal

• Pei-Luen Li

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ABSTRACT

The temperature dependence of the magnetic susceptibility of pure aluminum (99.9999+%) and Al-Mn (0.04 at.%) have been investigated using Faraday's method from 2°K to 300°K. In this temperature region, the susceptibility is independent of magnetic field indicating the absence of any ferromagnetic impurities. From room temperature to 50°K, the susceptibility changes by 18% and exhibits a T^2 dependence which is the same (within an experimental error of ± 0.3 %) for both the pure aluminum and the Al-Mn alloy. This T² dependence is an intrinsic property of the aluminum and can be interpreted in terms of the band structure of aluminum. The difference in susceptibility $(\Delta \chi = \chi_{alloy} - \chi_{pure})$ due to the manganese is temperature independent to $\pm 0.04 \times 10^{-7}$ emu/gm over the temperature range 50°K to 250°K. The present work does not confirm the presence of localized spin fluctuations in Al-Mn. However, the ratio of the enhancement factor to the width of the virtual bound d-state from low temperature susceptibility measurements is in good agreement with that determined from resistivity measurements by Caplin and Rizzuto.

CHAPTER I

INTRODUCTION

The addition of small amounts of transition metal impurities in non-transition metals such as Cu, Zn, Al, etc., gives rise to relatively large changes in various properties. According to the Friedel-Anderson theory, the characteristic changes observed are due to the formation of virtually bound d-states which may or may not possess localized magnetic moments.

It is known that a transition metal impurity added to a monovalent metal gives rise to a Curie-Weiss law at high temperatures such as in Cu-Mn. In a di-valent host matrix, the d-states of the transition metal impurity may be partially filled by the conduction electrons of the host due to the higher concentration of electrons. In Zn-Mn, the Curie-Weiss law is still obeyed. Both systems, Cu-Mn and Zn-Mn, exhibit the Kondo effect, i.e., a log T term in the resistivity.

In contrast to the above situation when manganese is introduced substitutionally into a trivalent solvent, such as aluminum, the Curie-Weiss law is not obeyed [Taylor (1959), Hedgcock (1963), Aoki (1968), Wheeler (1968)] and no Kondo log T term in the resistivity is observed.

In the Hartree-Fock (static) sense, the 3d-transition impurities in aluminum should therefore behave as "non-magnetic" impurities at low temperatures. After more complete analysis, Schrieffer (1967), etc., suggests that Al-Mn alloys are best

described as Kondo-compensated states (with a large Kondo temperature) in the low temperature region (i.e. $T < T_K$) instead of treating the Mn as "non-magnetic" at all temperatures. This means that the susceptibility for $T >> T_K$ is governed by a Curie-Weiss law, and saturates to a finite value for $T << T_K$.

Recently, the theory of localized spin fluctuations indicates the physical equivalence between the spin compensated state and the localized spin fluctuations on a dilute "non-magnetic" alloy. This theory considers the case of Al-Mn as an unmagnetized state at 0°K but capable of short-lived spin fluctuations with a relaxation time τ_0 at finite temperatures. This theory leads to the prediction of a resistivity and a susceptibility due to Mn impurity having a T^2 dependence at low temperatures and can be written as

$$\rho(\mathbf{T}) = \rho_{0} (1 - \pi^{2} (\frac{\mathbf{T}}{\mathbf{T}_{K}})^{2}]$$

$$\chi(\mathbf{T}) = \frac{Ng^{2} \mu_{B}^{2}}{\pi k T_{K}} [1 - \frac{\pi^{2}}{3} (\frac{\mathbf{T}}{\mathbf{T}_{K}})^{2}]$$

where T_{K} is the Kondo temperature, $kT_{K} \sim \frac{1}{\tau_{O}}$.

Caplin and Rizzuto (1967) observed a \overline{T}^2 resistivity in the Al-Mn system. The present paper reports the measurement of the susceptibility of (6-9) pure aluminum and Al-Mn (400 ppm) in the temperature range 2°K to 300°K.

CHAPTER II

THEORY OF THE MAGNETIC SUSCEPTIBILITY

II.1. Magnetic Susceptibility

In the case of a normal (non-ferromagnetic) metal the atoms may be treated as diamagnetic cores while the valence electrons outside the cores may be treated as free or conduction electrons. Hence the expression for the total susceptibility of pure aluminum may be written in the form

$$\chi^{\text{total}} = \chi^{\text{Al}^{3+}} + \chi^{\text{para}}_{\text{el}} + \chi^{\text{dia}}_{\text{el}}$$
(11.1)

where χ^{Al}^{3+} is the diamagnetic susceptibility of the triply ionized atom Al³⁺, χ^{para}_{el} and χ^{dia}_{el} are the spin paramagnetism and the diamagnetism of the conduction electrons, respectively.

The diamagnetic susceptibility of the Al³⁺ ion has been evaluated by Henry and Rodgers (1956) using a self-consistent field approximation to give a value of -1.16 x 10^{-7} emu/gm. With the correction for exchange interaction, the susceptibility is increased by a factor of 0.8 to yield a value of -9.3 x 10^{-7} emu/ gm. This diamagnetism depends only on Σr^2 where r is the radius of the electron orbits about the nucleus. Since any changes in r with temperature are unlikely, it is assumed that the core diamagnetism is temperature independent and hence any temperature dependence of the susceptibility is attributed to the conduction electrons. The spin paramagnetism and diamagnetism of the conduction electrons will be discussed in the next two sections.

II.2. Spin Paramagnetism

(a) Density of States and the Effective Mass.

The equilibrium properties of metals, such as the electronic specific heat, Pauli spin paramagnetism, etc., depend on the density of states at the Fermi level. In general, the density of states at the Fermi level $N(E_F)$ can be written as a surface integral of the form

$$N(E_{F}) = \frac{1}{4\pi^{3}h} \oint_{FS} \frac{dS_{F}}{v}$$
(II.2)

where v is the magnitude of the electron velocity on the element dS_F of Fermi surface. A large value of N(E_F) may arise for several reasons. If the Fermi surface is distorted, such as near the Brillouin zone boundaries, the velocity may become small, giving a large contribution to the integral. Overlapping bands occurring near the Fermi surface, such as s and d bands in transition metals, give rise to a large N(E_F). Strong many body effects (e.g. electron-phonon, electron-electron interactions, etc.) affect the velocity of the electrons at the Fermi level and may also influence the density of states at the Fermi level. These effects are normally included in terms of a renormalized mass, called the effective mass, m*. Since many body effects only influence the total energy, one may still use a parabolic band approximation and write the conduction electron energy as $E=\frac{\hbar^2k^2}{2m^*}$. It may be shown that the density of states is related to the effective mass by

$$N(E_{F}) = \frac{m^{*}k_{F}}{\pi^{2}5^{2}}$$
 (II.3)

where fik_r is the free electron Fermi-momentum.

Pytte (1967) has shown that the ratio of density of states $N^*(E_F)$ to its free electron value is proportional to the ratio of the effective mass m* to its free electron mass. The many body effects are assumed to be additive to the effective mass, and hence the density of states may be written as

$$\frac{N^{\star}(E_{F})}{N_{O}(E_{F})} = \frac{m}{m_{O}}$$

$$= \frac{m_{BS}}{m_{O}} (1 + \lambda + \mu)$$
 (II.4)

where m_{BS} is the average band mass. The contribution of electronphonon and electron-electron interactions is represented by the parameters λ and μ , respectively.

