Quantum Corrections to the Conductivity in Simple Metallic Glasses

by

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To Monika

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ABSTRACT

The validity of the theories of quantum corrections to the electrical conductivity, namely weak localization and enhanced electron electron interaction, has been tested quantitatively in well characterized, free-electron-like Mg-Cu and Mg-Zn metallic glasses containing various amounts of Ag and Au through measurement of the electrical resistivity between 1.5K and 20K in magnetic fields up to 5.6T. It is found that the theories give an excellent description of the magnetoresistance at low fields, in both the weak and strong spin-orbit scattering limit but that at higher fields they break down. The electron spin-orbit scattering and dephasing rates have been deduced. Above 4K the dephasing rate is controlled by inelastic electron phonon scattering, below 4K it saturates to a value consistent with a new model of dephasing of the quantum back scattering interference by ionic zeropoint motion. The first direct measurement of the effect of superconductivity on the magnetoresistance in bulk amorphous metals is also presented. The temperature dependence of the resistivity between 1.5 and 6K is in qualitative but not quantitative agreement with the quantum correction theories.

RÉSUMÉ

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La validité des théories de corrections quantiques à la conductivité électrique, c'est-à-dire la localisation faible et l'interaction électron-électron renforcée, a été vérifiée quantifativement dans des verres métalliques bien caractérisés du type électrons libres, à base de Mg-Cu et de Mg-Zn et contenant divers niveaux de Ag et de Au par mesure de la résistivité électrique entre 1.5K et 20K dans des champs magnétiques allant jusqu'à 5.6T. Il a été trouvé que les théories fournissent une excellente description de la magnétorésistance à de faibles champs, à la fois dans les limites de faible et de forte diffusion spin-orbitale mais qu'à des champs plus élevé, elles ne s'appliquent plus. Les taux de diffusion spin-orbitale et les taux de déphasage ont été déduits. Au dessus de 4K le taux de déphasage est controlé par la diffusion inélastique électron-phonon, alors qu'en dessous de 4K il sature à une valeur qui est en accord avec un nouveau modèle de déphasage de l'interférence de la rétrodiffusion quantique par mouvement ionique de point zéro. La première mesure directe de l'effet de la superconductivité sur la magnétorésistance dans les métaux amorphes tridimensionnels est également présentée. La dépendance de la résistivité sur la température entre 1.5K et 6K est en accord qualitatif mais non quantitatif avec les théories de corrections quantiques.

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1. Introduction

Amorphous metals are metals whose atoms do not show long range structural order. They were first produced in bulk in 1959 by Duwez¹ and his coworkers at the California Institute of Technology, using a technique of rapid quenching of the liquid. Since that time, and in particular since 1970, the unique properties of amorphous metals have inspired much research and have also lead to several industrial applications.

The absence of structural order "is illustraited on Fig.1.1, where the atomic structure factor of an amorphous solid is compared with that of a liquid and a crystal.





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It is clear that the atomic arrangement is more like a liquid and it is this combination of the atomic disorder of a liquid with the mechanical integrity of a solid which gives amorphous metals many of their unique properties, examples of which are high tensile strength, low magnetic hysteresis energy losses and strong corrosion resistance.

To date amorphous metals have been produced using a variety of techniques such as vapor phase condensation, chemical deposition, ionbeam mixing, solid state reaction and continuous rapid cooling from the melt⁴. The group of amorphous metals produced by melt-quenching, the last of the above techniques, is often referred to as metallic glasses, though the distinction may be largely semantic.

The underlying principle in all of the methods is to form the metastable amorphous phase at a rate faster than its transformation to the energetically more favorable crystalline phase. In the case of the melt-quenching method (which is the only one used for the research in this thesis) this is best demonstrated by a Time-Temperature Transformation (TTT) diagram, as displayed in Fig.1.2.





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This diagram shows the time taken by an undercooled liquid to crystallizé, as a function of temperature. It is characterized by the interplay between thermodynamic driving force and atomic kinetics. When a liquid is cooled below the ideal melting temperature, T_, the free energy of the crystal phase becomes less than the free energy of the liquid phase causing, initially, a decrease in crystallization time. But lowering the temperature also reduces the atomic mobility, and eventually the point is reached when the crystallization time starts to increase leading to the "nose" at T_n, t_n in the TTT-diagram. At some temperature T the atomic mobility is so small (this point is usually defined by a viscosity exceeding 10¹² poise) that the atomic rearrangement necessary for crystallization becomes impossible on laboratory time scales, leaving the undercooled liquid frozen in a single configuration called an amorphous solid. Because of the nondirectional nature of the metallic bonding (in contrast to the directional covalent bonding in silicates and borates) the cooling rates necessary to bypass the "nose" are relatively high. In the case of elemental metals T_g is so low (typically 40K) that the cooling rates necessary have been estimated to be of the order 10^{13} K/sec, which is inaccessible by any practical melt-quenching device. However, in many alloys particularly those close to a deep eutectic the melting ${}^{\mathcal{Y}}$. temperature T_m and the glass transition temperature T_g may_c be quite close (e.g $T_{g}/T_{m} > 0.45$) and a metallic glass can be produced relatively easily by rapid quenching from the melt (see Chapter 3 for more details) using cooling rates of about $2 \cdot 10^6$ K/sec.

So far research on amorphous metals has been directed towards applications. However there has been a substantial body of work on fundamental properties, work whose aim has been to examine how the properties are influenced by the absence of long range periodicity. In particular the electrical resistivity has been the subject of intense research for about 20 years, and it is one aspect of this which is the topic of the present thesis.

At first sight the electrical resistivity in amorphous metals is much simpler than in crystalline metals. An ideal perfect crystal offers

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no resistance to electron flow, and the resistance of a real crystalline metal reflects deviations from ideality as a result of defects, impurities and thermal vibrations. Hence the resistivity of a crystalline metal is very temperature dependent, system dependent (e.g compare Cu and Fe) and, at low temperatures, sample dependent. By contrast the gross atomic disorder tends to constrain the resistivity of amorphous metals to a certain uniformity. The mean free path of the electrons is of the order of a few interatomic spacings which leads to a resistivity of about 100μ Cm, and indeed almost all amorphous metals have resistivities in the range 40 to 300μ Cm. Furthermore the influence of thermal vibrations on the already severe structural disorder is almost negligible so that the resistivity of amorphous metals has a comparatively small temperature dependence. The contrast between the behavior of crystalline and amorphous metal is illustrated in Fig.1.3.





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On deeper examination, however, amorphous metals prove to be less simple:

i) The room temperature resistivity, ρ , and the room temperature resistivity temperature coefficient, $\alpha = \frac{1}{\rho} \left(\frac{d\rho}{dT} \right)_{RT}$, are correlated. They fall into either of two groups, as shown in Fig.1.4, depending on whether the current is predominantly carried by s,p. or d-electrons. This is known as the Mooij correlation after the person who first pointed it out in sputtered transition metal films⁸.





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fi) At low temperatures the registivity of all disordered metals has a negative temperature coefficient, provided the metals are not close to a superconducting transition. Typically below 15K the resistivity shows a slow negative temperature variation regardless of the specific high temperature behavior. In addition, one observes in this temperature regime a very large magnetoresistivity which is difficult to explain by the usual Lorentz-force-derived effects seen crystalline metals. Some representative graphs of these unusual low temperature resistivity properties are shown in Fig.1.5a,b.

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Figure 1.5 a) The resistivity temperature dependence of three amorphous metals below 20K (from reference 6).

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Figure 1.5 b) The magnetoresistance of amorphous Mg₇₀Cu₃₀ (ref. 9) amorphous Ni₅₀Zr₅₀ (ref. 10).

The temperature dependence of the electrical resistivity at higher temperatures, i.e above 20K, has been discussed and studied by many workers⁷ and is not the topic of this thesis.

¹ The studies on the slow temperature dependence of the resistivity at low temperatures have a long history. At first, since the behavior could be regarded as roughly logarithmic, most authors assumed it was caused by the Kondo effect in which electrons scatter off magnetic impurities. The fact that all early amorphous metals contained some magnetic elements lent credence to this idea, but it was shown in 1975 by Cochrane and coworkers¹¹ that the effect also existed in systems <u>without</u> magnetic impurities and was of about the same magnitude. These

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authors preferred an explanation of structural origin and proposed that the effect was caused by electrons scattering off a vibrational degree of freedom (rather than magnetic as for the Kondo effect), a so-called "two-level system". The progress on this controversial subject up to 1980 is reviewed by Harris and Strom-Olsen¹² who point out that neither of the two models should be considered as satisfactory as they do not explain consistently the observed temperature dependence of the resistivity and fail altogether to account for the very large magnetoresistance mentioned in point ii) above.

The discussion over the true nature of the low temperature resistivity took a new direction with the publication of articles by Abrahams, Anderson, Licciardello and Ramakrishnan¹³ and Altshuler and Aronov¹⁴ on the role of disorder in the behavior of the electrical conductivity. Following ideas of Thouless¹⁵, Abrahams et al. presented a scaling theory of electron localization. They identified the first perturbation correction to the conductivity due to disorder to arise from coherent backscattering processes first discussed by Langer and Neal¹⁶. Shortly after, Anderson and coworkers¹⁷ associated the slow temperature dependence of the resistivity observed in thin disordered metal wires with this correction. Altshuler and Aronov¹⁴ on the other hand, showed that in disordered metals (these include thin metallic films, strongly doped semiconductors and amorphous metals) the intense elastic scattering interferes with the electron-electron interaction and causes a correction to the density of states. As a consequence a slow temperature dependent correction to the resistivity arises; in three dimensional conductors it varies as $-\sqrt{T}$.

The work by Abrahams et al. and Altshuler and Aronov triggered an avalanche of theoretical investigations into the nature of the conductivity of disordered conductors which resulted into the formulation of theories known today as quantum corrections to the conductivity. All of these theories are based on the idea that the electron motion through a disordered conductor *J*- such as an amorphous metal - is diffusive rather than ballistic as in crystalline conductors. The diffusive nature of the electron motion leads to two additional

effects on the conductivity at low temperatures by causing a quantum interference of backscattered electrons, which is referred to as the weak localization effect^{18,19}, and by decreasing the dynamical electronic screening and thus enhancing the electron-electron interaction^{20,21,22}.

The theoretical studies on the quantum corrections to the conductivity were accompanied by numerous experimental investigations.[®] Much of the early work concentrated on the wide field of strongly doped semiconductors (the reader is referred to reviews in reference 23). Bergmann²⁴ was the first to study systematically the weak localization effect in amorphous thin films. He reported an excellent agreement,

The success of the quantum correction theories in three dimensional amorphous metals is less clear. Bieri and coworkers²⁵ were the first to carry dut measurements of the magnetoresistance in a bulk metallic glass $(Cu_{57}Zr_{43})$ to study the quantum correction theories. Even though they find good agreement between data and theory at small magnetic fields some serious deviations are apparent at larger fields which become more pronounced at lower temperatures. Studies on the magnetoresistance by Poon et al.²⁶ in $Cu_{60}Zr_{40}$ and $Y_{75}Al_{25}$ followed. They too report significant discrepancies between theory and measurement. Olivier and coworkers²⁷ find that the magnetoresistance in amorphous Y-Al ribbons cannot be fitted consistently to the theory over the entire field and temperature regime. Only Howson et al.²⁸ report semi-quantitative success of the theories in Cu-Ti metallic glasses. However, all the experiments carried out to date on bulk amorphous metals have suffered from a number of serious drawbacks: The electrical transport properties were complicated by one or more of d-band conduction 25,26,27,28, superconductivity^{28,29}, magnetic ordering³⁰ or a significant level of magnetic impurities ^{31,32}. These complications introduce sufficient uncertainties into the analysis that they do not allow an unambiguous assessment of the success of quantum correction theories. Furthermore, it should be noted that some workers have treated some of the parameters^{†)} entering the formulae beyond what is physically reasonable; such as large, resistivity prefactors 32 and variable superconducting fluctuation parameters²⁵.

t) The significance of these parameters and the importance of their proper handling is explained in detail in Chapters 2 and 4.

The objective of this thesis is to investigate the quantum corrections to the conductivity in the most simple bulk amorphous metals available and to provide a stringent and unambiguous test of the existing theories. One of the simplest metals which can be cast without much effort into an amorphous solid by quenching from the melt is $Mg_{70}Cu_{30}$. Amorphous $Mg_{70}Cu_{30}$ has been been well characterized as a simple free-electron system, with electrical transport characteristics above the low temperature resistivity anomaly which are well understood within the Faber-Ziman theory 33,34,35. In this sp-band amorphous alloy the expansion parameter, $(k_{\rm F}1)^{-1}$, of the quantum correction theories, is well defined and small enough (i.e 0.06) that higher order contributions are negligible. Parameters that enter the quantum correction theories, such as resistivity, Fermi wave vector, density of states, electron diffusivity and electron screening factor, are either known from experiment or can be calculated with sufficient confidence from free electron theory^{33,34,35}. The alloy is neither superconducting nor does it exhibit any magnetic ordering; in fact it is diamagnetic. Also, it can be manufactured with a magnetic impurity level of the order, parts per million. This leaves only two main parameters of the theories of quantum corrections to the conductivity undetermined. These are the the spin-orbit and inelastic electron scattering rates which control both the magnitude and signa of the corrections. Measuring the quantum corrections to the magnetoresistance at different temperatures allows us to resolve the temperature dependent inelastic scattering rate. Also, the spin-orbit scattering rate will be studied systematically: The Mg-Cu system allows progressive increase of the spin-orbit scattering rate by substitution of up to half of the Cu by the heavier metals Ag and Au. Other electrical transport properties will not change significantly, since Cu, Ag, Au are elements with the same valence and almost identical covalent radii. It is expected from quantum correction theories that the magnetoresistance changes sign from negative to positive when going from weak to strong spin-orbit scattering.

The advantages of Mg based alloys are not yet exhausted. One can replace all of the Cu by Zn. Though being remarkably similar

otherwise³⁶, the two alloys $Mg_{70}Cu_{30}$ and $Mg_{70}Zn_{30}$ differ in one very fundamental aspect; $Mg_{70}Zn_{30}$ is a superconductor³⁷ with a transition temperature of 0.12K whereas $Mg_{70}Cu_{30}$ is not superconducting. This implies that the sign of the electron-electron goupling constant is changed and thus offers a unique-chance to resolve the effect of enhanced electron-electron interactions and superconducting fluctuations on the electrical transport in amorphous metals.

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Through_deliberate doping of the high purity Mg based alloys with Manganese and Gadolinium it is demonstrated in this thesis how the weak localization quantum interference is suppressed by magnetic impurity scattering.

In the following chapter the theories of quantum corrections to the conductivity will be briefly reviewed to give the discussion of the experimental data in Chapter 4 a proper theoretical footing. The experimental methods employed in this work are described in detail in Chapter 3. The conclusions of this research are drawn in Chapter 5. Some numerical recipes and analysis techniques are presented in the appendices.