In aluminum, the parameter λ has been calculated to be 0.49 by Ashcroft and Wilkins (1965), 0.46 by Pytte (1967), 0.50 by Janak (1968), and 0.46 by Carbotte (1969). In future calculations an average value of 0.48 will be chosen. The contribution of the electron-electron interaction in aluminum is very small, having a value of -0.01 as calculated by Rice (1965). From equation (II.4) and the average band mass 1.06 m_{O} as calculated by Ashcroft and Wilkins (1965), the total density of states at the Fermi level is found to be 1.53 times the free electron value. This is in good agreement with 1.5 determined by Dick and Green (1967) from the low temperature electronic specific heat and with 1.55 to 1.6 determined by Spong and Kip (1963) from cyclotron resonance. The theoretical value of the density of states and the effective mass as calculated from equation (II.4) will be used in the calculations of the magnetic susceptibility of aluminum.

(b) Modified Pauli Spin Paramagnetism

As mentioned in section II.2(a), a factor of 1.53 is introduced in the total density of states due to the electron-phonon and the electron-electron interactions. The Pauli spin paramagnetism is thus given by

$$\chi = 2\mu_{\rm B}^2 \, N^* (E_{\rm F})$$

= 3.06 $\mu_{\rm B}^2 \, N_{\rm O}(E_{\rm F})$ (II.5)

The exchange interactions between electrons of different spins have been calculated by Falicov and Heine (1961), by the method of quasi-particle excitations. Their detailed formulation shows the Pauli spin paramagnetism in equation (II.5) is modified by an additional factor to give

$$\chi_{\text{pauli}}^{*} = 2\mu_{\text{B}}^{2} \, N^{*}(E_{\text{F}}) \, (\frac{1}{1-\nu})$$
 (II.6)

where v is a parameter of the exchange interaction. It is important to point out that the parameter v depends only on the spin; hence this interaction does not appear in the electronic specific heat and the diamagnetism of the conduction band which are only related to the density of states.

The factor $\frac{1}{1-\nu}$ can be calculated from the ratio of the paramagnetic susceptibility to the electronic specific heat coefficient $\gamma_{exp} = 2/3\pi^2 k^2 N^* (E_F)$ in the limit T $\rightarrow 0$. Hence

$$\frac{1}{1-\nu} = \frac{\left[\chi^{\text{para}}(T \to 0)\right]_{\text{exp}}}{\gamma_{\text{exp}}} \cdot \frac{\pi^2 k^2}{3\mu_B^2}$$
(II.7)

II.3. Diamagnetism of the Conduction Electrons

The conduction electrons contribute a diamagnetic effect through their translational motion, which is exactly one-third of the paramagnetic susceptibility in the free electron approximation. However, under the assumption of introducing an effective mass into the kinetic energy term to account for the periodic potential and electron-electron and electron-phonon interactions, it is reasonable to presume the diamagnetism to involve the corrected density of states, N*(E_F), and the effective Bohr magneton $\mu_{eff} = \frac{e\pi}{2m^*c}$. The diamagnetism of a group of electrons can then be written as

$$\chi_{dia} = -\frac{1}{3} \left(\frac{m}{m^*}\right)^2 \cdot 2\mu_B^2 \cdot N^* (E_F)$$
 (II.8)

where m* is given by equation (II.4).

II.4. Temperature Dependence of the Magnetic Susceptibility

The temperature dependence of the spin paramagnetism is mainly attributed to the variation of $N^*(E_F)$ as the Fermi level varies with the temperature. For a parabolic band with effective mass m*, the spin paramagnetism can be written as (Ref. Wilson, 1965)

$$\chi_{p} = \begin{cases} \chi_{p}^{o} \left[1 - \frac{\pi^{2}}{12} \frac{T^{2}}{T_{o}^{2}}\right] & \text{for } T << T_{o} \\ \frac{2}{3} \frac{\chi_{p}^{o} T_{o}}{T} & \text{for } T >> T_{o} \end{cases}$$
(II.9)

where
$$\chi_p^o = 2\mu_B^2 N^*(E_F)$$
, $N^*(E_F)$ is the density of states of this
particular band at E_F ;

 T_{o} is the degeneracy-temperature of the electron in this particular band where $E_{o} = kT_{o}$;

and E is the Fermi energy measured from the bottom of the band.

The temperature dependence of χ_p/χ_p^0 predicted by these relations is shown below (Verkin, 1957). The curves a and b correspond to equations (II.9) and (II.10), the dotted line is the complete theoretical expression for the temperature dependence of the susceptibility (Wilson, 1965)



Fermi surface studies indicate that the Fermi surface of aluminum can be divided into several sheets corresponding to the complex band structure of aluminum. If it is assumed that the bands are non-interacting, then all the conduction electrons can be classified into various bands which will each contribute to $N*(E_F)$ separately. Each band has its own characteristic temperature $(T_0)_i$ measured from the bottom of its band, where the band index i is indicated for i-th band of electrons. In summary, the total susceptibility can be written as the diamagnetism of the cores and the sum of the contributions of each band of electrons.

$$\chi = \chi^{\text{Al}^{3+}} + \frac{\Sigma}{i} [(\chi^{\text{para}}_{\text{el}})_{i} + (\chi^{\text{dia}}_{\text{el}})_{i}] \qquad (\text{II.11})$$

Combining equations (II.6), (II.8) and (II.11), one obtains

$$\chi = \chi^{Al^{3+}} + \frac{\Sigma}{i} \left[\frac{1}{1-\nu} - \frac{1}{3} \left(\frac{m}{m_i^*} \right)^2 \right] \left[\chi_p(T) \right]_i$$
 (II.12)

which gives

$$\chi(\mathbf{T}) = \chi^{\mathrm{Al}^{3+}} + \begin{cases} \sum_{i}^{\Sigma} \left[\frac{1}{1-\nu} - \frac{1}{3} \left(\frac{m}{m_{i}^{*}}\right)^{2}\right] \left[\chi_{\mathrm{p}}^{\mathrm{o}}\right]_{i} \left[1 - \frac{\pi^{2}}{12} \left(\frac{T}{T_{\mathrm{o}}^{\mathrm{i}}}\right)^{2}\right], \ \mathbf{T} << \mathbf{T}_{\mathrm{o}} \quad (\mathbf{II.13}) \\ \\ \sum_{i}^{\Sigma} \left[\frac{1}{1-\nu} - \frac{1}{3} \left(\frac{m}{m_{i}^{*}}\right)^{2}\right] \frac{2}{3} \cdot \frac{\left[\chi_{\mathrm{p}}^{\mathrm{o}}\right]_{i} \left(T_{\mathrm{o}}^{\mathrm{i}}\right)}{T}, \ \mathbf{T} >> \mathbf{T}_{\mathrm{o}} \quad (\mathbf{II.14}) \end{cases}$$

2

In the case of aluminum, the usual quoted Fermi energy is 11.64 ev (Ashcroft, 1963) measured from the bottom of the first conduction band. This corresponds to a degeneracy temperature of 1.35 x 10^{5} °K, the T² dependence of such a band of electrons being practically negligible over the measured temperature range. However, the results of soft X-rays measurements (Rooke, 1963, and Wooton 1966), de Haas-van Alphen effect (Shoenberg, 1957) and band calculation (Ashcroft, 1963) show that there exists a small band of electrons with a degeneracy temperature of 387°K which gives rise to a large contribution to N*(E_F) and a T² variation of the susceptibility.

CHAPTER III

APPARATUS

The present work is concerned with the absolute magnetic susceptibility which is measured by Faraday's method using specially designed Faraday's pole-tips and a sensitive servobalance. A metal dewar is set up permitting the investigation to be carried out in the temperature range from 2°K to 300°K. Photograph 1 shows the complete low temperature susceptibility apparatus.

III.1. Methods of Measuring Susceptibilities

The force exerted on a small body suspended in an inhomogeneous magnetic field is given by (Ref. Bates, 1963)

$$F_{z} = \frac{m}{\rho}(k - k_{o}) H \frac{\partial H}{dz}$$
 (III.1)

where F_z is the force in the z direction, m and ρ are the mass and the density of the body, k and k_o are the volume susceptibilities of the body and its surrounding medium, respectively, H is the field and the field gradient is confined to the z direction. When the sample (k ~ 2 x 10⁻⁶ emu/cm³) is suspended in a vacuum (k_o = 0), or in a helium atmosphere (k_o ~ 10⁻¹¹ emu/ cm³ at N.T.P.) the expression reduces to

Photograph 1

- 1. Helium Gas Cylinder
- 2. Stoke's-Pump Line (for the Sample Chamber)
- 3. Oscilloscope
- 4. Strip Chart Recorder
- 5. Wallace and Tiernan Pressure Gauge
- 6. Balance
- 7. Metal Dewar
- 8. Magnet
- 9. Battery Charger
- 10. Battery (6V)
- 11. Temperature Measurement and Temperature Control
- 12. Pirani-Penning Pressure Gauge
- 13. Edward-Pump Line for the Balance Chamber and the Insulation Space of the Metal Dewar
- 14. Current Power Supply for the Magnet





$$\mathbf{F}_{\mathbf{z}}^{\mathbf{He}} = \frac{\mathbf{m}}{\rho} \operatorname{KH} \frac{\partial \mathbf{H}}{\partial \mathbf{z}} = \mathbf{m} \chi \mathbf{H} \frac{\partial \mathbf{H}}{\partial \mathbf{z}}$$
 (III.2)

where χ is the mass susceptibility.

In the present case, we determine the absolute magnetic susceptibility by determining the forces exerted on the specimen when suspended in an atmosphere of helium and of oxygen gas. From equations (III.1) and (III.2), the magnetic susceptibility of the specimen at temperature T can be found as follows

$$\chi_{s}(T) = \frac{F_{He}}{F_{He} - F_{Ox}} \cdot \frac{1}{\rho_{s}} \left[\rho_{O}(T-P)\chi_{O}(T)\right]_{Oxygen} \qquad (III.3')$$

Bates (1963) gives the susceptibility of oxygen at 293°K and 760 Torr as 106.2×10^{-6} emu/gm. Using this value the susceptibility of the sample is

$$\chi_{s}(T) = 1.60 \times 10^{-5} \times \frac{F_{He}}{F_{He} - F_{OX}} \frac{1}{\rho_{s}} \frac{P}{T^{2}} emu/gm$$
 (III.3)

The absolute magnetic susceptibility at room temperature $\chi(R.T.)$ is measured on a Cahn balance (section III.7) using the method described as above. The low temperature susceptibilities are obtained from the room temperature susceptibility and the reduced susceptibilities, $\chi(T)/\chi(R.T)$. If the thermal expansion of the suspension wire is negligible (Appendix II), the reduced susceptibility at temperature T, can be determined by

 $\chi(\mathbf{T})/\chi(\mathbf{R}.\mathbf{T}) = F(\mathbf{T})/F(\mathbf{R}.\mathbf{T})$

where F(T), F(R.T) are the forces measured in a vacuum at temperature T and at room temperature, respectively.

III.2. The Balance and its Associated Circuitry

Many metals become such good conductors at low temperatures that eddy current effects so overdamp the sample motion that good measurements on susceptibilities are difficult to obtain. Actually, two effects are present: the damping due to the sample moving in an inhomogeneous field, and the transient forces arising when the field is turned on and off. In order to overcome this damping effect, a sensitive, stable, and fast response servobalance, similar to that of Hedgcock and Muir (1960), was used.

A schematic diagram of the servobalance is shown in Fig. 1. When a force is exerted on the specimen, the slight deflection of the mirror gives rise to an unbalanced current in the photocell bridge circuit. This current is amplified by a Sanborn Wideband amplifier and supplied to the feedback coil, in such a way as to oppose any change from the initial condition. The feedback current is measured by reading the voltage generated across a tapped resistor in series with the feedback coil. This allows changes in sensitivity in the measurement of susceptibility by a factor of 1000. A dummy load, R, was also introduced in the output of a DC amplifier so that the balance could be operated in the open loop mode which allows the alignment of the specimen to be checked by a method to be described in a later section.



μ. Diagram of the Servo-system and

the

Photograph 2

- 1. Photocell
- 2. Lamp
- 3. Balance
- 4. Balance Chamber
- 5. Throttle Valve
- 6. Wallace and Tiernan Pressure Gauge
- 7. Shock Mount
- 8. Pumping Line





In order to reduce high frequency noise and increase the stability of the servobalance, the light source for the split photocells was operated from a heavy duty, 6V battery. The split photocells and the mechanical balance were completely shielded from the room light by a black cloth. The input circuits of the DC amplifier were guarded and electrostatically shielded.

The circuit used for measuring the feedback current is also shown in Fig. 1. The voltage generated across the decade resistors which were in series with the feedback coil was fed to a 1.2 mv Hewlett-Packard 680M Strip Chart Recorder through a low pass filter. A zero suppression device made it possible to back off to new zero while still keeping the recorder on scale.

In order to isolate the servobalance from mechanical vibrations, a pair of shock mounts (shown in Photograph 2) and rubber hose connections for the pumping system were used (Ref. T. Raudorf M.Sc. Thesis, McGill University, 1967).

III.3. Magnet and Control

As mentioned in section III.1, Faraday's method requires that the value of $H\frac{dH}{dz}$ be fairly constant over a short distance, otherwise, in addition to difficulties of stability, serious errors may arise through failure to maintain the specimen in a fixed position. Specially designed Faraday pole tips, similar to those described by Garber et al (1960), were used. Fig. 2 is a plot of $H\frac{dH}{dz}$ vs z, the vertical distance from the minimum pole-tip separation which is indicated by zero in the figure.









This plot was obtained by a measurement on a germanium sample (500 mg, 5 x 5 x 3 mm) at various distances from the minimum pole-tip separation. The distance was measured by a meter stick (\pm 0.5 mm). The constant force region (2% variations in $H\frac{dH}{dz}$), also shown in Fig. 3, was approximately 10 mm and 25 mm above the minimum pole-tip separation.

The magnet used was a fifteen inch Harvey Wells HS 1365B model, with a 1-1/2 inch minimum pole-tip separation. With this separation and the maximum magnet current (65 Amp) a field of 18.9 kG at minimum pole-tip separation (shown in Fig. 3, point A) and 14.8 kG at constant force region (point B) were produced. Fig. 3 shows the variation of the average magnetic field with the current through the magnet in the constant force region.

As mentioned in section III.1, the reduced susceptibility did not require an exact knowledge of the value of the field but rather only the reproducibility of previously selected fields, so that the method did not need an accurate field calibration. For ferromagnetic corrections, the fields could be measured by a gaussmeter with 1% accuracy. There was a slight hysteresis in the magnet (the coercive field $H_c = 25$ gauss) below 10 kG. To eliminate this difficulty, most of the measurements were taken at the maximum field of 14.8 kG.