2. THEORY OF QUANTUM CORRECTIONS TO THE CONDUCTIVITY

2.1 General Remarks

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> Following the work of Abrahams and coworkers¹³, and Altshuler and Aronov¹⁴ a large number of theoretical studies of the quantum corrections to the conductivity in disordered conductors has been published during the last 8 years. This chapter gives a review of those aspects of the quantum correction theories which are relevant to the understanding of the resistivity measurements on the Mg-based metallic glasses studied in this thesis.

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A rigorous mathematical derivation of the theories is far beyond the scope of the thesis. It is merely intended to make the quantum correction theories plausible to the reader, and to provide a physical picture of electrical conduction in amorphous metals.

Prior to any discussion it is necessary to define what is meant by disordered conductors. An ordered conductor is one in which, 1, the average distance between lattice defects and impurities or the extent of strict translational symmetry, is larger than the length, 1,, over which the conduction electron wave-function maintains phase coherence. In such conductors correlations between scattering events at different lattice defects or impurity sites are unimportant since the electron keeps no memory of its phase. Any conductor which does not obey this restriction is considered disordered. Examples of the latter group are: all amorphous metals, many fine polycrystalline conductors, icosahedral and quasicrystalline metals, strongly doped semiconductors (metallic regime), chemically disordered (or random substitutional) alloys and conductors with a high density of defects (such as ion-irradiated metals). In these materials the elastic scattering length can vary between one and several hundred interatomic spacings. The phase coherence length depends critically on the temperature and lies also in the above range.

In ordered conductors the motion of the charge carriers is essentially ballistic, i.e between scatterings the electron propagates undisturbed over many interatomic distances. A non-zero resistivity arises from the fact that electrons scatter off the occasional lattice defect, impurity atom or thermal_lattice vibration (phonon). Using simple kinetic theory, as first shown by Drude³⁸ in 1900, the resistivity can be written as

$$p = \frac{m}{e^2 n\tau}$$
(2.1)

(2.2)

where m is the current carrier mass, e the carrier charge and n the carrier volume density. The characteristic inverse time $1/\tau$ is the total effective scattering rate due to the different scattering mechanisms listed above. This result can also be obtained more rigorously using linear response theory³⁹. Matthiessen's rule³⁸ states that independent scattering rates are additive and thus one can write the resistavity of a metal as

$$\dot{\rho} = \rho_0 + \rho(T)$$

 ρ_0 is the residual resistivity arising from lattice defects impurities etc., and is temperature independent, and $\rho(T)$ is generally due to dynamic disorder such as electron-phonon scattering. Ideally if no correlation effects between single scattering events are present, $\rho(T)$ reduces to zero at T=0 and one then speaks of ρ_0 as the residual resistivity (see for example measurements on potassium in reference 40,41).

In disordered conductors the picture of ballistic motion of electrons breaks down. With increasing disorder the spatial separation of independent elastic scattering events eventually becomes smaller than the coherence length and correlation effects arise. Naively speaking one can say that for sufficient disorder the conduction electrons undergo numerous random elastic scatterings before they lose phase memory, i.e $l_e << l_{\phi}$. In this limit the electron path can be viewed as a random walk. Consequently it is appropriate to define an electron diffusivity D from the velocity-velocity correlation function as

 $D = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle_{t,OM}$ (2.4)

where \vec{v} is the velocity of electrons and the averaging is carried out both over the ensemble of electrons at the Fermi surface and over time.

For a system where the relaxation time approximation 38 is valid,

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$$\vec{v}(t) >_{t,OM} = \vec{v}(0) e^{-t/\tau}$$

(7 is the momentum relaxation time), one can calculate D as

$$D = \frac{1}{3} r_{p}^{2} \tau^{2}$$
 (2.5)

 v_p is the Fermi velocity, and the factor of 1/3 arises from a spherical average of the velocity vector product in eq.2.4. Given the expression for D, it is possible to rewrite the Drude expression, eq.2.1, for the resistivity as

$$\rho = \frac{1}{e^2 DN(\epsilon_F)}$$
(2.6)

where $N(\epsilon_F)$ is the density of states at the Fermi level. Eq.2.6 is usually referred to as the Einstein relation. To be more precise one should write D as $D(\epsilon_F)$ to indicate that an average over the Fermi surface was taken in calculating D. Though derived here for the free electron model, the Einstein relation for the resistivity is valid for all disordered conductors regardless of the detailed electronic structure⁴⁵.

The change of the resistivity due to an applied magnetic field is identically zero in the free-electron, single band model⁴². In real single crystal simple metals, a longitudinal magnetoresistance may appear from the Lorentz force on the electrons because of a nonspherical shape of the Fermi surface⁴³. It usually increases linearly or quadratically in $\omega_{c^{\intercal}}$, ω_{c} is the cyclotron frequency, and saturates eventually when $\omega_{c^{\intercal}}$ is of the order 10 (see Kohler's rule^{42,44}). In strongly disordered conductors such as metallic glasses however, the elastic scattering time and hence the product $\omega_{c^{\intercal}}$ is so small, of the order 10⁻⁵, that Lorentz-force driven magnetoresistance is negligible. It will not be discussed any further (in the Mg-based glasses studied here, it is four five orders of magnitude smaller than the observed magnetoresistance, even at fields of several Tesla).

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It is important to realize that eq.2.6 does not take account of correlation effects. Strictly speaking it was only assumed that the elastic scattering length is shorter than the coherence length. The

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conduction electrons were still assumed to be a non-interacting Fermi gas without any interference between the individual scattering events. Abrahams, Anderson, Licciardello and Ramakrishnan¹³, and Althuler and Aronov¹⁴ investigated the changes of the conductivity which arise when these assumptions are dropped. Following the work of Abrahams et al., Anderson and coworkers¹⁷ showed that a temperature dependent correction to the conductivity arises in disordered conductors from the dephasing of coherent electron backscattering by inelastic electron-phonon scattering. Later it was shown by Kawabata⁴⁶ that a magnetic field also has a strong effect on the coherent backscattering conductivity 6 correction. Altshuler and Aronov¹⁵, on the other hand, argued that electron-electron interactions in disordered conductors are strongly enhanced by intense, correlated scattering which leads to yet other significant corrections to the conductivity expression (eq.2.6) which depend on both, temperature and magnetic field.

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In the following section the effect of interference between elastic scattering events is discussed and in section 2.3 the combined effect of electron-electron interactions and disorder is considered. The expressions for the magnetoresistivity given in the following sections involve some weakly convergent series and rather intractable integrals. The formulae used for the numerical evaluation for these expressions are given in appendix A. The reader should note that all expressions for the quantum corrections to the conductivity are written in terms of $\delta\rho/\rho$ and not in terms of $\delta\sigma/\sigma$ as in the original articles. Since $\frac{\delta\sigma}{\sigma} < 10^{-4}$ one can identify $\delta\rho/\rho = -\delta\sigma/\sigma$. This notation was chosen to facilitate the comparison of theory and experiment and to emphasize on the small size of the signal. 2.2 Veak Localization

In the previous section it was argued that in a disordered conductor the resistivity can be written as $\rho = 1/e^2 D(\epsilon_F) N(\epsilon_F)$. In the following heuristic picture it is shown that, quantum interference effects lead to corrections to this expression.

Consider an electron moving from A to B along the paths 1,2,3 shown in Fig.2.1a.



Figure 2.1 Non-intersecting a), and intersecting b), electron diffusion paths.

The total probability of the electron transferring from A to B is given by the modulus of the sum of the probability wave amplitudes A_1 , i.e.

$$P(A,B) = \left| \sum_{i} A_{i} \right|^{2} = \sum_{i} |A_{i}|^{2} + \sum_{i \neq j} A_{i}A_{j}^{*} = \sum_{i} |A_{i}|^{2} = A^{2} \qquad (2.7)$$

The first term in eq.2.7 is the simple sum of the independent probabilities of the individual paths, i, leading to a resistivity as in eq.2.6. The mixed term cancels to zero as the paths have different lengths and the product $A_i A_j^*$ averages to zero over the ensemble of possible paths. For a diffusing electron it is however possible that some of the paths contain a loop as shown for path 2 in Fig2.1b. If only elastic scattering invariant under time-reversal and rotation - is

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considered, the electron has an equal probability of moving clockwise or counterclockwise through the loop, so that path 2 consists of two separate paths of identical length. The mixed term for these two paths does not vanish and leads to an enhanced probability of finding the electron at the point 0. Therefore the resistivity of the conductor is increased²⁰. One can investigate the interference at point 0 further by simply letting A and B tend to 0 as shown in Fig.2.2.



Figure 2.2 Closed electron diffusion paths (loops).

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Each loop represents two complementary paths the electron can traverse with equal probability. The probability of the electron returning to its origin is therefore

$$P(0,0) = 2 \left| \sum_{i} A_{i} \right|^{2} = 2 \sum_{i} |A_{i}|^{2} = 2A^{2}$$
 (2.8)

In other words, because of the interference of the probability wave amplitudes at 0, there is an enhanced probability for the electron to return to its initial position - it is weakly localized^{†)}.

f) This phenomenon is not restricted to diffusing electrons. It is common to all diffusive wave propagations. It has been observed for the zero angle backscattering of laser light⁴⁷ and it was observed (buts not understood then) in radar echoes during second world war.

One can estimate the relative magnitude of the conductivity correction by estimating the probability that an electron ray of volume $dV = v_p \lambda^2 dt$ intersects itself²⁰, i.e.

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$$\frac{\Delta\sigma}{\sigma_0} \approx -\int_{\tau_0}^{\Phi} dt \frac{v_F^{\lambda^2}}{(Dt)^{d/2}} \frac{1}{a^{3-d}}$$
(2.9)

Here λ is the electron wavelength, v_p the Fermi velocity, D the electron diffusivity, d the effective dimension and a the transverse size of a film or a wire (a<<l_{\phi}). τ_e and τ_{ϕ} have the same meaning as in the previous section. Evaluating the integral gives

$$\Delta \sigma \approx \frac{e^2}{\hbar l_{\phi}} + \text{const.} \qquad \text{in 3D and} \qquad (2.10)$$

$$\Delta \sigma \approx -\frac{e^2}{\hbar} \ln(l_{\phi}/l_e) \qquad \text{in 2D}$$

where $l_{\phi} = \sqrt{D_{\tau_{\phi}}}$ is the distance over which the electron diffuses coherently.

The temperature dependence of the weak localization conductivity correction is a consequence of the temperature dependence of 1_{ϕ} . In the presence of a magnetic field the electron acquires a phase shift when it moves around a loop. The sign of the phase shift depends on the direction. Therefore the two complementary electrons return to the origin with a relative phase shift of $\Delta \phi = (2e/\hbar)\Phi$, where Φ is the magnetic flux through the loop. When the phase shift is of the order 1, the two complementary electron waves are out of phase and the <u>interference</u> is suppressed. This will happen if the electrons take longer than the time $\tau_{\rm H}$ to traverse the loop. This magnetic dephasing time is usually defined by

$$\Delta \phi = \frac{4 e D B}{\hbar} \tau_{\rm H} \approx 1 \quad \text{or} \quad \tau_{\rm H} \approx \frac{\hbar}{4 e D B}$$

Here, $2BD_{\tau_{\rm H}}$ is the average magnetic flux through the loop. In the Mgbased metals studied here $\tau_{\rm H}$ is of the order 10^{-13} sec at a field of 1T. If $\tau_{\rm H}$ is shorter than all other dephasing time scales involved, e.g the dephasing time $\tau_i^{\rm e-ph}$ due to electron-phonon scattering, then the cut off $\tau_{\rm A}$ in eq.2.9 is identical with $\tau_{\rm H}$ and a magnetoconductance arises. Further insight into the weak localization problem can be gained by looking at the two complementary paths (Fig.2.2) ine the equivalent K-space representation. These are the the maximally crossed diagrams (also called fan diagrams) in Fig.2.3a first studied by Langer and Neal¹⁶. Fig.2.3b shows the more physical interpretation of Fig.2.3a by Bergmann¹⁹.



Figure 2.3 a) The fan diagram for particle-hole propagators. The solid lines stand for electron (>) and hole (<) propagators and the dashed lines indicate scattering by impurities (×).



An electron in an initial state \vec{k} undergoes a sequence of scatterings $\vec{k} - \vec{k_1}' \cdot \cdot \cdot - \vec{k_n}' = -\vec{k}$ into the final state $-\vec{k}$. The momentum transfers

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in this sequence are $\vec{g}_1, \vec{g}_2, \cdots, \vec{g}_{n-1}, \vec{g}_n$. The complementary scattering sequence $\vec{k} - \vec{k}_1'' \cdots - \vec{k}_n'' = -\vec{k}$ results from the above momentum transfers in reverse order, i.e. $\vec{g}_n, \vec{g}_{n-1}, \cdots, \vec{g}_1$. If the individual scatterings are time-reversible and symmetric (i.e. no inelastic, magnetic or spin-orbit scattering) the products of the scattering transfer matrices for the complementary paths will be identical. i.e.

$$\prod_{i=1}^{n} T(\vec{g}_{i}) = \prod_{i=n}^{1} T(\vec{g}_{i}) ,$$

and thus the amplitudes and phases of the final states of the complementary scattering sequences are equal which leads to constructive interference. Using Green's function techniques and the Kubo linear response theory^{19,39} it is possible to calculate the exact contribution to the conductivity of the weak localization effect from the maximally crossed diagrams in Fig.2.3 as will be shown in the following paragraphs.

The simplest Kubo diagram that contributes to the conductivity is shown in Fig.2.4a.



Figure 2.4 a) The simplest Kubo conductivity diagram.



Figure 2.4 b) Sum of Kubo diagrams with maximally crossed impurity scattering.

It yields a conductivity

$$\sigma_{ij}(\omega) = \int \frac{d\epsilon f(\epsilon - \hbar\omega) - f(\epsilon)}{2\pi} \int \frac{d\vec{k}}{(2\pi)^3}$$

$$\times \sum_{s} v_{i}(\vec{k}) v_{j}(\vec{k}) G_{s}^{R}(\epsilon, \vec{k}) G_{s}^{A}(\epsilon - \hbar\omega, \vec{k})$$
(2.11)

Here $v_i(\vec{k}) = \frac{dE(\vec{k})}{\hbar dk_i}$ is the electron velocity at the energy $E(\vec{k})$.

$$G_{s}^{R/A}(\epsilon,\vec{k}) = \frac{1}{\epsilon \pm (i\hbar/2\tau) - B(\vec{k})}$$

, are the impurity averaged retarded and advanced Green's functions which are suitable to describe the propagation of an electron of spin s in a disordered conductor 48,20 . Evaluating the expression for σ leads to the well known Drude formula for the conductivity

$$\sigma = \lim_{\omega \to 0} \left(\sigma_{i,j=x}(\omega) \right) = \lim_{\omega \to 0} \delta_{ij} \frac{ne^2 \tau/m}{1 - i\omega\tau}$$
(2.12)

which reduces to eq.2.1 at $\omega=0$. The additional effects of the coherent backscattering can be incorporated into the Kubo formalism by simply inserting the maximally crossed diagrams into Fig.2.4a and summing over all possible fans. This is shown in Fig.2.4b. The resulting conductivity correction **c**an be written as

$$\Delta \sigma_{ij}(\omega) = \int \frac{d\epsilon f(\epsilon - \hbar \omega) - f(\epsilon)}{2\pi} \int \frac{d\vec{k}}{(2\pi)^3} \int \frac{d\vec{k}}{(2\pi)^3} \sum_{s,s'} v_i(\vec{k}) v_j(\vec{k}') \qquad (2.13)$$
$$\times G_s^R(\epsilon, \vec{k}) G_s^A(\epsilon - \hbar \omega, \vec{k}) M_{s,s'}(\vec{k}, \vec{k}'; \epsilon, \omega) G_s^{R^A}(\epsilon, \vec{k}') G_s^A(\epsilon - \hbar \omega, \vec{k}')$$

 $M_{s,s}$, $(\vec{k}, \vec{k}'; \epsilon, \omega)$ is the mathematical equivalent of the maximally crossed diagrams in Fig.2.4b. To facilitate the calculation of the integral in eq.2.13 one can rearrange the terms in a way which is equivalent to "twisting" around the lower hole propagator lines of the maximally crossed diagrams in Fig.2.3a. This yields the so-called ladder diagrams in the particle-particle channel shown in Fig.2.5a.