III.4. Cryostat

In order to fit a moderately strong dewar with a maximum working space within a minimum pole-tip separation, a metal dewar

Fig. 4. Metal Dewar

- 1. 1-1/2" union.
- Electrical leads for the temperature control. (Black wax sealed; German Silver tubing).
- 3. Thin rubber connection.
- 4. Throttle valve (needle valve) V.
- 5. Helium Fill.
- 6. Exhaust line of sample chamber, E.
- 7. Exhaust line of Insulation Space.
- 8. Waffer.
- 9. Insulation Space.
- 10. Beryllium Copper Suspension wire (2/1000 inch in diameter).
- 11. Liquid Helium Indicators (100 Ω , 1/4 watt Carbon Resistor).
- 12. Liquid N₂ reservoir.
- 13. Liquid He reservoir.
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- 18. Sample tube, B.
- 19. Counterweight.
- 20. Ga-As Temperature Sensing Diode as a Thermometer.
- 21. Cold Helium Gas.
- 22. 22 ohms Cu-Ni Heater.



Fig. 4. Metal Dewar




was used. Fig. 4 shows the detailed construction of such a vessel, manufactured by Andonian Associated, Inc.

As shown in Fig. 4, the stream of cold helium gas controlled by a throttle valve, V, through a capillary tube from the helium reservoir, diffused into the sample chamber, A, and surrounded the bottom part of the sample tube, B. To make a good thermal contact with the specimen, exchange gas of 1-2 mm Hg of helium gas was introduced into the sample tube. To minimize helium boil, there were four stainless steel radiation shields inside the liquid helium reservoir and the bottom shield was placed between the helium level and the top of the liquid nitrogen level. Beside the radiation shields, the cold helium gas at the bottom of the sample chamber was shielded by an aluminum tail cooled by the conduction from the top liquid nitrogen container, C. The helium reservoir would be only precooled slowly by radiation after the outer container was filled with liquid nitrogen. For the same reason of thermal isolation, the dewar vacuum was maintained at 10^{-5} to 10^{-6} mm-Hg, by continuously pumping with an Edward oil diffusion pump and a forepump.

A maximum of five watts of electrical energy through a 22 ohms (Cu-Ni) heater, H, would raise the sample tube temperature above the boiling point of nitrogen when liquid helium was being used as the refrigerant.

It was necessary to have some form of level indicator in a metal dewar because one could not see into the vessel when filling it. Three carbon resistors (shown in Fig. 4) with a bridge circuit, similar to the Aremco portable cryo-gauge 402, were used as helium level indicators, Fig. 5 shows the circuit diagram of level indicator.

III.5. Temperature Measurement and Temperature Control

A gallium-arsenide diode made by the Precision System Corporation was used as a thermometer between 2°K and 300°K during the measurement of magnetic susceptibility, because the Ga-As diode is not affected by the magnetic field. It is necessary to calibrate the Ga-As diode before using as a thermometer. The procedure of calibration will be discussed in Appendix I.

As shown in Fig. 4, the Ga-As diode was fixed at the bottom of the sample tube, about 15 cm below the sample position (constant force region). The schematic diagram for temperature measurement and control of such a diode is shown in Fig. 7. A constant current of 100 microamps was driven through the diode in the forward direction and the voltage across it was measured as a function of temperature. The voltage was measured by a Guildline potentiometer of range from 1 μ V to 2 V. Fig. 6 shows the voltage across the diode with the temperature variation over the whole temperature range studied.

The schematic diagram for temperature control is also shown in Fig. 7. A servomechanism, working on the error signal between the voltage of the temperature sensing diode V_D , and a preset voltage on the potentiometer, V_p , controlled the current in the heater and the rate of heating. The rate of cooling was controlled by the throttle value through a capillary tube and the pumping







Fig. 7. Schematic Diagram of Temperature Measurement of the Diode and Temperature Control

speed of the exhaust line of the sample chamber. In this way, the temperature can be stablized to within $\pm 1/2$ °K at 150°K and ± 20 millidegree at 10°K.

III.6. Balance Chamber and Vacuum System

As shown in Fig. 8, the balance chamber and the insulation space of the metal dewar could be evacuated by an Edward diffusion pump and a forepump. The vacuum was indicated by an Edward Pirani-penning gauge (Pirani gauge: $10-10^{-2}$ mm-Hg, Penning gauge: $10^{-2}-10^{-6}$ mm-Hg).

To minimize the thermal conduction into the cryostat, the upper part of the sample tube was made of stainless steel. To minimize the temperature gradient in the sample position, the lower part was made of copper about 25 cm in length. The overall inner diameter of the sample tube was 1/2 inch. In order to eliminate outgasing in the sample tube, overnight pumping was needed and gave final pressure of 10^{-5} - 10^{-6} mm-Hg.

A thin rubber connection, from the metal dewar to the servobalance and a rubber hose connection, from the exhaust line of the sample chamber to the Stoke's pumping line, were introduced to eliminate unwanted vibrations (Fig. 8).

III.7. Cahn Balance

As mentioned in section III.1 and 2, the servobalance is sensitive and designed mainly for measuring the reduced



Fig. 8. The Balance Chamber and the Vacuum System

susceptibility $\chi(T)/\chi(R.T)$. It is necessary to use an auxiliary balance for measuring the absolute susceptibility at room temperature.

The Cahn RG Electrobalance, having a 2.5 g capacity and a sensitivity of 0.1 μ g, was chosen for measuring the absolute susceptibility at room temperature by using helium and oxygen as calibrating agents. The characteristics and operation of the Cahn balance have been described by S. Mahajan, thesis, McGill (1967). Two modifications were made: one, water jackets were put over the magnet coils to increase magnet stability, and two, the balance was mounted on a lathe cross feed to facilitate the adjustment of the sample position. The experimental error of measuring the absolute susceptibility was l.l%, and the probable error within 0.5%.

III.8. Experimental Procedure

(a) Specimen Preparation and Ferromagnetic Correction.

For the present research it was desired to measure the magnetic susceptibility of polycrystalline pure aluminum and an Al-Mn alloy as a function of temperature. In order to check the purity of the aluminum and the concentration of manganese in the Al-Mn alloy, the resistance ratio [R(4.2/R(296)-R(4.2)] was measured.

The pure aluminum was made from Cominco 69 Grade Aluminum (99.9999+% purity). The Al-Mn alloy (nominal concentration

0.045 at.%) was made by Aluminum Company of Canada Ltd. The spectroscopic analysis of both materials is shown in Table 1.

	Cu	Fe	Mg	Mn	Si	Ca	Ag	
Al	0.2	-	0.1	0.2	-	0.1	0.1	
Al-Mn	10	15	10	450	10	10	10	ppm

Table 1. Spectroscopic Analysis of Al and Al-Mn Alloy.

Strips were rolled from pieces taken from the same ingot adjacent to the susceptibility sample and were used for the measurements of the resistance ratio. The pure aluminum specimens were annealed 24 hours at 450°C to relieve strain. The Al-Mn specimens were annealed 60 hours at 600°C and then quenched in cold water. Specimens were heavily etched in an Aqua-regia-HF solution (75 ml HCl, 25 ml HNO₃, 5 ml HF) after the cutting and the heat treatment.

The resistance ratios of pure aluminum and Al-Mn are 0.00035 and 0.125 respectively. Table 2 shows the comparison of nominal Mn concentrations with impurity concentrations deduced from the resistance ratio and the susceptibility at room temperature.

Table 2. Impurity Concentrations in Al-Mn Alloy.

Nominal Concentration	0.045%	
Concentration from Resistance Ratio	0.039%	*
Concentration from $\chi(296^{\circ}K)$	0.040%	*

(*The value is inferred from the measurements of Aoki).

To check the ferromagnetic impurity in the sample, a Honda plot, $\chi_{\rm H}$ vs $\frac{1}{\rm H}$ was made both at room temperature and at low temperatures. Both samples showed the susceptibility to be independent of the magnetic field indicating the absence of any ferromagnetic impurity (Figs. 9, 10, 11).

(b) Specimen Alignment.

One of the difficulties before measuring the susceptibility is to make sure that the balance is in a condition of freeoscillation which includes the sample not touching the wall of the sample tube and the feedback coil not dragging. There are indirect tests deduced from the oscilloscope and the chart recorder about balance conditions, listed in Table 3.

One can approximately set up the balance by using the horizontal balance leveling feet and level and the final adjustments made using the above tests.

(c) Operating Procedure.

After the entire system is aligned with the vertical, the sample was hung by a thin copper-beryllium wire (0.002 inches in diameter). A test on the balance conditions (section III.8b) was made before evacuating the balance chamber. After the servobalance with the sample attached was observed to swing freely, the system was pumped down overnight (to minimize the residual outgas).

	Free	Touch	Small
	oscillation	the wall	dragging
1. Chart Recorder	straight line	irregular	irregular
2. Zero shift after			
small disturbance	no	yes	yes
3. From oscilloscope	6-7 oscilla-	oscillations	2-3 oscil-
(open loop servo-	tions in l	hardly	lations
mechanism, switch	atm pressure	stopped	
on the dummy load	and 12-14 os-		
R) .	cillations in		
	vacuum		
4. Shape of the os-	irregular,	same, but am-	same, but
cillation in the	changing with	plitude is	amplitude
oscilloscope	time, but am-	3-4 times	is 3-4
when the servo	plitude is	bigger.	times
is on.	small.		bigger.

Table 3. Characteristic Behaviour of Balance.

Some pure helium exchange gas of 0.1 mm-Hg - 1 mm Hg was then introduced into the system. Temperatures below room temperature were obtained by introducing liquid nitrogen into the inner dewar as a refrigerant. For temperatures below the nitrogen point, liquid helium was introduced and temperatures below the helium point were obtained by pumping on the liquid helium. A heater of maximum 5 watts power formed the heating element of a feedback circuit used to control the temperature below the nitrogen point.

Measurements of the susceptibility of a given sample as a function of temperature were all made at the maximum magnetic field.

CHAPTER IV

EXPERIMENTAL RESULTS

IV.1. Room Temperature Susceptibility

Fig. 9(a) shows the room temperature susceptibilities of pure aluminum (99.9999+%) and Al-Mn (400 ppm) as a function of magnetic field and also shows two sets of measurements for each of the samples. A germanium sample is used to check the condition of the Cahn Balance and the same plot for germanium is shown in Fig. 9(b). All of the samples show field independence within the experimental error ± 0.5 % (Appendix II). However, it is interesting to note that the $\chi_{\rm H}$ of Al and Al-Mn are more scattered from the average value than that of germanium. This is because the balance is usually more stable in measuring the diamagnetic specimen. The average value of $\chi_{\rm H}$ obtained from Fig. 9 and the comparisons with some previously published values of these specimens are listed in Table 4.

IV.2. Measurements of Susceptibilities at Low Temperatures

Figs. 10 and 11 show that the variations of the reduced susceptibilities $\chi(T), \chi(296)$ with magnetic field are essentially independent of field within the experimental error (±0.3%) at low temperatures. Combining this fact with the field independence of the room temperature susceptibility indicates that there is no trace of a ferromagnetic component either in Al or Al-Mn to the



Fig. 9. Room Temperature Susceptibility as a function of inverse magnetic field for samples of pure aluminum, Al-Mn (0.04 at.%) alloy and germanium.



Fig. 10. Honda Plot of Pure Aluminum at Low Temperatures



Fig. 11. Honda Plot of Al-Mn Alloy at Low Temperatures

Table 4. Room Temperature Susceptibilities of pure

Sample	$\chi \times 10^7$ (emu/gm)	Remarks		
Ge	1.060 ± 0.05	Stevens (1955)	(298°K)	
	1.054 ± 0.05	present work	(296°K)	
Al (49)	6.193 ± 0.1	Taylor (1959)	(290°K)	
(49)	6.03 ± 0.06	Hedgcock (1963)	(300°K)	
(59)	6.10 ± 0.1	Aoki (1969)	(293°K)	
(69)	6.02 ± 0.03	present work	(296°K)	
Al-Mn	6.24 ± 0.1	Hedgcock (1963)	(300°K)	
(400 ppm)	6.26 ± 0.03	present work	(296°K)	

Ge, Al and Al-Mn Alloy.

lowest temperature (2°K).

It is noted that the Honda plot $(\chi_{\rm H} \text{ versus H}^{-1})$ for aluminum at 4.2°K shows a small oscillation. It is believed those points scattered from the average value are attributable to forced oscillation of the overdamped servobalance below 10°K.

The temperature dependence of the absolute susceptibilities of aluminum and Al-Mn are shown in Fig. 12. Below 40°K the curvature of $\chi(T)$ of aluminum or Al-Mn is changed from concave downward into concave upward. This kind of behaviour is in qualitative agreement with that found by Aoki (1968) and Wheeler (1968) in the same temperature range. The $\Delta\chi(T)$, defined as the difference between the mean curve of $\chi_{Alloy}(T)$ and $\chi_{pure}(T)$, is essentially constant from 40°K to 250°K and has a slight increase from 250°K to 300°K which qualitatively agrees with that found by Flynn (1965) in the temperature range 1000°K to 1400°K.



Fig. 12. Magnetic Susceptibility of pure aluminum and Al-Mn (0.04 at.%) alloy as a function of temperature from

CHAPTER V

ANALYSIS OF EXPERIMENTAL RESULTS

V.1. Aluminum

Combined with the high temperature susceptibility results measured by Auer (1934), the temperature dependence of the susceptibility of aluminum from 2°K to 800°K is shown in Fig. 13. The general behaviour of $\chi(T)$ from 50°K to 800°K looks similar to the theoretical curve of the temperature dependent susceptibility in section II.4. Hence, it will be attempted to fit the experimental results to the model, described in Chapter II, which has $\frac{1}{\pi}$ dependence at high temperatures and to π^2 dependence at low temperatures. Fig. 14 shows a straight line above 450°K in $\chi(T)$ vs T^{-1} curve and gives $\chi(T \rightarrow \infty) = 4 \times 10^{-7}$ emu/gm which can be interpreted as the temperature independent susceptibility. Fig. 15 shows a T^2 dependence from 50°K to 200°K and the value of the slope of T^2 dependence, $s = 1.385 \times 10^{-12}$ emu/gm-(°K), is obtained by a least square fit. Because $\chi(T)$ is turning up below 40°K, the susceptibility at 0°K, $\chi(T \rightarrow 0)$, is defined by the value of extrapolating T^2 dependence of susceptibility to 0°K and gives $\chi(T \rightarrow 0^{\circ}K) = 7.13 \times 10^{-7} \text{ emu/gm}.$