Figure 2.5 a) Ladder diagrams in the particle-particle channel.



Figure 2.5 b) Dyson equation for ladder diagrams.

The order of the scattering sequence remains unchanged. The infinite series of the ladder diagrams can be summed easily giving a Dyson equation which is shown in Fig.2.5b. It follows for the conductivity that

$$\Delta\sigma(\omega)_{\omega\to 0} = -\frac{2\pi N(\epsilon_F)^{\tau}e}{\hbar} \frac{e^2}{\pi\hbar} D_{\tau}e \sum_{s,s'} \int \frac{d\vec{q}}{(2\pi)^3} C(\vec{q};\omega) \qquad (2.14)$$

with
$$C(\vec{q} = \vec{k} + \vec{k}'; \omega) = \frac{\hbar}{2\pi N(\epsilon_F)\tau_e^2} \frac{1}{D\vec{q}^2 - i\omega}$$

this yields

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$$\Delta \sigma(\omega)_{\omega \to 0} = -\frac{e^2}{2\pi^2 \hbar} \frac{q_0^2}{0 \, dq \frac{q^2}{2 - i\omega}}$$
(2.15)

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The quantity $C(q,\omega)$ in above equation and in Fig.2.5b (the particleparticle diffusion propagator) is often referred to in the literature as

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the Cooperon as it has a pole (the diffusion pole) at small total momentum $\vec{q} = \vec{k} + \vec{k}$ ' analogous to the Cooper pair propagator in superconductivity theory.

The upper integration limit, $q_0 = (D\tau_e)^{-1/2}$, in the above equation reflects the fact that the coherent backscattering sequence lasts longer than the time, τ_e , which elapses between two elastic scatterings. $(D\tau_e)^{1/2}$ corresponds to the length of the smallest diffusion step, i.e the distance the electron travels between two elastic scatterings. The temperature dependence of the above weak localization conductivity is, as Anderson, Abrahams and Ramakrishnan¹⁷ have pointed out, a consequence of the fact that the coherent backscattering sequence can not last longer than the diffusing electron wave packet maintains phase coherence, i.e. τ_{ϕ} . The cut off at τ_{ϕ} is achieved by replacing $-i\omega$ with h/τ_{ϕ} in the Cooperon¹⁹. Some authors⁴⁸ prefer to add h/τ_{ϕ} to the denominator of the Cooperon and take the limit ω -0 later; the result remains the same. Calculating the conductivity with the cut off, τ_{ϕ} , yields for three dimensional conductors⁴⁹

$$\Delta \sigma = -\frac{e^2}{2\pi^2 h \sqrt{D_{T_{\phi}}}}$$
(2.16)

The dephasing time τ_{ϕ} is, among other effects, due to inelastic electron-phonon or electron-electron scattering with a characteristic temperature dependence $\tau_{\phi} \propto T^{-p}$, p>0.

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In a magnetic field, the Green's functions in eq.2.11 acquire an additional phase factor. In real space representation the Green's function can be written as 39,19

$$G(\vec{r},\vec{r}') = G_{B=0}(\vec{r},\vec{r}') \cdot \exp\left(\frac{ie}{\hbar} \int_{\vec{r}}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s}\right)$$
(2.17)

where \vec{A} is the magnetic vector potential. This phase factor is absorbed into the Cooperon by replacing \vec{q}^2 in eq.2.14 by the generalized momentum $(\vec{q} + 2e\vec{A}/c)^2$. Substituting the generalized momentum by its quantum mechanical eigenvalue (for the motion perpendicular to \vec{B} only) 4eB/h(n+1/2), the integration over d \vec{q} becomes a summation over all Landau levels; n, plus an integration over the q-component parallel to the applied magnetic field. A magnetoconductivity follows then from eq.2.15 (which is given later in eq.2.23 and 2.24).

In addition to the spin conserving inelastic dephasing and the dephasing due to a magnetic field, scattering mechanisms that change the spin state of the backscattered electrons have to be considered. This is quite obvious since the interference at point 0 in Fig.2.2 involves the total wave function and not just its spatial part. The interference will not be constructive if the electron spin has been changed along one of the two complementary paths. There are two important mechanisms which change the electron spin state. The electron spin can interact with a localized magnetic moment (impurity spin) or with the electron's angular moment when it is scattered by an Fron (spin-orbit scattering). Each process leads to a characteristic dephasing time, τ_s and τ_{so} respectively. The related Hamiltonians of either process have a symmetry different from the orthogonal symmetry of the previously discussed processes. Magnetic impurity scattering is described by a unitary Hamiltonian and spin-orbit scattering by a symplectic Hamiltonian. They cause the vertex C in eq.2.14 (the Cooperon) to have a more complex structure. Hikami and collaborators⁵⁰ showed that the vertex should be written, as

$$C = \frac{1}{2\pi N(\epsilon_{\rm F})\tau_{\rm e}^{2}} \left[\frac{3}{2} \frac{1}{Dq^{2} - i\omega + \frac{4}{3\tau_{\rm so}} + \frac{2}{3\tau_{\rm s}}} - \frac{1}{2} \frac{1}{Dq^{2} - i\omega + \frac{2}{\tau_{\rm s}}} \right]$$
(2.18)

The factors 3/2 and 1/2 are a consequence of the multiplicity of the spin triplet and singlet states^{†)}. In the absence of magnetic impurity scattering $(1/\tau_s = 0)$ and for weak spin-orbit scattering $(\tau_{so} \text{ large})$ the vertex C reduces to the expression given in eq.2.14. If the opposite limit is assumed for spin-orbit scattering $(\tau_{so} \text{ very small})$ the triplet term in eq.2.18 vanishes, while the singlet term remains unchanged.

(t) Isotropic scattering is assumed here, i.e.

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 $\frac{1}{x} = \frac{1}{y} = \frac{1}{z} = \frac{1}{3\tau}$ and similarly for $1/\tau$. Even though τ so and τ_s are not isotropic in general, this simplification makes a negligible difference in bulk metallic glasses.

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Therefore the vertex C reduces to that in eq.2.14, but with an additional factor of 1/2. This implies that in changing from weak to strong spin-orbit scattering the sign of the weak localization quantum interference effect reverses and its magnitude is halved. If magnetic impurity scattering is present in the conductor (finite $1/\tau_s$) the triplet and singlet part of C are both reduced. The quantum interference disappears entirely in the concentrated magnetic impurity limit.

The various dephasing times introduced above have been calculated by several authors. Takayama⁵¹ derived the inelastic scattering rate for electron-phonon scattering at low temperatures as

$$\frac{1}{\tau_{4}} = \frac{2\pi^{2}\lambda}{3Dm} \frac{\left(k_{B}T\right)^{2}}{k_{B}\theta} + \frac{3\pi\lambda\hbar\log^{2}}{(3Dm)^{2}}(k_{B}T) \stackrel{\text{e}}{\longrightarrow} .$$
(2.19)

where $\lambda=0(1)$ and thus $1/\tau_1^{e-ph}$ is of the order $1\times10^{11} \sec^{-1}$ at 10K. This is two orders of magnitude larger than the Bloch-Grüneisen inelastic scattering rate, which falls off as T^5 . Chakravartry and Schmid⁴⁵ have presented another calculation of the inelastic electron-phonon scattering rate. They find that it can vary anywhere between T^2 and T^4 depending on the particular phonon modes and their respective velocity of sound. The magnitudes are comparable with the above result.

The electron-electron scattering rate for three dimensional conductors has been calculated by Schmid⁵². It can be written as²⁴

$$\frac{1}{\tau_{1} e^{-e}} = \frac{\pi}{8\hbar} \frac{(k_{\rm B}T)^{2}}{\epsilon_{\rm F}} + \frac{1}{6\hbar} \left(\frac{\hbar}{2m}\right)^{\frac{3}{2}} \frac{(k_{\rm B}T)^{3/2}}{\epsilon_{\rm F}}$$
(2.20)

yielding a rate $1/\tau_i^{e-e}$ of approximately 10^8sec^{-1} at 10K which is negligible compared to the inelastic electron-phonon scattering rate in eq.2.19.

It is important to note that the inelastic scattering times τ_i^{e-ph} and τ_i^{e-e} which follow from eq.2.19 and eq.2.20 are not necessarily identical with the dephasing time due to the respective inelastic process. The effectiveness, i.e the size of the energy transfer in the scattering process, has to be accounted for. However, Altshuler and Aronov²⁰ and also Chakravartry and Schmid⁴⁵ have pointed out that large
energy transfers dominate in three dimensional disordered metals and the distinction is therefore unnecessary. For scattering mechanisms which cause a change of the electronic spin state the scattering time is identical with the dephasing time.

The spin-orbit scattering rate has been derived by Werthamer and coworkers 53,54 as

$$\frac{1}{\tau_{so}} = \frac{8\pi}{3\hbar} n_{i} N_{b}(\epsilon_{F}) |\langle M_{so} \rangle|^{2} = \frac{3\pi k_{B}T_{c}\lambda_{so}}{2\hbar}$$
(2.21)

where $\langle M_{SO} \rangle$ is the spin-orbit scattering matrix element. The second equality is valid for superconductors only. With $\lambda_{SO} = 0(1)$ one finds for $Mg_{70}Zn_{30}$ that $1/\tau_{SO} \approx 10^{-11}$ sec-1, which is of the same order as $1/\tau_1^{e-ph}$. This is about the best estimate one can give since $\langle M_{SO} \rangle$ is not known for Mg-Cu and Mg-Zn glasses. One does however expect a strong dependence of τ_{SO} on the concentration of heavy elements in the alloy. It has been shown that $1/\tau_{SO}$ should vary as Z^8 in metals if the single conduction electron wave function is approximated by atomic orbitals⁵⁵.

The magnetic spin scattering rate can be determined from Fermi's Golden Rule, which gives)

$$\frac{1}{\tau_{\rm g}} = c \frac{2\pi}{\hbar} N(\epsilon_{\rm F}) \Omega J^2 S(\underline{S+1})$$
(2.22)

c is the magnetic impurity concentration, Ω the atomic volume, J the spin exchange integral (scattering matrix) and S(S+1) the degeneracy of the magnetic spin S. In amorphous Mg-Cu and Mg-Zn alloys only manganese holds a magnetic moment. With $S \approx 2.2$ and $J \approx -0.25 \text{eV}^{-56,57}$ one finds $1/\tau_e$ to be of the order of $2 \times 10^9 \text{sec}^{-1}$ per ppm of manganese.

We have seen above that the scattering times due to inelastic electron phonon, magnetic spin and spin-orbit scattering have comparable magnitudes. Consequently we expect the weak localization conductivity correction to be sensitive to variations of any of the above time scales, i.e to temperature, to the concentration of metals with large Z and to magnetic impurities. All the major aspects of the weak localization quantum interference effect have now been sketched out. It only remains to calculate the temperature and field dependence according to eq.2.14, with the various scattering mechanisms included. Unfortunately this is a rather complicated and long calculation, the details of which do not contribute to any additional insight into the phenomenon. For this reason only the results of such calculations are presented and the reader is referred to the original articles for the exact treatment.

Fukuyama and Hoshino⁴⁹ have calculated the field and temperature dependence of the weak localization resistivity for three dimensional disordered conductors in the presence of inelastic and spin.orbit scattering in the limit $\tau_e \ll \tau_{so}$, τ_{ϕ} . They find:

$$\left(\frac{\delta\rho}{\rho}\right)_{WL} = \rho \frac{e^2}{2\pi \hbar} \sqrt{\frac{eB}{\hbar}} \left[\frac{1}{2\sqrt{1-\gamma}} \left\{ f_3 \left(\frac{B}{B_-} \right) - f_3 \left(\frac{B}{B_+} \right) \right\} - f_3 \left(\frac{B}{B_2} \right) \right]$$

$$- \sqrt{\frac{4B_{so}}{3B}} \left[\frac{1}{\sqrt{1-\gamma}} \left(\sqrt{t_+} - \sqrt{t_-} \right) + \sqrt{t_-} - \sqrt{t_+} \right]$$

$$(2.23)$$

The parameters are defined as

$$t = \frac{3B_{1}}{4B_{so}} \text{ and } t_{\pm} = t + \frac{1}{2} (1 \pm \sqrt{1 - \gamma})$$

with $\gamma = \left(\frac{3g^{*} \mu_{B}B}{8eDB_{so}}\right)^{2}$

 g^* is the effective g-factor and has a value of 2 in metals, and

$$B_{\pm} = B_{1} + \frac{2B_{so}}{3} (1 \pm \sqrt{1-\gamma})$$

 $B_2 = B_1 + \frac{4}{3}B_{so}$

 B_i and B_{so^3} are usually referred to as the inelastic and spin-orbit fields. They are related to the dephasing times discussed earlier

(similarly to $\tau_{\rm H}$ and B) by

$$B_x = \frac{h}{4eD\tau_x}$$

 f_3 is an infinite series resulting from the evaluation of the integral in eq.2.14 for all Landau levels n. Its properties are discussed on page 36. The expression in eq.2.23 includes the effect of the spin-up and spin-down band splitting (Zeeman effect) in the presence of spin-orbit scattering. In a magnetic field the energies of the two bands are split by $2\mu_B$ which alters the admixture of spin-up and spin-down states due to spin-orbit (or magnetic spin) scattering. Trudeau and Cochrane⁵⁸ pointed out only recently that in systems with a considerable paramagnetic enhancement, the g-factor should be multiplied by the Stoner factor $1/(1-\chi/\chi_p) = 1/(1-\overline{1})$ to reflect the fact that the band splitting is increased by strong electron correlations. In systems with no paramagnetic enhancement and a large electron diffusivity, the Zeeman contribution is negligible and eq.2.23 reduces the following expression which Altshuler and Aronov²⁰ have derived based on calculations by Kavabata⁴⁶ and Hikami et al.⁵⁰:

$$\left(\frac{\delta\rho}{\rho}\right)_{WL} = \rho \frac{e^2}{2\pi^2 h} \sqrt{\frac{eB}{\hbar}} \left[\frac{1}{2}f_3\left(\frac{B}{B_{\phi}}\right) - \frac{3}{2}f_3\left(\frac{B}{B_{3}}\right)\right]$$
(2.24)
Here $B_{\phi} = B_1 + 2B_s$ and $B_3 = B_1 + \frac{2}{3}B_s + \frac{4}{3}B_{so}$

 B_1 and B_{so} have been defined above. The dephasing effect due to magnetic spin scattering has been included in this expression through the spin scattering field B_s , which is related to the magnetic spin scattering rate, given in eq.2.22, by $B_s = \hbar/4eD\tau_s$. A similar extension of eq.2.23 to finite magnetic spin scattering has not yet been presented in the literature. However, Maekawa and Fukuyama¹⁸ have calculated the corresponding magnetoresistance in two dimensional conductors including the additional magnetic spin scattering effects. In a simple calculation one can take their calculation of the vertex C (which has no dimensional dependence) and carry out a low impurity concentration expansion (B_s small, i.e $B_s << B_{so}$). One finds that B_{\pm} and B_2 in eq.2.23

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should be replaced by

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$$B_{\pm} = B_{1} + 2B_{s}^{4} + \frac{2(B_{s0}^{-}B_{s})}{3} (1 \pm \sqrt{1-\gamma})$$

$$B_{2} = B_{1} + \frac{2}{2}B_{s} + \frac{4}{2}B_{s} = B_{2}^{4}$$

To test the validity of this extension one needs only to consider the limit of zero Zeeman splitting (i.e g^{+} -0) and one finds that eq.2.23 still reduces to eq.2.24 as required.

Ins the high purity Mg-Cu and Mg-Zn glasses studied here, B_s is much smaller than B_s so that one can write

$$\mathbf{B}_{\pm} = \mathbf{B}_{\phi} + \frac{2\mathbf{B}_{so}}{3} \left(1 \pm \sqrt{1-\gamma}\right)$$

 $B_2 = B_{\phi} + \frac{4}{3}B_{so} = B_3$

The magnetoresistance is thus conveniently defined by only four parameters, the known resistivity ρ and diffusivity D and the unknown spin-orbit scattering field B_{so} and the (as we call it) dephasing field B_{ϕ} . B_{ϕ} combines the dephasing effects of, to first order temperature independent, magnetic impurity scattering and temperature dependent inelastic electron-phonon and electron-electron scattering. As we shall see in Chapter 4 this definition allows us to analyse the magnetoresistance measurements with a minimal number of adjustable parameters. The error the above definition of B_2 introduces into B_{so} is, in the materials studied in this thesis, always less than 2% and therefore negligible (see Chapter4).

Representative plots of eq.2.23 and eq.2.24 are shown in Fig.2.6a-d for different sets of scattering fields B_i , B_{so} , and B_s . A comparison between eq.2.23 and eq.2.24 is plotted in Fig.2.6e with a value for the electron diffusivity D of $0.2 \text{cm}^2/\text{sec}$, typical for amorphous d-band metals, and $6 \text{cm}^2/\text{sec}$, typical for amorphous sp-band metals such as Mg-Cu or Mg-Zn. We find that for the alloys studied here the Zeeman splitting has no effect on the magnetoresistivity in the field range under consideration. The effect of D on the magnetoresistance can be made more transparent by the following argument: the dephasing effectiveness of the applied magnetic field is proportional to the flux through the area of the self-intersecting loops (Fig.2.2) and hence proportional to $(1_{\phi})^2 = D\tau_{\phi}$ (the diffusion length 1_{ϕ} was defined in eq.2.10). In contrast, the dephasing due to the Zeeman splitting in the presence of spin-orbit scattering depends on the number of spin-orbit scatterers along the loop and is therefore proportional to the length of the loop $v_{F}\tau_{\phi}$. It follows that for small D the Zeeman dephasing is more effective than the magnetic field dephasing, whereas for large D the reverse is true.

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Figure 2.6 a) Normalized weak localization magnetoresistance (eq.2.23) for varying dephasing fields, B_{ϕ} , at constant, weak spin-orbit scattering. $\rho = 50 \mu\Omega cm$ and $D = 6 cm^2/sec$.



Figure 2.6 b) Normalized weak localization magnetoresistance (eq.2.23) for varying dephasing fields, B_{ϕ} , at constant, strong spin-orbit scattering. $\rho = 50\mu\Omega cm$ and $D = 6cm^2/sec$.



Figure 2.6 c) Normalized weak localization magnetoresistance (eq.2.23) for several spin-orbit scattering fields, B_{go} , at constant dephasing field B_{ϕ} . $\rho = 50 \mu \Omega cm$ and $D = 6 cm^2/sec$.



Figure 2.6 d) Normalized weak localization magnetoresistance (eq.2.23) for several spin-scattering fields, B_s , at constant inelastic dephasing and spin-orbit scattering fields. $\rho = 50\mu\Omega cm$ and $D = 6cm^2/sec$.

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Figure 2.6 e) Normalized weak localization magnetoresistance (eq.2.23) for small and large diffusivities.. Eq.2.24 gives identical results for $D = 6 \text{ cm}^2/\text{sec.}$ $\rho = 50 \mu\Omega \text{ cm}$ and $B_{\phi} = 1\text{ mT.}$

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The functional form of $f_3(x)$ was first derived by Kawabata⁴⁶ as:

$$f_{3}(x) = \sum_{n=0}^{\infty} a_{n}(x)$$
 (2.25)

with
$$a_n(x) = 2(n+1+\frac{1}{x})^{1/2} - 2(n+\frac{1}{x})^{1/2} - (n+\frac{1}{2}+\frac{1}{x})^{-1/2}$$

The function is plotted out in Fig.2.7. Details of the algorithm used to calculate this curve are given in Appendix A. The asymptotic forms of f_3 are

$$f_3 \approx \frac{x^{3/2}}{48} \left(1 - \frac{7x^2}{64} + \cdots \right)$$
 for x << 1 and

$$f_3 \approx 0.6049 - \frac{2}{\sqrt{x}}$$
 for x >> 1.

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One can therefore expect the magnetoresistance to vary at low fields as $+B^2$. Specifically, for B << B_A << B_{SO} $\neq 0$

$$\left(\frac{\delta\rho}{\rho}\right)_{WL} = \rho \frac{e^2}{2\pi^2 h} \sqrt{\frac{e}{h}} \frac{1}{B_{\phi}^{3/2}} \frac{B^2}{96}$$
(2.26)

and for large fields (B >> B_{ϕ} , B_{so}) the magnetoresistivity should vary as

$$\left(\frac{\delta\rho}{\rho}\right)_{\rm WL} = -\rho \frac{e^2}{2\pi^2\hbar} \sqrt{\frac{eB}{\hbar}} \times 0.6049 \qquad (2.27)$$

This means that as long as the disordered conductor has a finite spinorbit scattering strength B_{so} , the low field magnetoresistivity will always be proportional to $+B^2$ with a slope depending on the dephasing field B_{ϕ} . In contrast, the high field magnetoresistance has a universal $-\sqrt{B}$ field dependence. Whether the low or high field asymptotic regimes can be resolved experimentally depends critically on the size of B_{ϕ} and B_{so} .

Maekawa and Fukuyama¹⁸ have also derived the temperature dependence of the weak localization correction to the conductivity three

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dimensional conductors:

$$\frac{\left(\frac{\delta\rho}{\rho}\right)_{\rm WL}({\rm T})}{\times \left[\left(\frac{1}{\tau_{\rm i}} + \frac{2}{\tau_{\rm s}}\right)^{1/2} - 3\left(\frac{1}{\tau_{\rm i}} + \frac{2}{3\tau_{\rm s}} + \frac{4}{3\tau_{\rm so}}\right)^{1/2}\right]$$

$$(2.28)$$

Fig.2.12 shows this correction compared with other temperature dependent conductivity corrections (to generate the plot the values given in section 4.2.4 were used for τ_i and τ_{so}).



2.3 Enhanced Electron-Electron Interactions

. In the previous section the direct effect of quantum, interference on the resistivity was discussed. In this section two indirect quantum interference effects will be discussed briefly.

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The diagrams in Fig.2.8 show the lowest order electron-electron interaction processes in the absence impurity scattering.



Figure 2.8 a) The simplest Hartree electron-electron interaction diagram in the absence of impurity scattering. The closed line may be an electron or hole propagator. The thin wavy line denotes the bare Coulomb interaction. b) The simplest exchange (or Fock) electron-electron interaction

diagram in the absence of impurity scattering.

The Hartree term in Fig.2.8a symbolizes the interaction of an electron with a fluctuation of the vacuum. It can be viewed as the basic interaction of an electron with the mean field of the surrounding electron gas and leads (in connection with higher order terms) to the screening of the electron charge (it is discussed in more detail by Ascroft and Mermin³⁸ and Mahan³⁹). The exchange term in Fig.2.8b is the simplest correction to the electron self-energy due to electron-electron scattering. It is similar to the self-energy correction due to virtual phonon exchange (where the e-e interaction line is replaced with a phonon line) which has to be considered in more detailed density of states calculations. In disordered conductors, the intense inelastic scattering interferes with the electron-electron interactions, leading to scattering processes which are represented by the diagrams in Fig2.9a-f. The bare e-e interaction (thin vavy line(in Fig.2.8a,b) is replaced by a renormalized e-e coupling λ and a coherent impurity scattering sequence D or C is added. The Cooperon, C, was defined in Fig.2.5. The diffuson, D, is similar to the Cooperon, a summation of ladder diagrams in the particle-hole channel as is demonstrated graphically in Fig.2.10a,b. The renormalized electron-electron coupling in the particle-hole (diffusion) channel, λ_D , and in the particleparticle (Cooper) channel, λ_c , are defined in Fig.2.10c,d. In the literature, the processes in Fig.2.9a-f are usually referred to as the Hartree and exchange (Fock) terms in the Cooper and diffusion channel. Hartree

Exchange

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p-h

a)



b)





λ

e)

Figure 2.9 Hartree and exchange diagrams in the particle-hole (p-h) and particle-particle channel (p-p).

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E H

p-p

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Figure 2.10 b) The Cooperon.



Figure 2.10 c) The "dressed" electron coupling in the diffusion channel (thick wavy line). The thin wavy line is the bare coulombic electron interaction.



Figure 2.10 d) The "dressed" electron coupling in the Cooper channel.

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Physically, the Hartree terms in Fig.2.9a,c,e lead to a decrease of the electronic screening and therefore to an enhanced electron-electron interaction. This is because the intense elastic scattering in a disordered conductor prevents the "sluggish" electron screening-cloud from following a scattered electron as perfectly as it does in an ordered conductor. The exchange terms in Fig.2.9b,d,f should be considered as higher order corrections to the electron self-energy in the presence of static impurity and electron-electron scattering. For this reason Altshuler and Aronov²⁰ refer to them as the density of states corrections.

A different picture of the enhanced electron-electron interaction has been proposed recently by Bergmann⁵⁹. He has argued that the Hartree term (and similarly the exchange term) should be understood as an interference effect similar to the weak localization effect. In Bergmann's view the effect comes about from an electron scattering around a loop exactly as Fig.2.2. When the electron wave returns to its starting point it interferes with the local charge distribution. The interference creates a charge modulation which contains all phase information of the scattering events along the loop path, much like a hologram but with charge flow replacing light flow. A second electron scattering around the loop from a different starting point will be scattered by this "charge hologram" and return to its starting point. Because the hologram contains all phase information of the loop, the phase change of the second electron exactly cancels when it returns to its starting point. It therefore interferes constructively with the local charge distribution at its starting point. This leads to a change in the resistance similar to that discussed in section 2.2 for the weak localization effect, and should therefore, as Bergmann argues, be sensitive to magnetic fields, inelastic, spin-orbit and magnetic spin scattering in much the same manner.

Some insight into the magnetoresistance can be gained from the diagrams in Fig.2.9. The exchange processes in Fig2.9b,d,f can not lead to a Zeeman type magnetoresistance as the spin is conserved in these processes. Also, the processes in the particle-hole channel in

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Fig.2.9a,c,e (with small momentum difference, i.e $\vec{k}' = \vec{k} + \vec{q}$ with $|\vec{q}| \langle \langle |\vec{k}| \rangle$ can not give rise to an orbital magnetoresistance. A magnetoresistance can, however, arise from the Zeeman band splitting of the Hartree particle-hole diagram because the two propagators may have a different spin state. It is usually referred to as the diffusion channel . magnetoresistance. Because the size of the total momentum is not restricted, one has to average the screened Coulomb potential over the total momentum. This leads to a size factor $\boldsymbol{\tilde{F}}_{\sigma}$ of the magnetoresistivity which depends on the details of the electron screening and the Fermi surface of the conductor under consideration. The functional form of the diffusion channel magnetoresistance has been derived by Lee and Ramakrishnan 60,21 as

$$\left(\frac{\delta\rho}{\rho}\right)_{DC} = \rho \frac{e^2}{2\pi^2 h} \sqrt{\frac{eB}{\hbar}} \frac{\tilde{F}_{\sigma}}{2\sqrt{\pi}} \left(\frac{\pi k_B T}{2DeB}\right)^{\frac{1}{2}} g_3\left(\frac{g\mu_B B}{k_B T}\right)$$

$$: \tilde{F}_{\sigma} = -\frac{32}{3F} \left[1 + \frac{3F}{4} - (1 + F/2)^{3/2}\right]$$

$$(2.29)$$

where

$$F = \frac{\int d\Omega \ V(q = 2k_F \sin(\Theta/2))}{\int d\Omega \ V(q = 0)}$$

$$g_3(x) = \int_0^\infty d\omega \ \left(\frac{d^2}{d\omega^2}[\omega \ N(\omega)]\right) \left(\sqrt{\omega + x} + \sqrt{|\omega - x|} - 2\sqrt{\omega}\right)$$

$$N(\omega) = \left[e^{\omega} - 1\right]^{-1}$$

V(q) is the Fourier transform of the static screened Coulomb potential, and F is the electron electron interaction at the Fermi energy averaged over the solid angle Ω . For the simple metals studied here one can calculate F quite easily, by treating them as free-electron metals and using the Thomas-Fermi screening theory 38. In transition metals F is more difficult to evaluate since the electronic structure is more complex and the Thomas-Fermi theory does not apply.

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For the simple Mg based alloys studied here we find

$$\mathbf{F} = \left(\frac{\mathbf{k}_{o}}{2\mathbf{k}_{F}}\right)^{2} \ln\left[\left(\frac{2\mathbf{k}_{F}}{\mathbf{k}_{o}}\right)^{2} + 1\right] \approx 0.5$$

 $k_0^2 = \frac{4me^2k_F}{\pi \hbar^2}$ is the Thomas Fermi screening vector

The numerical evaluation of $g_3(x)$ is given in the appendix A.2. Lee and Ramakrishnan point out that the above equation is calculated under the assumption that the Zeeman splitting of the spin-up and spin-down bands is so large that no significant admixture of the two bands by spin-orbit or magnetic spin scattering occurs as this would suppress the magnetoresistivity. Hence the following restriction applies to eq.2.29

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$$\frac{g\mu_B^B}{4eD} >> B_{so}, B_{s}$$

In the Mg-Cu and Mg-Zn alloys under consideration here, eq.2.29 is therefore only valid in the weak spin-orbit scattering alloys. Fortunately, the size of the Diffusion channel magnetoresistivity is so small in these alloys that the above limitations are not significant. Recently Trudeau and Cochrane⁵⁸ have shown experimentally that the band splitting in the diffusion channel magnetoresistance is, like the weak localization magnetoresistance, enhanced by the Stoner factor $1/1-\overline{I}$. A plot of the diffusion channel magnetoresistivity is shown in Fig.2.11.