Lingelbach and Vogt (1959) first pointed out that the temperature dependence of the susceptibility of pure aluminum could be fitted into a T^2 law from 100°K to 300°K. This T^2 temperature dependence was attributed to a peak in the density of states at the Fermi level and was based on a band calculation of Matyas (1948)



Fig. 13. Temperature dependent susceptibility of pure aluminum from 50°K to 800°K



Fig. 14. Magnetic susceptibility of pure Al as a function of inverse temperature from 450°K to 800°K



Fig. 15. Magnetic susceptibility of pure aluminum and Al-Mn alloy as a function of T^2 from 50°K to 200°K

The coefficient of the T^2 term derived theoretically was not in good agreement with the experimental results. Extrapolation of the experimental χ to T = 0°K yielded a value for density of states at the Fermi level which agreed with the theoretical calculations of Matyas and with the value that derived from the electronic specific heat, however, their treatments neglected the corrections due to the diamagnetism of the conduction electrons and the electron exchange interactions which would be very important in the calculation of magnetic susceptibility.

In aluminum, a simplified model similar to Lingelbach and Vogt model, based on experimental results is proposed. It is assumed that the Fermi surface can be divided into two parts, one is the average spherical Fermi surface and the other part is the rest of the Fermi surface. The electrons inside the average spherical Fermi surface essentially give the temperature independent spin paramagnetism and the electrons in the rest of the Fermi surface contribute to the T^2 dependence of the susceptibility. Because of the lack of detailed information about the <u>average</u> effective mass for <u>each</u> group of electrons, the correction on diamagnetism is made only by using the average effective mass of <u>total</u> electrons in the conduction band which can be derived from electronic specific heat.

Hence equations II.10 and II.11 can be written as

$$\chi = \chi^{\text{core}} + \left[\frac{1}{1-\nu} - \frac{1}{3}\left(\frac{1}{1.53}\right)^2\right] \left\{ 2\mu_{\text{B}}^2 N_{\text{O}}(\text{E}_{\text{F}}) + 2\mu_{\text{B}}^2 \Delta N(\text{E}_{\text{F}}) \left[1 - \frac{\pi^2}{12}\left(\frac{\text{T}^2}{\text{T}_{\text{O}}^2}\right)\right] \right\} \quad \text{T} << \text{T}_{\text{O}}$$
(V.1)

$$\chi = \chi^{\text{core}} + \left[\frac{1}{1-\nu} - \frac{1}{3}(\frac{1}{1.53})^2\right] \left\{ 2\mu_B^2 N_O(E_F) + \frac{2}{3} \frac{2\mu_B^2 \Delta N(E_F) \cdot T_O}{T} \right\} \qquad T >> T_O \qquad (V.2)$$

At 0°K the equation can be reduced to

$$\chi(T=0^{\circ}K) = \chi^{core} + \left[\frac{1}{1-\nu} - \frac{1}{3}\left(\frac{1}{1.53}\right)^2\right] 2\mu_B^2 \cdot N^*(E_F)$$
 (V.3)

The enhancement factor $\frac{1}{1-\nu}$ introduced by Falicov and Heine can be found experimentally and the value of 1.31 listed in Table 5 is in good agreement with the value 1.3 for aluminum estimated by Pines (Redfield 1955) and 1.35 estimated by Geldart (private communications). The experimental values listed in Table 6 are in good agreement with the theoretical calculations which are based upon the model described in Chapter II. The

Table 5. Comparison of experimental results and theoretical calculations in aluminum (I).

Average effective mass

X ^{core}	-0.93 x 10 ⁻⁷ emu/gm
N*(E _F) specific heat	4.03 x $10^{33} \text{ erg}^{-1} \text{ gm}^{-1}$
$\chi(T \rightarrow 0)$ measured	7.13 x 10 ⁻⁷ emu/gm
$\frac{1}{1-\nu}$	1.31
	1

agreement in the second row in Table 6 indicates that the

Table 6. Comparisons of experimental results and theoretical calculations in aluminum (II).

N*(E _F) specific heat	4.03 x $10^{33} \text{ erg}^{-1} \text{ gm}^{-1}$
N _O (E _F) (Free electron)	2.675 x $10^{33} \text{ erg}^{-1} \text{gm}^{-1}$
$\Delta N(E_{F}) [=N*(E_{F}) - N_{O}(E_{F})]$	1.355×10^{33}
$\chi_{el}^{sph F.S.} = 2\mu_{B}^{2}N_{O}(E_{F})$ χ_{cal} (Temp. Indep.) $\chi_{measured}$ (Temp. Indep.)	4.6 x 10 ⁻⁷ emu/gm 4.42 x 10 ⁻⁷ emu/gm 4 x 10 ⁻⁷ emu/gm
χ_2 (calculated): $2\mu_B^2[\Delta N(E_F)]$ χ_{el} (calculated) χ_{el} (measured)	2.33 x 10^{-7} 2.71 x 10^{-7} 3.13 x 10^{-7}
T_{O} (measured from χ)	401°K
T _O (dHvA) Gunersen	387°K

Average effective mass

temperature independent susceptibility can be attributed to the electrons in the spherical Fermi surface which is essentially the first and second zone of the Fermi surface of aluminum based on the Ashcroft model (1963). It is important to point out that the degeneracy-temperature $T_0 = 401^{\circ}K$ obtained from the susceptibility measurements is in good agreement with the limiting energy ($E_0 = kT_0$) from the long period dHvA oscillation

found by Gunnersen (1957). The third zone of the Fermi surface of aluminum based on the Ashcroft Model (1963) is essentially a "ring structure".



(iii)

The free electron Fermi surface of aluminum (i) filled first zone, (ii) second zone hole surface, (iii) third zone electron surface, (iv) fourth zone pockets of electrons. In (iii) and (iv) the zone centre has been shifted in the reduced zone mapping.

(iv)

The long period found by Gunnersen essentially can be divided into two, α and β orbits in the third zone. Hence, it can be interpreted that the electrons inside the "neck" (α orbits) and "corner" (β orbits) of the "ring structure" give rise to the T² dependent susceptibility. It is noted that the effective

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mass of this small group of electrons in the third zone from dHvA effect (m* ~ $0.1m_0$) is not supported by the fact of the large paramagnetism in aluminum. However, it is not a serious discrepancy in the Ashcroft "ring structure". Based upon the Ashcroft model the effective mass of the long period dHvA oscillations is attributed to the electrons moving in the α and β orbits, and the other components of the effective mass are essentially highly anisotropic so that the average effective mass of this group of electrons gives rise to the large observed paramagnetism[•]. In conclusion, the experimental facts can be qualitatively described by the model based upon the knowledge of the band structure of aluminum.

It is interesting to note that the susceptibility of aluminum increases monotonically with decreasing temperature below 30°K. The susceptibility of aluminum below 200°K can be fitted to the following equation

$$\chi(T) = [7.13 \times 10^{-7} - 1.38 \times 10^{-12} T^2] + \frac{1.47 \times 10^{-7}}{T}$$
 emu/gm

If
$$\partial \chi_{T<50^{\circ}K}^{A1} \equiv \chi(T) - [7.13 \times 10^{-7} - 1.38 \times 10^{-12} T^2]$$
 (V.4)

therefore
$$\partial \chi_{T<50^{\circ}K}^{Al} = \frac{1.47 \times 10^{-7}}{T}$$
 emu/gm

Fig. 16 shows the plot of $\partial \chi_{T<50^{\circ}K}^{A1}$ vs T^{-1} .