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 $\rho = 50 \mu \Omega cm, D = 6 cm^2 sec, B_{\phi} = 1mT, B_s = 0$.

- (1) Maki-Thompson, eq.2.35, with $T_c = 0.12K$
- (2). Cooper channel, eq.2.32, with $T_o = T_F = 85000K$

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- (3) diffusion channel, eq.2.29, with $\tilde{P}_{a} = 0.5$
- (4) Cooper channel, eq.2.31, with $T_0 = 0.12K$
- (4) Cooper channel, eq.2.32, with $T_0 = 0.12K$, and eq.2.30 with $\alpha = 1/\pi$
- (6) negative MR due to 25ppm of Mn (eq.2.39)
- (7) Cooper channel, eq.2.30, with $\alpha=1$

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An orbital magnetoresistance arises from processes in the particle-particle (Cooper) channel shown in Fig.2.9c,d,f.e (with small total momentum, i.e $|\vec{p} + \vec{p}'| = |\vec{q}| \ll |\vec{p}|$). The Hartree processes in the particle particle channel also give rise to a Zeeman type magnetoresistance which is however negligible⁶¹. Several authors have calculated this contribution, but their results are not consistent and there has been some controversy in the literature as to which should be considered correct. The individual results are therefore discussed in

some detail here in order to determine which should be used for the analysis in this thesis. Under the assumption electron pair-interaction constant, g, does not depend on the resulting (small) total momentum, Althuler and Aronov⁶¹ find for Cooper channel magnetoresistance

$$\left(\frac{\delta\rho}{\rho}\right)_{\rm CC} = \alpha\rho \frac{e^2}{2\pi^2\hbar} \sqrt{\frac{eB}{\hbar}} g(T,B) \Phi_3\left(\frac{2DeB}{\pi k_BT}\right)$$
(2.30)

where $\Phi_3(x) = \left(\frac{\pi}{2x}\right)^{1/2} \int_0^\infty dt \, \frac{t^{1/2}}{\sinh^2 t} \left(1 - \frac{xt}{\sinh(xt)}\right)$

In superconducting metals the coupling constant g(B,T) is written as

 $T^* = max \left(T, \frac{4DeB}{k_p}\right)$ where

In non-superconducting it has a different form, i.e

 $g^{-1}(B,T) = \left(-\ln\left(\frac{T}{T_c}\right)\right)$

$$g^{-1}(B,T) = \frac{1}{\lambda} + \ln\left(\frac{\gamma T_F}{\pi T^*}\right)$$

 $\ln(\gamma) = C = 0.577$ and λ is the dimensionless electron-phonon coupling constant which is approximately 0.1 in Mg-Cu glasses (this is an upper bound given by the McMillan fomula¹²³ for $T_{c}=0$). We note that the Cooper channel magnetoresistance is negative in superconductors and positive in non-superconductors because of the sign of g(B,T). In calculating the above magnetoresistance, the authors have neglected terms of the order of B/T in the expression of g(B,T). In how far these higher order terms become important in the field and temperature regime

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considered in this thesis is not known and still subject of ongoing research[†]). Altshuler and Aronov argue in reference 61 that the factor α is 1 in the limit of weak spin-orbit scattering and 1/4 in the limit of strong spin-orbit scattering because the Kubo formular of the diagrams in Fig.2.9 which lead to eq.2.30 involve the square of the Cooperon (eq.2.18). It was discussed earlier for the weak localization effect that and strong spin-orbit scattering suppresses the triplet part

pointed out that there is an exact cancellation of the Cooper channel exchange terms with the parallel spin part of the Cooper channel Hartree term and only the singlet Cooper channel Hartree term contributes. The factor α should therefore be 1/4 in either spin-orbit scattering limit^{††}). In a later publication²⁰ Altshuler and Aronov present a different expression for the Cooper channel magnetoresistivity where they also include the Zeeman splitting and magnetic impurity scattering effects:

of the Cooperon and halves its size. However, Isawa and Fukuyama²² have

$$\begin{pmatrix} \frac{\delta\rho}{\rho} \end{pmatrix}_{CC} = \rho \frac{e^2}{2\pi^2 \hbar} \left(\frac{k_B^T}{\hbar D} \right)^{\frac{1}{2}} \frac{g(T,B)}{2} F_{-1} \left(\frac{2eDB}{\pi k_B^T}, \frac{g\mu_B^B}{\pi k_B^T}, \frac{\hbar/\tau_s}{\pi k_B^T} \right)$$
(2.31)

The function F_{-1} is defined as (after an analytical continuation^{20,64}):

$$F_{-1}(x_1, x_2, x_3) = \int_0^\infty dt \frac{t^{1/2}}{\sinh^2 t} \left(1 - \frac{x_1}{\sinh(x_1 t)} \right) \cos(x_2 t) e^{-x_3 t}$$

We note that the prefactor in the above equation differs by $\frac{1}{\alpha\pi}$ from that in eq.2.30. As both equations have been calculated from the same Feynman diagrams in Fig.2.9 such a difference should not occur and we conclude that the above results should not be used.

t) McLean and Tsuzuki⁶² have suggested that g(B,T) should be extended as

$$g(B,T) = \left(\ln \left(\frac{T_c}{T} \right) + \Psi \left(\frac{1}{2} \right) - \Psi \left(\frac{1}{2} - \frac{DeB}{2\pi k_B T} \right) \right)^{-1}$$

However Lopes Dos Santos and Abrahams⁶³ have pointed out that this is unphysical.

††) This is underlined by the fact that for $\alpha = 1$ the Cooper channel magnetoresistance is too large compared to the size of the magnetoresistance measured in the Mg-Cu and Mg-Zn glasses here.

The Cooper channel magnetoresistivity has also been calculated by Isawa and Fukuyama²² for repulsive electron-electron interaction (nonsuperconductors). The authors explicitly consider the cancellation of the exchange terms with the parallel spin part of the Hartree term mentioned above and find

$$\left(\frac{\delta\rho}{\rho}\right)_{CC} = \rho \frac{e^2}{2\pi^2 h} \sqrt{\frac{eB}{\hbar}} \frac{3\pi^2}{2} \left(\frac{k_B T}{4eDB}\right)^2 g(T,B) \Phi_F(B,T) \qquad (2.32)$$

where $\Phi_{\mathbf{F}}(\mathbf{B},\mathbf{T}) = -\sum_{k=0}^{\infty} k \left[\zeta \left(\frac{5}{2}, \frac{1}{2} + \frac{\mathbf{k} + \gamma}{\gamma \mathbf{h}} \right) - \frac{2}{3} \left(\frac{\gamma \mathbf{h}}{\mathbf{k} + \gamma} \right)^{3/2} \right]$

$$\gamma = \frac{2eDB_i}{mk_BT}$$
, $h = B/B_i$

ζ = generalized Riemann ζ-function

$$g(T,B) = \frac{1}{\frac{2}{F} + \ln\left(\frac{1.13T_F}{T^*}\right)} \setminus$$

The other parameters have been defined earlier. The expression is derived from perturbation theory to first order in the disorder parameter, $(k_{\rm p}l_{\rm p})^{-1}$, and to infinite order in the electron-electron interaction. As the disorder parameter is small in the Mg.based glasses studied here, i.e. $(k_{\rm p}l_{\rm p})^{-1} \approx 0.06$, the above expansion should be valid without restriction. The expression for the coupling g(B,T), however, is not exact. Similar to the expression by Altshuler and Aronov, it is correct only to lowest order in B/T. We note that the two expressions have a very similar form (for non-superconductors), they differ by only about 20%. Although Isawa and Fukuyama have derived the Cooper channel magnetoresistance for the mutual electron repulsion only, it should be valid for the attractive case (superconductor) as well, because the underlying Feynman diagrams are the same and only the sign of the coupling g(B,T) differs. One can therefore use eq.2.32 for superconducting metals as well with $g(B,T) = -1/\ln(T^*/T_c)$ for the electron-electron coupling. The dephasing effect of inelastic

electron-phonon scattering on the Cooper channel magnetoresistance has been included in eq.2.32 through the inelastic scattering field B_i . In the range of temperatures and fields studied here it is however very small. Not included in the derivation of eq.2.32 were the Zeeman band splitting and magnetic impurity scattering effects which decrease the Cooper channel magnetoresistance. Judging by the corresponding factor

$$\cos\left(\frac{g\mu_{B}B}{\pi k_{B}T}t\right)\exp\left(\frac{\hbar/\tau}{\pi k_{B}T}t\right)$$

in eq.2.31 they are negligible in the high purity, large diffusivity glasses studied here. For typical values of D, B_1 , and $1/\tau_s$ and using the same coupling g(B,T) we find that eq.2.32 and 2.31 are very similar as is shown in Fig.2.11. On the scale of this figure the two expressions are identical for B<3T and differ by only 10% for B=6T. We also find that eq.2.30 falls onto the curve of eq.2.32 if the factor α is set to $-1/\pi$. We therefore conclude that eq.2.32,eq.2.31 and eq.2.30 (with $\alpha = 1/\pi$) give consistent descriptions of the Cooper channel magnetoresistance. For the analysis of the data eq.2.32 is used as it includes the dephasing due to inelastic electron-phonon scattering.

To complete the discussion on enhanced electron-electron interactions, the temperature dependence of the diffusion and Cooper channel resistivity correction is given in the following equation^{20,21}:

$$\left(\frac{\delta\rho}{\rho}\right)_{e-e}(T,B=0) = \left(\frac{\delta\rho}{\rho}\right)_{e-e}^{DC}(T,B=0) + \left(\frac{\delta\rho}{\rho}\right)_{e-e}^{CC}(T,B=0)$$
(2.33)

$$= -\rho \frac{e^2}{2\pi^2 h} \left(\frac{k_B^T}{hD} \right)^{\frac{1}{2}} \left[\frac{2}{3} - \frac{3}{4} \tilde{P}_{\sigma} - g^{-1} \right] \times 0.915$$

The quantities \tilde{F}_{g} and g^{-1} were introduced in eq.2.29 and 2.30. It is not clear from the discussion by Altshuler and Aronov²⁰ whether the Cooper channel part in eq.2.34 also applies to the repulsive electron interaction case. Plots of eq.2.34 for typical values in Mg.based glasses are shown in Fig.2.12.

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Figure 2.12 Normalized quantum corrections to the resistivity. $\rho = 50\mu\Omega cm$, $D = 6cm^2/sec$. The abreviations have the followin meaning: $DC = diffusion channel with \tilde{F}_{\sigma} = 0.5$ $CC s/c = Cooper channel with T_o = T_c = 0.12K$ $CC non-s/c = Cooper channel with T_o = T_p = 85000K$ $WL = weak localization with B_{so} = 1T$, for B_see eq.4.2

 $\dot{M}T = Maki \cdot \dot{T}hompson with T_c = 0.12K$

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2.4 Superconducting Fluctuations

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In addition to the resistivity corrections discussed in the previous sections, a temperature and magnetic field dependent resistivity arises in disordered superconductors from superconducting fluctuations above the transition temperature. In contrast to ordered superconductors, superconducting fluctuations, i.e Cooper pairs with a small correlation length and a short lifetime, can exist in disordered superconductors far above the transition temperature ($T \approx 50T_c$). One distinguishes between two types of contributions to the resistivity: one from the current carried by the superconducting fluctuations, which is referred to as the Aslamasov-Larkin term⁶⁵, and one from the scattering of normal electrons by the superconducting fluctuations, which is referred to as the Maki-Thompson term⁶⁵.

Ami and Maki⁶⁵ have investigated both the Aslamasov-Larkin and Maki-Thompson terms in great detail. They find that the Aslamasov-Larkin contribution decreases rapidly above the transition temperature. This is in agreement with experimental results by Johnson and collaborators⁶⁶, who reported that it is negligible above 1.3T. In contrast, the Maki-Thompson term persists to well above T. Ami and Maki show that it consists of two parts: one with a large magnetic field and small temperature dependence, and a second with a small field and drastic temperature dependence. The latter term decays with temperature as $\exp(-\gamma | \overline{t})$ (t is the reduced temperature $t = T - T_c / T_c$ and $\gamma = O(1)$) as was shown experimentally by Johnson et al. 66 in type II amorphous superconductors. In Chapter 4 it is shown that such a decay is also observed in the Mg-Zn glasses studied here. Unfortunately, the expressions Ami and Maki give for the Maki-Thompson resistivity temperature and field dependence are long and extremely complex and are therefore not reproduced here. Altshuler, Varlamov and Reiser⁶⁷, however have given a simpler expression for the temperature dependence in the absence of a magnetic field as

$$\left(\frac{\delta\rho}{\rho}\right)_{\rm MT}(T) = \rho \frac{e^2}{2\pi^2 \hbar} \left(\frac{k_{\rm B}T}{\hbar D}\right)^{\frac{1}{2}} g^2(T) \times 6.8 \qquad (2.34)$$

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and Larkin⁶⁸ has calculated the magnetoresistance as

$$\left(\frac{\delta\rho}{\rho}\right)_{\rm MT}(B) = \rho \frac{e^2}{2\pi^2 h} \sqrt{\frac{eB}{\hbar}} \beta(T) f_3\left(\frac{B}{B_{\phi}}\right) \qquad (2.35)_{\psi}$$

g(T) is the bare electron coupling introduced in eq.2.30, and f_3 and B_{ϕ} were defined in eq.2.24. The coupling constant β is related to $g(T) = -1/\ln(T/T_{\phi}) \frac{4}{5}y$

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$$B(T) = \frac{\pi^2}{4} \sum_{m=-\infty}^{\infty} (-1)^m \Gamma(|m|) - \sum_{n=0}^{\infty} \Gamma''(2n+1)$$
(2.36)

where[†])
$$\Gamma(|m|) = \left[-g^{-1} + \Psi(1/2 + |m|) - \Psi(1/2)\right]^{-1}$$

and Ψ is the digamma function.

The magnitude of the two expressions above reduces only logarithmically with increasing temperature above T_c . We therefore expect the Maki-Thompson term to contribute significantly to the magnetoresistance in the Mg-Zn glasses even at temperatures as high as 10K. It was pointed out by Altshuler and Aronov²⁰ that only a singlet term contributes to the Maki-Thompson magnetoresistance in eq.2.36 and it is therefore not limited by the strength of spin-orbit scattering in the alloy. According to Larkin⁶⁸ however the validity of eq.2.36 is limited to small applied fields and small inelastic electron-phonon scattering, i.e

B,Bi <<
$$\frac{k_BT}{4eD}\ln(T/T_c)$$

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At larger applied fields, as was mentioned by Lopes Dos Santos⁴ and Abrahams⁶³, the Maki-Thompson magnetoresistivity (which increases monotonically according to the above equation) is expected to saturate; the magnetic field can only destroy that extra finite conductivity which is due to superconducting fluctuations. Close to this saturation the magnetoresistance should vary as 1/B.

†) There is a typographical error in Larkin's paper. The first digamma function carries a minus sign in his article which causes an unphysical divergence of Γ for certain values of T. Lopes Dos Santos and Abrahams⁶³ have corrected this; however their expression for Γ is in error by a factor of 2 in the argument the digamma function⁶⁹.

Strictly speaking, the coupling constant β has to be field dependent since the bare $coupling g^{-1}$ is field dependent. Within the above field limitations this can however be neglected. Also, it is not known how sensitive β is to the strong pair-breaking which is believed to exist in amorphous superconductors⁶⁶. Values for β were tabulated by Larkin⁶⁸. As a precaution the table was recalculated using the method described in the appendix A.4. Surprisingly the obtained values were 30% larger than Larkin's. Presumably Larkin made an error either in the remainder approximation (which is essential to the calculation because of the slow convergence of the series) or he was not aware of round-off errors intrinsic to some computers. The difference^{†)} between Larkin's and our result for β is shown in Fig.2.13. A plot of the Maki-Thompson magnetoresistance is shown in Fig.2.11 in comparison with other magnetoresistance contributions discussed in the previous section. The temperature dependence superconducting fluctuation resistance of eq.2.34 is included in Fig.2.12.

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†) The calculation in appendix A.4 agrees with results by Richter, Baxter and Trudeau 64 who used a different estimation of the remainder of the series in eq.2.36.

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2.5 Magnetic Impurity Scattering

In section 2.2 and 2.3 it was shown that magnetic impurity scattering causes a dephasing of the coherent backscattering and therefore decreases the quantum corrections to the resistivity. This is not the only effect magnetic impurities have on the temperature and field dependence of the resistivity. Scattering of the conduction electrons by dilute localized magnetic moments gives rise to a resistivity $\rho_{mag} = m/e^2 n \tau_s$. $1/\tau_s$ is the magnetic scattering rate introduced in section 2.2. Taking the temperature dependence of $1/\tau_s$ into account leads to the well known Kondo resistivity^{70,71}. It is a third order effect in the conduction-electron local-moment exchange integral, J, and is written as

$$\left(\frac{\delta\rho}{\rho}\right)_{mag}(T) = \frac{c}{\rho} \frac{3\pi m\Omega}{2\hbar e^2 \epsilon_{R}} \left[V^2 + J^2 S(S+1) \left(1 + \frac{3Jz}{\epsilon_{P}} \ln \left(\frac{k_{B}T}{2\epsilon_{P}}\right) \right) \right]$$
(2.37)

V is the direct Coulomb interaction potential. J consists of two parts, i.e $J = J_a - |V_m \uparrow^2 / \Delta E$. J_a is a direct ferromagnetic exchange term and the second part is an indirect antiferromagnetic admixture term. For dilute 3d transition elements such as Mn the antiferromagnetic term dominates because the energy difference, ΔE , between the localized d-states and the Fermi energy is small; J is then negative. For dilute rare earths the f-shell configuration is very stable. ΔE is therefore large and the overall exchange J is small. In some rare earths such as Gd ΔE is so large that J is in fact positive⁷¹. In the high-purity metals studied here this Kondo resistivity is negligible.

Beal-Monod and Weiner⁵⁶ have carried out a detailed study of the field dependence of $1/\tau_s$. With increasing field the magnetic impurity spins are progressively aligned which gives rise to a negative magnetoresistance⁷². Assuming that the direct Coulomb potential V is much larger than the indirect spin-exchange potential J the two authors

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find to second order in J:

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$$\left(\frac{\delta\rho}{\rho}\right)_{mag} = K J^{2} A(\alpha) \qquad (2.39)$$
where $K = \frac{c}{\rho} \frac{3\pi m\Omega}{2he^{2}\epsilon_{F}}$

$$A(\alpha) = 4\langle S_{z}\rangle^{2} + \langle S_{z}\rangle \left(\coth \alpha/2 - \frac{\alpha/2}{\sinh^{2}\alpha/2}\right)$$
with $\alpha = \frac{g\mu_{B}B}{k_{B}T}$

and
$$\langle S_z \rangle = \frac{M}{g\mu_B N/V} = S B_S(S\alpha)$$

 B_{S} is the Brillouin function, M the magnetization, S moment of the impurity spin and c the impurity concentration. The important point to notice is that $\Delta \rho_{m} / \rho$ as well as $B_{s} = \hbar / 4eDr_{s}$ both depend on the product cJ^{2} so that the above negative magnetoresistivity can not be neglected at low temperatures (T<6K) if B_{s} is of the order 3mT or larger. A plot of the impurity magnetoresistance $\Delta \rho_{m} / \rho$ is included in Fig.2.11.

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2.6 Application to Amorphous Mg-Cu and Mg-Zn

The bulk Mg-Cu and Mg-Zn glasses studied in this thesis are simple metals. We can therefore calculate the expansion parameter $(k_F l_e)^{-1}$ of the theories of the quantum corrections to the conductivity from the measured resistivity and free electron theory, i.e

$$(k_{F}l_{e})^{-1} = \frac{\hbar}{3m} \rho e^{2}N(\epsilon_{F})$$

We find that it ranges from 0.05 to 0.07 and is therefore small enough in all alloys that higher order terms of the perturbation expansion need not be considered^{\dagger}.

Our knowledge of the above alloys is such that <u>all</u> parameters appearing in the various expression in the previous sections, with the exception of the dephasing field B_{ϕ} and the spin-orbit scattering field B_{so} , are known. Specifically we know the resistivity, diffusivity, Fermi temperature, superconducting transition temperature of $Mg_{70}^{2n}_{30}$ and therefore the Maki-Thompson parameter β , and the electron screening parameter \tilde{F}_{σ} . The relevant parameters are listed in Table 2.1.

This allows us to make the following predictions for the magnetoresistance arising from the quantum corrections. The weak localization magnetoresistance is expected to positive at small fields (B<0.5T) in all high-purity Mg based alloys studied here because off finite spin-orbit scattering. Its total magnitude at 6T is of the order $\Delta\rho/\rho \approx 10^{-4}$. Since the electron diffusivity is large (D= 5-8cm²/sec) the Zeeman band-splitting effect on the weak localization magnetoresistance (eq.2.23) is negligible. For the same reason the diffusion channel magnetoresistance (eq.2.29) is small, i.e less than 5% of the weak localization magnetoresistance. Neither of these two terms is enhanced by the Stoner factor since Mg-Cu and Mg-Zn glasses are only very weakly paramagnetic and or even diamagnetic. The Cooper channel magnetoresistance is positive in Mg-Cu glasses. At 6K its magnitude at

†) The size of these contributions for larger $(k_{\rm P}l_{\rm e})^{-1}$ is still the subject of current research. From theoretical considerations some authors claim that they are zero.

a field of 6T is about 15% of the weak localization magnetoresistance. In Mg-Zn it is negative and about 30% larger than in Mg-Cu. The additional magnetoresistance contribution from superconducting fluctuations in Mg-Zn increases the positive magnetoresistance at small fields by about 10-30% compared to the corresponding Mg-Cu alloys. The very low concentration of magnetic impurities in all alloys (see Table 3.4) precludes magnetic effects on the electrical transport.

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Table 2.1

Alloy	ρ	k _. F	D	Fo	т _р
^{Mg} 70 ^{Cu} 30	44.0	1.38	'6 .9	0.50	84000
^{Mg} 70 ^{Cu} 27 ^{Ag} 3	45.7	1.38	6.6	0.50	84000
Mg ₇₀ Cu ₂₄ Ag ₆	46.4	1.38	6.5	0.50	84000
Mg ₇₀ Cu ₁₅ Ag ₁₅	51.8	1.38	5.8	0.50	84000
^{Mg} 70 ^{Cu} 29.9 ^{Au} 0.1	48.4	1.38	6.1	0.50	84000
^{Mg} 70 ^{Cu} 28.5 ^{Au} 2.5	49.0	1.39	6.1	0.50	86 000
Mg70 ^{Cu} 27 ^{Au} 3	50.4	1.39	5.9	0.50	86000
Mg ₇₀ Cu ₂₁ Au ₉	55.8	1.39	5.3	0.50	86000
^{Mg} 70 ^{Zn} 30	45.1	1.43	6.0	0.49	0.12 ^{†)}
Mg ₇₀ Zn ₂₇ Ag ₃	49.8	1.43	5.3	0.49	0.04 ^{†)}
$Mg_{70}Zn_{27}Au_{3}$	50.4	1.43	5.3	0.49	0.04 ^{†)}
Mg ₇₀ Zn ₂₉ Gd ₁	45.6	1.43	5.9	0.49	90000
Mg ₇₀ Cu ₃₀ (170ppm Mn)	45.0	1.38	6.7	0.50	84000

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Units: $\rho \neq n \mu \Omega cm$, k_F in $10^8 cm^{-1}$, D in cm^2/s , T_F in K 'Error: ρ : $\pm 5\%$, D: $\pm 10\%$. †) : T_c in K

3. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

3.1 Preparation of Samples

The preparation of glassy Ng Zn and Mg-Cu samples is described in detail in the following sections. In the preparation of the samples particular attention is paid to their quality and purity. The quality of the glass, i.e the level of crystalline precipitates, and the level of magnetic impurities both strongly influence electric transport measurements. In particular, a small number of crystalline grains in the amorphous matrix can significantly alter electrical transport properties (see reference 73 and 74 and Fig.1.3). Also, as is shown later in section 4.2.4, as little as 10ppm of Manganese impurities in the glasses studied here would prevent an unambiguous analysis of their magnetoresistivity by the theories of quantum corrections to the conductivity.

3.1.1 Rav Materials

The starting metals for the alloys were purchased from the following suppliers with the quoted specifications:

Mg: Alfa Products (Thiokol/Ventron Products) Danvers, MA 01923, USA Purity: m99.95%, specifically 40ppm Mn, 20ppm Fe, 10ppm Ni according to the batch analysis suplied by Alfa Products
Zn: American Cominco Spokane, Washington, USA Purity: 99.9999%

Cu: ASARCO Ltd., New York, USA Purity: 99.999%, less than lppm transition metal impurities

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Ag:	Johnson Matthey Chemicals Ltd.				
	London, U.K.				
	Purity: Specpure (registered trademark),				
-	specifically 3ppm Fe, 1ppm Cu, <1ppm of Bi,Cd,Mg				
Au:	Alfa Products (Thiokol/Ventron Products)				
	Danvers, MA 01923, USA				
	Purity: m99.9999%				
Mn:	Mackay Inc.				
	New York, N.Y. 10038, USA				
	Purity: 99.99%				
Gd :	Alfa Products (Thiokol/Ventron Products)				
	Danvers, MA 01923, USA				

Purity: m99.9%, main impurities are rare earth oxides

3.1.2 Distillation of Magnesium

It is evident from the previous section that the impurity level of the Magnesium as purchased is far from being acceptable ven though it is the purest commercially available at the present time. Specifically, 40ppm of Manganese is a high enough magnetic impurity concentration to destroy most of the weak localization magnetoresistance (see Chapter 4.2.5). For this reason a vacuum distillation technique, developed by Revel and coworkers⁷⁵, was used to refine the "dirty" magnesium. A sketch of the Magnesium still \cdot a simplified version of the one used by Revel et al. • is shown in Fig.3.1. It consists of a 60cm long stainless steel tube of 25mm diameter which is inserted into a vertical furnace and evacuated by a rotary pump. The stainless steel tube encloses a 6cm long and 22mm 'in diameter high-purity carbon crucible at its bottom. The carbon crucible is closed with a carbon lid, a small orifice (1mm diameter) in the lid allows the Mg vapor to escape. An open-ended quartz tube, 50cm long and 19mm in diameter, rests on the carbon crucible. The stainless steel tube was positioned in the furnace so that its end (and hence the graphite crucible) was in the hottest area of the furnace. The quartz tubing was long enough to reach the cold

area above the furnace. Prior to the distillation the carbon crucible and the quartz tubing were thoroughly etched in a solution of 1:1:1 HCl, HNO3, H2O to remove metallic contaminants off its surface, and dried in the evacuated steel tube at 1000K for several hours. Pieces of Mg rod were placed into the graphite crucible and the still was assembled as shown in Fig.3.1. Upon heating the center of the furnace to 1000K . 180K above the melting point of Mg - Magnesium evaporates; its vapor pressure is approximately 10mbar at this temperature 76 . The Mg vapor passes through the small orifice in the lid of the carbon crucible and ascends until it condenses on the cold quartz substrate at the top of the still. When the Magnesium had evaporated and the still had cooled down, the quartz tube was removed and cut open with a diamond saw to recover the purified Magnesium. The majority of the Magnesium deposited at a temperature of between 800K and 600K. The vertical temperature profile was measured with a Cromel thermocouple. Only this material was used; it contains according to Revel and coworkers the least transition metal impurities. Before further processing, the Magnesium was thoroughly etched in acid with the composition given above. The Magnesium distillate is essentially transition metal free, because the Mg vapor pressure at 1000K (as shown in Fig.3.2) is at least 5 orders of magnitude larger than the vapor pressure of transition metals. specifically that of manganese, nickel, chromium and iron. Therefore primarily Mg and in addition some more volatile elements such as Zn, Na, Cd evaporate from the liquid and condense on the quartz substrate. However, the latter elements do not have a significant effect on our measurements.

A major advantage of the purification method described above lies in its simplicity. Small variations of the residual gas pressure in the still (here about 10^{-2} mbar), the temperature of the Mg liquid (as long as it is above 970K) or the condensation temperature have only little effect on the purity of the distillate which allows good results without technical sophistication. The magnetic impurity concentration of the distillate was determined by magnetic susceptibility and neutron activation measurements as described in section 3.2.4 and 3.2.5 of this chapter and was found to be (0.4 ± 0.2) ppm of Mn and (3 ± 3) ppm of Fe.




1) furnace.

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- 2) stainless steel crucible
- 3) carbon crucible
- 4) carbon lid with orifice
- 5) liquid magnesium
- 6) quartz tube
- 7) condensed magnesium
- 8) vacuum connection
- 9) valve
- 10) rotary vacuum pump

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Figure 3.2 Equilibrium vapor pressures of pure elements (p°) normalized by the magnesium vapor pressure $(p^{\circ}Mg)$ (from reference 75).