Within the experimental error (±1% at 4.2°K), Al-Mn (0.04 at.%) shows the same temperature behaviour.

The "spin only" Curie Law for the nuclear paramagnetism of aluminum with a nuclear moment 3.64 $\mu_{\rm N}$ can be written as



Fig. 16. Magnetic susceptibility of aluminum below 25°K

$$\chi_{A1}^{Nuclear} = \frac{0.251 \times 10^{-7}}{T} \text{ emu/gm}$$
 (V.5)

This nuclear paramagnetism only contributes one-sixth of the 1/T component.

There is no definite explanation of the rest of the 1/Tcomponent in aluminum. It corresponds to 8 parts in 10^7 paramagnetic ions with spin $\frac{5}{2}$. However, it is believed that this Cuire-like tail is not contributed by any 3d-transition metal impurity in aluminum, because it is known that the Curie-Weiss law for the 3d impurity up to a concentration 0.04% is not obeyed. There are two possible sources of the observed paramagnetism: one is due to <u>molecular</u> oxygen dissolved in the aluminum ingot during fabrication; the other is due to the intrinsic property of aluminum. To check the first possibility, it is suggested that the molecular oxygen can be evacuated at very high vacuum from the melted aluminum and then re-measure the susceptibility of this "oxygen-free" aluminum.

It should be pointed out that the line width of conduction electron spin resonance in aluminum is essentially independent of temperature and <u>sample thickness</u> below 25°K. S. Schultz, G. Dunifer and C. Latham (1966) point out that it is possibly due to another relaxation mechanism in aluminum, as yet not understood, at low temperatures. It is not known whether there is any connection between the anomaly in conduction electron spin resonance and that in susceptibility below 30°K.

V.2. Aluminum-Manganese Alloy

The magnetic susceptibility of Al-Mn (0.04 at.*) exhibits the same temperature dependence as that of pure aluminum. A T^2 dependent susceptibility for Al-Mn alloy is shown in Fig. 15. Within the experimental error (±0.6% in slope), aluminum and the Al-Mn alloy have the same slope in the plot of $\chi(T)$ vs T^2 . No additional T^2 dependence contributed by the manganese impurities is observed in this 0.04 at.% Al-Mn system.

The constant $\Delta \chi = \chi_{Alloy} - \chi_{pure}$ (from 50°K to 250°K) can be interpreted as follows: if the Mn impurity is near to being magnetic, the Pauli paramagnetism of the Lorentzian virtual bound state with fivefold orbital degeneracy is enhanced and can be written as

$$\chi_{\text{pauli}}^{\text{d electron}} = 2\mu_{\text{B}}^{2}[\partial N(E_{\text{F}})]_{\text{Mn}} \cdot \eta$$
$$= \frac{10N\mu_{\text{B}}^{2}}{\pi} \frac{\eta}{\Delta} \qquad (V.6)$$



where η is the enhancement factor of the d-state

 Δ is the width of the virtual bound state and N is the number of the Mn impurities.

This has been discussed for the Al-Mn system by Caplin and Rizzuto (1968). The parameter $\frac{\Lambda}{\eta}$ can be estimated from susceptibility and resistivity measurements independently and is shown in Table 7.

Table 7. $\frac{\Delta}{\eta}$ values from resistivity and susceptibility measurements.

	·	Susceptibility			
	Resistivity	present work	others*		
$\frac{\Delta}{\eta} \times 10^2 \text{ eV}$			6.9 ± 1.0 (300°K)		
for Al-Mn	8.3 ± 0.5	8.05 ± 0.5	8.6 ± 0.7 (300°K)		
	(1.5°K to 4.2°K)	(50°K to 250°K)	9.0 ± 0.2 (1360°K)		

The width of the virtual bound state for Al-Mn, derived from superconductivity 0.8 eV (Boato et al 1967), specific heat 0.17 eV (Aoki 1968) and thermopower 0.27 eV (Boato 1967), is consistently found to be of the order 0.5 eV. For $\Delta \approx 0.5$ eV the enhancement factor n from present susceptibility measurements is approximately 6.2. It is also noted that $\frac{\Delta}{\eta}$ from low temperature susceptibility measurements has a better agreement with that from the resistivity measurements than that from high temperature susceptibility measurements. It is consistent with the fact that the theoretical formulation of the enhanced pauli paramagnetism is valid at T = 0°K.

The slight increase in $\Delta \chi = \chi_{Alloy} - \chi_{pure}$ from 250°K to 300°K is in qualitative agreement with the contribution of the impurities dissolved in liquid aluminum from 1000°K to 1400°K (Flynn 1967). Flynn suggestes that the increase of magnetization with temperature can be tentatively interpreted as the effect of thermal expansion on the band structure. Friedel (1968) has argued that the impurity bandwidth should increase with the solvent Fermi energy because the overlap integral between the conduction band and atomic d states increases. The Stoner (1935) formula for the thermal expansion of the solid modified by the same enhancement factor n in equation (V.6) for the d state can be written as

$$\frac{1}{\chi_{\mathbf{p}}} \frac{\partial \chi_{\mathbf{p}}}{\partial \mathbf{T}} \simeq \frac{2}{3} \alpha_{\mathbf{v}} \eta \qquad (\mathbf{V.7})$$

where α_{v} is the volume thermal expansion coefficient of the solvent. For Mn in aluminum at 300°K with $\eta = 6.2$ and $\alpha_{v} \approx 0.23 \times 10^{-4} (°K)^{-1}$, $\frac{1}{\chi_{p}} \frac{\partial \chi_{p}}{\partial T} = 0.95 \times 10^{-4} (°K)^{-1}$ is in good agreement with the value of $1.02 \times 10^{-4} (°K)^{-1}$ determined from the bottom curve $\Delta \chi(T)$ in Fig. 12.

Narath and Weaver (1969) reported the nuclear resonance shifts and spin-lattice relaxation rates of dilute "non-magnetic" V, Cr, and Mn impurities in aluminum and similar data for the "magnetic" alloys AuV ($T_k \sim 300$ °K) and MoCo ($T_k \sim 24$ °K) at temperatures below the Kondo temperature (1.3 to 4.0°K). They demonstrated that the magnetic properties of both systems were qualitatively indistinguishable at sufficiently low temperatures. Hence, the impurity susceptibility is saturated at temperatures below the Kondo temperature and effectively temperature independent

Brettell and Heeger (1967) reported the NMR of Al nuclei in dilute Al-Mn alloys. Within the limits of experimental error, the line width, line shape, and Knight shift were found to be independent to the impurity concentration, temperature and magnetic field. No satellite line of the Al nuclei resonance was reported.

Launois and Alloul (1969) investigated the NMR of both Al and Mn nuclei in dilute Al-Mn alloy. The Al resonance in the alloy was reported to consist of a central unshifted Al line corresponding to pure Al and a satellite line which they suggested results from an interaction with Mn nearest neighbours. They pointed out that the magnitude of the observed Knight shift due to Mn impurities was much too large to be explained other than on the basis of an enhanced polarization of the conduction electrons. The first nearest neighbour Knight shift, which was assumed to be proportional to the impurity susceptibility, exhibited a linear temperature dependence.