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3.1.3 Induction Melting

Magnesium is extremely difficult to melt by arc-melting. Once struck by the electric discharge an oxide layer forms on the surface (Mg is an effective getter) and this layer impedes the alloying. To avoid these difficulties it was necessary to alloy Magnesium with other metals by induction melting. A sketch of the induction melting station built for this purpose is shown in Fig.3.3. It consists of a quartz vessel suspended in a radio frequency induction coil (powered by a 30kW LEPEL RF generator) and connected to a vacuum pumping system. The quartz vessel holds a high purity (less than 5ppm Fe) carbon crucible as shown in Fig.3.3a (the carbon was purchased from SPEER CANADA Ltd.). The crucible is 8cm long and 1.8cm in diameter. Its separate bottom piece allows easy removal of the alloyed metal pellet. The carbon lid on the crucible has a small orifice to prevent pressure build-up during the alloying. Both, quartz and carbon crucible were cleaned in a solution of 1:1:1 HCl, HNO, H₂O and dried at 1200K under vacuum prior to each melting. The stacking order of the constituent metals was found to be important. Best results were obtained with the Mg pieces (≈ 2.4 g) at the bottom of the crucible and the other materials on top as indicated in the figure. After placing the materials into the carbon crucible the quartz vessel was pumped down to a pressure of $\tilde{\langle 10}^{-5}$ mbar and flushed several times with purified Argon to remove Oxygen. Prior to melting, the quartz vessel was filled with Ibar of purified Argon. This; inert atmosphere of approximately lbar pressure is important to avoid evaporation of large quantities of Magnesium and Zinc. The carbon crucible and the metals it contained were then heated to between 1000K and 1100K within 10 to 30sec. The temperature was monitored with a Minolta-Land CYCLOPS 52 infrared pyrometer. Shaking the quartz vessel for one to two minutes was enough to ensure a sufficiently homogeneous mixing of the alloy; no phase separation was visible when the solidified alloy was cut, polished and inspected with a metallurgical microscope. After the alloy had solidified, the quartz vessel was evacuated; the alloy was removed when it had cooled down to room temperature. The weight loss of the sample was 2% to 7% and we attribute it to the

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evaporation of Mg and Zn as well as to some residue stuck to the walls of the carbon crucible. The alloy pellet was then cut with a diamond saw into pieces of appropriate size for melt-spinning, polished with 400 or 600grit sandpaper and cleaned in an ultra-sonic alcohol bath to remove silicon-carbide contaminants due to the sandpaper.



a)

b)

Figure 3.3 a) Schematic diagram of the induction melter.

- 1) high purity carbon crucible
- 2) RF heater coil
- 3) quartz crucible
- 4) vacuum connection
- 5) valves
- 6) argon inlet
- 7) pressure gauges
- 8) rotary and diffusion vacuum pumps
- b) Induction melter crucible.
 - 1) quartz crucible
 - 2) carbon lid
 - 3) carbon tube
 - 4) carbon bottom piece
 - 5) magnesium
 - 6) e.g Zn or Cu

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3.1.4 Melt-Spinning

Of many amorphisation techniques - such as e.g. sputtering, cryocondensation or solid-state reaction - melt-spinning is the most suitable for producing large quantities of bulk amorphous metals. The working principle[†]) is demonstrated in Fig.3.4. An alloy sample of 0.5g to 1g is placed in a quartz crucible. It is melted by induction heating and ejected through a small orifice at the bottom of the crucible onto the rim of a rotating copper wheel. The jet of molten alloy rapidly solidifies on the cold (300K) copper surface and forms a long amorphous ribbon. It was found empirically that the best ribbon quality was achieved with an orifice of 0.4mm diameter and a tangential wheel speed of 65m/s. The cooling rate of this technique can be estimated to be of the order $1-2\cdot10^{6}$ K/sec and is sufficient to produce glassy Mg-Cu and Mg-Zn alloys in the composition range of $\pm 10at$ % Mg around the eutectics at $Mg_{70}Cu_{30}$ and $Mg_{70}Zn_{30}$ (see phase diagrams in reference 77). To avoid oxidation of the sample, the melt-spinning was carried out in a Helium atmosphere at 0.35bar pressure, and the liquid alloy was ejected from the quartz crucible using high purity Argon at 0.5bar. The resulting glassy Mg-Zn and Mg-Cu ribbons were typically 1m long, 0.8-2mm wide and 15-30µm thick. Again it should be noted that the quartz crucible and the copper wheel were cleaned with 1:1 ENO2, H20 and alcohol before the spinning. Immediately after melt-spinning the samples were stored in liquid nitrogen to avoid oxidation and crystallization⁷⁸.

t) For a more detailed description of the melt-spinning technique the reader is referred to references 4 and 79.

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3.2 Quality Control and Sample Characterization

The melt-spun ribbons were subjected to detailed tests to ensure their amorphicity, homogeneity and purity and to establish their material characteristics. As mentioned before, intensive quality control and material characterization has been proven to be of extreme importance since for example electrical transport properties depend crucially on the material characteristics. A meaningful comparison between results on samples used in this thesis, and those by other workers, is only possible if the samples have been carefully characterized.

3.2.1 X-Ray Diffraction

The amorphicity of the as-spun ribbons was confirmed by X-ray diffraction using Cu-K_a radiation (λ =0.15418nm). A schematic picture of the computerized NICOLET L11 diffractometer with a STOE goniometer and Cu-tube is shown in Fig.3.5. This diffractometer has a resolution better than 0.05degree and is capable of detecting crystalline contaminants in the glass exceeding a concentration of about 2%. X-ray scans were taken in the range 20 = 30 to 50degrees. This scanning range brackets the entire amorphous reflection band. Some typical examples are shown in Fig.3.6. Samples which showed peaks in addition to the amorphous halo, as is the case for the scan of one Mg₇₀Cu₃₀ sample in Fig.3.6, were rejected. More than 80% of the ribbons melt-spun were found to be amorphous within the resolution of the diffractometer.

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Figure 3.6 X-ray diffraction patterns of some Mg-based alloys. The diffraction angle 20 is given in degrees, the intensity units are arbitrary. The bottom graph shows the diffraction pattern of a partially crystalline sample.

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3.2.2 Differential Scanning Calorimetry (DSC)

DSC data such as crystallization temperature, crystallization enthalpy and activation energy are important characteristics of a glass. It has been shown that they depend on melt-spinning parameters^{81,5}, oxygen contamination⁷³ and in some cases crystalline traces in the amorphous matrix. They can therefore be considered as a calibration of the quality of the metallic glass.

Samples of all the alloys investigated in this thesis were subjected to isochronal DSC scans with heating rates of 10,20,40,80 K/min using a Perkin-Elmer DSC 2C calorimeter. The working principle of such a DSC is best demonstrated by Fig.3.7. Approximately 5 to 15mg of sample contained in an aluminum pan is placed in a platinum sample holder. Sample, Al pan and sample holder are heated at constant heating rate by a small heater in the sample holder to a preset maximum temperature (here 600K). A resistive thermometer measures the temperature. The energy required to heat the sample at constant heating rate, Φ , is compared to that required to heat an identical platinum sample holder with an empty Al pan inside. The difference, i.e

$$\frac{\left(\Delta E_{s} - \Delta E_{r}\right)}{\Phi \Delta t} = \frac{\Delta E}{\Delta T}$$

is equivalent to the enthalpy change, $\frac{\Delta H}{\Delta T} = c_p$, of the sample. Changes in the atomic or magnetic structure (such as crystallization or magnetic ordering) result in a change of enthalpy. A microcomputer serves as a data acquisition system and allows convenient analysis of the resulting c_p against temperature curves. Some representative DSC scans are shown in Fig.3.8. The transformation temperature is taken to be the peak temperature (rather than the onset temperature which is not always well defined). The crystallization enthalpy was calculated by integrating the curves in Fig.3.8 over the temperature and normalizing the result by the sample mass. The activation energies of the transformations were deduced using Kissinger's method⁸². Results from the DSC measurements are combined in Table 3.1. They in good agreement with those found by Altounian et al.⁸³ and Mizutani et al.³⁴. The transformations causing the various exotherms in Fig.3.8 were identified by X-ray diffraction analysis (the X-ray diffraction patterns were compared to those listed in the JCPDS files⁸⁴).

In case of the $Mg_{70}Cu_{30}$ based alloys, with the exception of $Mg_{70}Cu_{15}Ag_{15}$ and $Mg_{70}Cu_{21}Au_{9}$, the crystallization characteristics are very simple. At the temperature T_x^1 the alloys crystallize into the stable phase Mg₂Cu. Whether there are small amounts of Mg present in the matrix in addition to Mg_2Cu or whether Mg_2Cu was formed slightly off stochiometry could not be resolved by X-ray diffraction as 7at% of Mg gives a minute X-ray signal compared to that of Mg₂Cu, and the systematics of the shifts diffraction lines could not be investigated because of their large width. It was not possible to discover the origin of the strong asymmetric form of the crystallization exotherm typical for all of the above mentioned Mg-Cu alloys; it may be caused by a small Avrami number of the reaction kinetics characteristic for surface crystallization. The crystallization of Mg₂Cu is followed by a growth of the crystallites of this phase at temperatures from 500K to 600K causing a very small exothermal DSC peak. No further transformation was observed before the alloys melt. The crystallization characteristics of the $Mg_{70}Cu_{15}Ag_{15}$ and $Mg_{70}Cu_{21}Au_{9}$ are different from those discussed above. This is not surprising since the amount of Ag and Au in the two samples is so large that not all Ag and Au can substitute stochiometrically for Cu in the Mg₂Cu compound. One expects a Mg Ag and Mg-Au phase to precipitate in addition to Mg₂Cu from the amorphous matrix. This is in fact observed. The primary exothermal peak in $Mg_{70}Cu_{21}Au_{9}$ was identified to be due to the crystallization of the $Mg_{3}Au$ phase, the following peak doublet being caused by the crystallization and growth of Mg_2Cu . $Mg_{70}Cu_{15}Ag_{15}$ crystallizes first into the Mg_3Ag phase which grows out of the amorphous matrix in the secondary DSC exotherm and partially decomposes into Mg₂Cu until a phase equilibrium is reached. Judging by the values for T_x^1 and for the activation energy of the primary peak found in the Mg-Cu glasses, it seems that $Hg_{70}Cu_{30}$ becomes thermally more stable on the addition of a third element, Ag or Au. Eventually, for large Au and Ag concentrations, the

stability must decrease however, as Mg-Ag and Mg-Au alloys, judging by the shallowness of their eutectics, can not be made amorphous by the melt-spinning with a quench rate of 10^6 K/sec or less. In fact, Mizutani³⁴ has shown that the limit of the glass forming range is reached in Mg₇₀Cu₃₀ if half of the Cu is replaced by Ag.

In case of the $Mg_{70}Zn_{30}$ -based alloys the first exothermal peak at temperature T_x^1 correspond to the nucleation of small crystallites of the stable phase $Mg_{51}Zn_{20}$. The secondary, somewhat larger, peak at temperature T_x^2 corresponds to the transformation of the entire amorphous matrix into this phase. The third peak, at temperature T_x^3 , is caused by the transformation of $Mg_{51}Zn_{20}$ into Mg + MgZn. No further transformation takes place until the alloys melt. The crystallization temperatures T_x^1 , activation energies E_a are comparable to those of the $Mg_{70}Cu_{30}$ -based glasses, the crystallization enthalpy however is only half as large.

The DSC measurements above have shown that the crystallization characteristics of the Mg-based glasses studied here are consistent internally and with the corresponding phase diagrams and agree with previous results^{83,34}. We can therefore conclude that the samples studied here are of equally good quality.

Figure 3.7 Schematic diagram of a Perkin-Elmer DSC 2C differential scanning calorimeter.

- 1) sample holder
- 2) reference holder
- 3) resistance thermometer
- 4) heater

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5) Argon inlet

6) Argon outlet

7) Aluminum heat sink

8) thermometer for sample and reference

9) power supply for sample and reference heater

10) sample enclosed in Al-pan

11) empty reference Al-pan



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Table 3.1

Results from differential scanning calorimetry at 40K/min. T_x^i is the transformation peak temperature, ΔH_x the transformation enthalpy and E_a^i its activation energy.

Alloy	T _x ¹	T _x ²	ΔH ^{*)} _x	E _a ¹	E ² a
Mg ₇₀ Zn ₃₀ 0)	380	391	1.67	1.90,±0.1	1.40 ±0.1
Mg ₇₀ Zn ₃₀	385	401	1.34	1.88 ±0.17	1.49 ±0.09
$Mg_{70}Zn_{27}Ag_3$	392	412	1.77	1.98 ±0.11	1.47 ±0.07
Mg ₇₀ Zn ₂₇ Au ₃	399	442	1.54	2.37 ±0.27	2.06 ±0.08

Alloy	T _x ¹	∆H x	^E a ¹
Mg ₇₀ Cu ₃₀	426	3.82	1.68 ±0.13
Mg ₇₀ Cu ₂₇ Ag ₃	415	3.42	1.64 ±0.04
Mg ₇₀ Cu ₂₄ Ag ₆	425	3.48	1.81 ±0.06
$Mg_{70}Cu_{15}Ag_{15}$	430	3.38	2.65 ±0.10
Mg ₇₀ Cu _{29.9} Au _{0.1}	408	4.32	1.36 ±0.20
Mg ₇₀ Cu _{28,5} Au _{1,5}	422	4.50	1.40 ±0.03
$Mg_{70}Cu_{27}Au_3$	427	3.79	1.68 ±0.03
Mg ₇₀ Cu ₂₁ Au ₉	466	4.87	3.19 ±0.18

Units: T_x in K, ΔH_x in kJ/mol, E_a in eV Error: T_x : $\pm 2K$, ΔH_x : $\pm 10\%$.

o) values by Altounian et al.⁸³

*) ΔH_{x} is the combined enthalpy change of first and second crystallization exothermal.DSC peak

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3.2.3 Election-Beam Microprobe

Electron beam microprobe is a convenient tool for the analysis of sample composition and homogeneity, as it is fast to carry out and accurate (the analysis was carried out by Dr. Rod Packwood at CANMET Labs, Ottawa). Similar to an X-ray cathode, the sample one wishes to analyse is irradiated with an electron beam of appropriate energy (here 20keV). The incident electrons excite electrons on the inner atomic shells. The excitations decay emitting X-rays of characteristic wavelengths (there is some Bremsstrahlung as well which is filtered out). The intensity of the emitted X-rays is proportional to the abundance of the corresponding element in the sample. Table 3.2 gives results for the composition of the alloys used in this thesis. No compositional inhomogeneities were detected on scales larger than of the electron beam diameter (1µm). The silicon traces detected in the samples originate from silicon present in the elemental starting materials as well as from the quartz crucible used for the melt-spinning. The electrical transport properties are not affected by these small Silicon concentrations. The reader should note that the nominal rather than the measured compositions will be used in the following in order to avoid unnecessary long alloy formulae. For detailed calculations of for example, the average atomic mass or the charge density, the measured compositions were used.

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Table 3.2

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Electron-beam microprobe results

nominal composition	detected composition					
	Mg	Cu	Zn	Ag	Au	Si
Mg ₇₀ Cu ₃₀	6°9.89	29.88				0.616
Mg ₇₀ Cu ₂₇ Ag ₃	71.11	25.92		2.91		0.0
$Mg_{70}Cu_{2/}Ag_{6}$	70.46	24.11		5.40		0.0
$Mg_{70}Cu_{15}Ag_{15}$	69.26	15.69		15.03		••
$Mg_{70}Cu_{20} a^{Au} 1$	70.61	29.26			0.11	••
$Mg_{70}Cu_{20} 5^{Au_{0}}5$	69.43	30.04			0.51	0.001
$Mg_{70}Cu_{29.5}O.5$	69.70	28.88			1.37	0.076
$Mg_{70}Cu_{27}Au_{3}$	71.20	25.87			2.90	0.019
$Mg_{70}Cu_{21}Au_{0}$	72.06	19.39	,		8.49	0.109
Mg _{zo} Zn _{ao}	72.74		27.25			0.019
$Mg_{70}Zn_{27}Ag_{3}$	72.97		24.23	2.77		0.042
$Mg_{70}Zn_{27}Au_3$	74.12		22.95	2.91		0.013
Mg ₇₀ ^{Zn} 29 ^{Gd} 1	73.12		26.12	Gd =	0.758	0.008

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Units: all concentrations are in atomic percent Error: 0.5%.