The present work on $\Delta \chi_{Mn}$ agrees with the enhancement of polarization of the conduction band by Mn impurities. However, the absence of any temperature dependence does not support the linear temperature dependent d-electrons susceptibility as found by Launois and Alloul.

In conclusion, the present work does not confirm the presence of localized spin fluctuations in the system of 0.04 at.% of Mn in aluminum. However, the ratio of the enhancement factor

to the width of the virtual bound state from the susceptibility measurements at low temperatures is in good agreement with that from the resistivity measurements by Caplin and Rizzuto (1968).

It is still an open question whether the localized spin fluctuations are present in the Al-Mn system. It is suggested that the susceptibilities of a higher concentration of the Al-Mn system (0.1% - 0.4%) should be very carefully measured from 50°K to 300°K, before we draw any further conclusions on the Al-Mn system.

SUMMARY

Measurements of magnetic susceptibility have been made on polycrystalline samples of pure aluminum (99.9999%) and Al-Mn metal alloy (0.04 at.%) using a Faraday method. A metal dewar is set up permitting the investigations to be carried out in the temperature range from 2°K to 300°K.

The magnetic susceptibility of pure aluminum shows a large temperature dependence from 2°K to 300°K. In this temperature region, the susceptibility is independent of the magnetic field indicating the absence of any ferromagnetic impurities. The absolute susceptibility of pure aluminum at room temperature $(296^{\circ}K)$ was measured as $(6.02 \pm 0.03) \times 10^{-7}$ emu/gm. From room temperature to 50°K the susceptibility changes by 18% and exhibits a T^2 dependence (50°K to 200°K) within an error of ±0.3%. The T² dependence of the susceptibility can be interpreted in terms of the band structure of aluminum. The susceptibility of pure aluminum increases rapidly with decreasing temperature below 30°K and shows a Curie-like behaviour. The nuclear paramagnetism of aluminum can only account for one-sixth of this 1/T component. A further investigation of the susceptibility of aluminum below 50°K has been suggested.

The temperature dependence of the susceptibility of Al-Mn is essentially attributable to the intrinsic properties of aluminum rather than a result of alloying with manganese. The difference in susceptibility, $\Delta \chi_{Mn} = \chi_{Alloy} - \chi_{pure}$, due to the

contribution of Mn impurity, is essentially constant from 50°K to 250°K and increases slightly from 250°K to 300°K. The slight increase in $\Delta \chi$, gualitatively agrees with the measurements of Mn dissolved in liquid aluminum (1000°K to 1400°K, Flynn, 1967) and can be interpreted in terms of the thermal expansion of the The susceptibility of Al-Mn also shows a T² dependence solid. between 50°K and 200°K. Within the experimental error (±0.6%), pure aluminum and Al-Mn have the same slope. No additional T^2 dependence due to Mn is observed in this 0.04% Al-Mn system. Therefore, the present work does not confirm the presence of localized spin fluctuations in this 0.04% Al-Mn alloy. However, the ratio of the enhancement factor to the width of the virtual bound state from the low temperature susceptibility measurements is in good agreement with that from the resistivity measurements by Caplin and Rizzuto (1967).
APPENDIX I

THERMOMETER CALIBRATION

A Ga-As diode (Section III.5) was used as the temperature measurements from 2°K to 300°K. In order to measure the true sample temperature, it is necessary to calibrate the temperature reading of this Ga-As temperature sensor diode (so-called "red spot" diode) which was fixed at the bottom of the sample tube. The procedures of the calibrations will be described as follows.

Initially, this "red spot" diode was calibrated against another Ga-As diode (so-called "pink spot" diode) which had been calibrated by the manufacturer. Fig. AI.1 shows the linearity of these two diodes. The calibrated "pink spot" diode was checked against a more reliable germanium thermometer made by Texas Instruments at temperatures below 30°K, and a difference of up to 5°K was found between the two thermometers. For high temperatures, the error decreased until at 30°K there was only 1°K difference between the two thermometers. Fixed-point checks at liquid nitrogen point and at ice point, showed a consistent error of half a degree in the calibrated "pink spot" diode. Hence, the "red spot" diode was calibrated against the germanium thermometer below 30°K, shown in Fig. AI.2, and against the "pink spot" diode at high temperatures, allowance being made for the 1/2°K error at room temperature. Fig. 6 is a plot of voltage across the "red spot" diode as a function of temperature from 2°K to 300°K.



Fig. AI.1. Linearity of Ga-As Temperature Sensing Diode



Fig. AI.2. Temperature Calibration of Ga-As Diode from 1.5°K

to 25°K against Germanium Thermometer

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A further investigation was made for the temperature at the sample position which is approximately 15 cm above the position of the "red spot" diode. The "pink spot" diode was suspended on the sample position with 1-2 mm-Hg helium exchange gas and tests were performed to check that both diodes registered the same temperatures. Differences of 1/2°K were found above 50°K and 1/5°K below 25°K.

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APPENDIX II

ERRORS

The magnetic susceptibility at room temperature was measured using a Cahn Balance (Section III.7) with oxygen gas as a calibrating agent. From equation III.3, the total error in susceptibility can be expressed as follows

$$\left| \frac{\Delta \chi}{\chi} \right|_{S} = \left| \frac{\Delta F}{F_{He}} \right| + \left| \frac{2\Delta F}{F_{He} - F_{OX}} \right| + \left| \frac{\Delta P}{P} \right| + \left| \frac{2\Delta T}{T} \right| + \left| \frac{\Delta \chi}{\chi} \right|_{Oxygen}$$

The absolute calibration of the equipment is dependent upon the use of oxygen as a standard and therefore can be no more accurate than the value for the susceptibility of oxygen. The uncertainty of the value 106.2×10^{-6} emu/gm at 20°C for oxygen (Bate 1963) is approximately ±0.3%. Errors from the pressure and temperature of the gas would be less than ±0.1%. The major uncertainty on the standardization was the purity of the oxygen gas (99.8% extra dry). Experiments indicated that, with continuous operation, the reproducibility of a given field was ±0.1% or better. The Cahn Balance has a sensitivity of 1 microgram, errors from this source being approximately ±0.4% in measuring the specimens studied. Therefore, on an absolute basis, the reported room temperature susceptibility may be as much as ±1.1% high. The maximum error relative to the oxygen gas is approximately ±0.8%.

The precision in the determination of the susceptibility of a sample as a function of temperature relative to its roomtemperature susceptibility is dependent upon the reproducibility of the magnetic field, the sensitivity of the servo-balance, and the measurement of the temperature. The measurement of the temperature was found to be the least source of error in that the susceptibilities of the samples were found to change less than 0.1% per degree change in temperature. Sample temperatures could be maintained within ±0.5°K, and error from this source would be less than ±0.05%. The reproducibility of a field with maximum magnet current was ±0.05%. The reproducibility in the determination of a susceptibility at a given temperature was ±0.3%. There is another major uncertainty attributed to the changing of the sample position with the temperature due to thermal expansion of the suspension wire. A rough estimation at 4.2°K results in the wire contracting about 1 mm from its room temperature value. Error from this source estimated from the constant force curve (Fig. III.2) was approximately ±0.15%, which was in good agreement with the measurement of a standard germanium sample as a function of temperature. Therefore the maximum error in reduced susceptibility is approximately ±0.6% at helium temperature and ± 0.5 % at temperatures from 50°K to 300°K.

Since in most cases, the points determining a given curve were obtained in a continuous run, the maximum probable error in the location of any point is approximately ±0.3%.

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