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3.2.4 Magnetic Susceptibility

The magnetic susceptibilities of the distilled Mg, all Mg.Zn and three Mg.Cu samples were measured at 300K and 5K using a lab-built alternating force magnetometer.

The working principle of the alternating force magnetometer is the Faraday method which relies on the fact that a magnetic moment placed in a non-uniform magnetic field experiences a force, i.e.

$$\mathbf{F}_{\mathbf{z}} = \mathbf{m} \left(\chi - \frac{\mathbf{d}_{\mathbf{o}}}{\mathbf{d}} \chi_{\mathbf{o}} \right) \mathbf{H}_{\mathbf{x}} \left[\frac{\partial \mathbf{H}_{\mathbf{x}}}{\partial \mathbf{z}} \right]_{\mathbf{z}}$$
(3.1)

where H_

A

m the sample mass and F, the resulting vertical force.

In our case the susceptibility χ_0 of the surrounding medium - He at 70mbar - is negligible. Compared to a conventional magnetometer with specially shaped pole faces to produce a vertical field gradient (Faraday balance⁸⁵) an alternating force magnetometer, see Fig.3.9, has the advantage that the vertical field gradient is generated by two Lewis coils⁸⁶ independent of the uniform horizontal field. Switching the sign of the field gradient and hence the direction of the force on the sample is simply achieved by reversing the current through the Lewis coils at constant horizontal field, and allows the elimination of signal drifts 'to first order. The suspended sample holder inside is kept in position by an electrical servo-mechanism. The nulling current of the servo system is proportional to the force on the sample holder, and sample and was calibrated with 99.9999% pure polycrystalline Zn and Al (supplied by Alfa Products). The system sensitivity was found⁸⁷ to be $1.2 \cdot 10^{-9}$ emu. The applied horizontal field ($H_{max} = 16.5k0e$) was measured with a calibrated Hall probe. The Hall voltage, nulling current, applied field and field gradient were measured and controlled by an, IBM personal computer through a lab-built analog-to-digital/digital-to-analog

interface. Fig.3.9 shows the entire alternating force balance including the cryogenic system which allows measurements down to 4.3K. The temperature is controlled by a flow of cold (4.2K) He gas (evaporated with a heater at the gas nozzle) around the sample holder chamber. The carbon-glass thermometers were calibrated with a calibrated Ge-diode suspended in place of the sample holder. At 5K the temperature was stable within 0.02K.

The measured room temperature susceptibilities are tabulated in Table 3.3. They are compared to the free electron value

$$x_{val} = \frac{2}{3} \left(\frac{2.59}{r_s/a_o} \right) 10^{-6} emu/ccm$$
(3.2)

with the diamagnetic atomic core-susceptibilities listed in reference 88 taken into account. Considering the size of the susceptibilities the agreement is excellent, which underscores again the fact that Mg-Cu and Mg-Zn alloys are good free-electron metals. The magnetization of three Mg-Zn alloys as a function of applied field at room temperature and 5K is compared in Fig.3.10 (points). Also shown in the figure is the additional magnetization one expects at 5K and 17k0e from 4ppm of Manganese diluted in the alloys (at room temperature their magnetization is negligible). It is calculated according to 89

$$M(H) = \chi_{\text{Langevin}} \cdot H = \frac{Ng\mu_B S}{V} B_S\left(\frac{g\mu_B SH}{k_B T}\right)$$
(3.3)

where g=2, $S\approx 2.2$ and B_S is the Brillouin function. Judging by the difference of the measured magnetizations at 5K and room temperature we conclude that the samples contain at most 4ppm of Mn. The accuracy of the alternating force magnetometer does not allow us to set a more precise limit on the impurity level.







Figure 3.10 Magnetization against applied field (points). The alloy compositions and temperatures are given in the figure. The horizontal bar indicates by how much the magnetization would change between 300K and 5K if 4ppm of Mn were dissolved in the alloys.

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Table 3.3

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Alloy .	^X exp .	Xcalc
Mg (crystalline)	5.25 ±0.14	2.64
Mg ₇₀ Cu ₃₀	-0.50 ±0,40	0.10
$Mg_{70}Cu_{28} S^{Au_{1}}S$	0.16 ±0.20	-0.10
$Mg_{70}Cu_{27}Au_3$	0.21 ±0.20	-0.16
Mg ₇₀ Zn ₃₀	1.06 ±0.14	0.86
Mg ₇₀ Zn ₂₇ Ag ₃	0.71 ± "	0.63
Mg ₇₀ Zn ₂₇ Au ₃	0.63 ± "	0.53

Measured and calculated magnetic susceptibility

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Units: 10⁻⁷emu/g Note : The CRC Handbook⁷⁶ gives 5.39·10⁻⁷emu/g for Mg.

3.2.5 Neutron Activation

 $\underline{\mathbb{Y}}$ Neutron activation measurements are better suited to measure traces of Mn or Fe impurities in Mg-Cu and Mg-Zn glasses than susceptibility measurements. Such measurements were carried out on all samples by Dr. Greg Kennedy at the SLOWPOKE scientific nuclear reactor of the École Polytechnique, Montreal, Canada. Neutron activation analysis exploits the fact that almost all stable elements capture a neutron and transform into an unstable isotope when exposed to a flux of slow neutrons 90 . These isotopes decay with a characteristic half-life and emit a characteristic γ -ray spectrum. One can detect the γ -ray emission of a sample exposed to neutrons with a Germanium solid-state y-ray counter. The number of detected γ -rays at a particular energy - with the halflife and neutron capture cross-section of the corresponding isotope accounted for - is proportional to the relative concentration of the respective elements in the sample. The most important impurity level to measure is that of manganese as it carries a magnetic moment in amorphous $Mg_{70}Cu_{30}$ and $Mg_{70}Zn_{30}$. Fe and Ni are only of secondary importance since neither holds a magnetic moment in amorphous Mg70Cu30 and $Mg_{70}Zn_{30}$ (see section 4.2.4b). The Fe level was measured nevertheless in the distilled high purity Mg to find out how much it can be reduced by the distillation described in section 3.1.2. The measured manganese concentrations are listed in Table 3.4. The Mn level in the Mg-Zn alloys is in fact so low that it could not have been resolved by the magnetic susceptibility measurements described in the previous section. Because of the weak activity of Fe^{5,7} it takes a long time to get a reliable value for the Fe concentration in any of the samples. First one has to irradiate the sample with a several times larger neutron doses and then one has to wait for a week to let the signal of the disintegrating Mg (and even more so of Cu and Zn) decay to a level which does not interfere with the Fe signal. The Fe level detected in purified Mg was 3 ± 3 ppm. 3

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Table 3.4

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Results of neutron activation analysis

Alloy	Mn	0
Mg, distilled	0.4)
Mg ₇₀ Cu ₃₀	2.6	
Mg ₇₀ Cu ₂₇ Ag ₃	1 [,] .7	L.
Mg ₇₀ Cu ₂₄ Ag ₆	0.3	
$Mg_{70}Cu_{15}Ag_{15}$	1.1	
Mg70Cu29.9Au0.1	0.1	•
Mg ₇₀ Cu _{28.5} Au _{1.5}	2.2	
$Mg_{70}Cu_{27}Au_3$	0.1	•
$Mg_{70}Cu_{21}Au_{9}$	0.3	
Mg ₇₀ Zn ₃₀	0.3	
Mg ₇₀ Zn ₂₇ Ag ₃	2.3	0
$Mg_{70}Zn_{27}Au_3$	0.8	
Mg ₇₀ Cu ₃₀ (170ppm. Mn)	166	

Units: parts per million (ppm) Error: Approximately 10% or 0.2ppp whichever is greater.

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3.2.6 Density and Resistivity Measurements

To complete the section, values for the room temperature resistivity and density are tabulated in Table 3.5. The density of both, amorphous ribbons and crystalline ingots, was measured by Archimedes' principle with Toluene as a working fluid $(d_{tol} = 0.866(9)g/ccm at 293K)$. It turned out that the error on the densities of the amorphous ribbons was rather large, i.e. 10%, as the low alloy density made it difficult to accommodate more than 50mg of sample ribbon in the buoyancy balance. This restriction does not apply to the crystalline ingots whose density was measured to a precision of 1% or better. Therefore we have used as density of the amorphous material the density of the crystalline ingots reduced by 2x to account for their volume difference 92. The values in Table 3.5 can therefore be considered as accurate to within 3%. The resistivity of the amorphous alloys was determined by measuring the resistance R of the sample ribbons (using a four terminal technique), their lengths 1, and mass m. The resistivity can then be calculated by

$$p = \frac{R \cdot m}{1^2 \cdot d} = \frac{R \cdot A}{1^2}$$

, ,

The main error on the resulting resistivity is due to a non-uniform cross-section A, i.e ribbon thickness and width vary over the length (10-50cm) of the ribbon measured. Therefore the values for ρ given in Table 3.5 are an upper bound for the resistivity with a possible error of 5%. Within these errors they are in good agreement with those reported by Mizutani and coworkers^{33-36,91}.

(3.4)

Table 3.5

Density and room temperature resistivity

alloy	d	ρ
Mg ₇₀ Cu ₃₀	3.11	44.0
Mg ₇₀ Cu ₂₇ Ag ₃	3.16	45.7
$Mg_{70}Cu_{24}Ag_{6}$	3.30	46.4
$Mg_{70}Cu_{15}Ag_{15}$	3.75	51.8
$Mg_{70}Cu_{20} a^{Au}$	3.19	48.4
$Mg_{70}Cu_{29} S^{Au}_{0} S$	3.30	48.8
$Mg_{70}Cu_{29,5}Au_{1,5}$	3.41	49.0
$Mg_{70}Cu_{27}Au_{3}$	3.48	50.4
$Mg_{70}Cu_{21}Au_{0}$	4.12	55.8
$Mg_{70}Zn_{30}$	2.92	45.1
$Mg_{10}Zn_{27}Ag_{3}$	3.04	49.8
$Mg_{70}Zn_{27}Au_{3}$	3.23	50.4
$Mg_{70}Zn_{20}Gd_1$	2.97	45.6
Mg ₇₀ Cu ₃₀ (170ppm Mn)	3.10	45.0

Units: d in g/cm^3 , ρ in $\mu\Omega cm$ Error: d: $\pm 3\%$, ρ : $\pm 5\%$

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3.3 Resistance and Magnetoresistance Probes

The longitudinal magnetoresistance, i.e. $\vec{B} \parallel \vec{J} \parallel \vec{E}$, of all samples was measured in fields up to 5.6T and at temperatures ranging from 1.4K to 20K in a standard ⁴He cryostat. The resistivity temperature dependence of the samples was also measured in the same temperature range and in case of Mg₇₀Zn₃₀ and Mg₇₀Zn₂₇Au₃ down to 100mK in a dilution refrigerator. Pictures of the magnetoresistance cryostat, resistance bridge, power supply and data acquisition system are shown Fig.3.11. In the following sections the individual components of this system are described. A brief description of the dilution refrigerator is given in section 3.3.6.



Figure 3.11 Pictures of the magnetoresistance cryostat, resistance bridge, power supply and data aquisition system.

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3.3.1 Cryogenics and Magnet

A sketch of the Hoffmann(Airco) dewar system with the Nb.Ti superconducting magnet (Type No.8000/5511) is shown in Fig.3.12 (purchased from Ferranti-Packard Electric Ltd., Toronto, Canada). The setup is conventional. The 1 inch bore superconducting magnet is kept at 4.2K in a stainless steel dewar filled with liquid Helium. The He bath itself is thermally shielded by liquid hitrogen. The level of liquid He is measured at several places above and along the magnet with a carefully balanced $1/8Watt 50\Omega$ Wheatstone bridge. The bore of the magnet contains a thin-wall stainless-steel dewar containing the sample holder. For measurements at 4.2K or below the sample chamber is filled with liquid Helium and evacuated. Temperatures as low as 1.4K can be reached this way. A system of valves, gauges and heaters allows one to keep the temperature stable within less than 1%. For measurements above 4.2K the 😓 sample holder and the sample are coupled thermally to the liquid He bath of the magnet by pressurising the sample chamber and the sample holder dewar with He gas (the pressures were typically 0.1mbar and 10^{-4} mbar respectively). A stable temperature was achieved by heating the sample holder to the particular temperature with the resistive heater wound non-inductively onto the sample holder (see Fig. 3.13). The heater current was adjusted to the appropriate level by an analog feedback mechanism. The stray field of the heater is less than 3µT.

For high field measurements the magnet was powered by a HP Harrison 6260A DC Power Supply through a diode protection stack. The DC power supply itself was controlled manually with a discrete Keithley Instruments K2601 nanovolt source. According to the manufactures specifications the superconducting solenoids field factor is B/I=0.1226T/Amp and the field is uniform (±1 in 10⁵) over all of the sample. The magnet is fully reversible and without a detectable hysteresis. The magnet current ($I_{max}=45Amp$) is sensed across a 0.50 standard resistor with a Keithley Instruments Model 175 digital multimeter.

In two cases continuous-sweep low-field (B \leq 50mT) magnetoresistance measurements were carried out. For this purpose a HP Figure 3.12 Schematic diagram of the magnetoresistance cryostat.

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-1) Cu sample holder

2) stainless steel tubes

3) terminal lead box

4) superconducting magnet solenoid

5) liquid Helium dewar

6) liquid Nitrogen dewar

7) sample holder dewar

8) liquid Helium level detectors

9) valves

10) small diameter valve

11) rotary vacuum pump

12) diffusion pump 🗸

13) 0-ring

14) Helium gas inlet[°]

15) liquid Helium transfer tube

16) Helium gas outlet

17) vacuum gauges

6824A bipolar DC power supply driven with a triangular wave frequency generator was used to power the superconducting magnet. Its current was sensed across a 0.1Ω standard resistor. The sweep time from full field to reversed full field was about 100sec, in order to keep the magnetic field synchronised with the power supply and resistance bridge signal.



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3.3.2 Sample Holder

A sketch of the 4-point resistance probe is shown in Fig.3.13. The copper sample holder block is held in position by four thin wall stainless steel tubes which also contain the 40gauge (0.08mm diameter) copper leads for the a.c. bridge contacts, carbon-glass thermometer, heater and He level detectors. The carbon glass resistor is placed inside the copper block, right under the sample, to ensure good thermal contact. Two samples can be mounted (one on each side) by simply sticking them with vacuum grease onto the thin film of mylar which serves as electrical insulator between sample and copper sample holder. Below 4.2K the sample and sample holder were in direct contact with the liquid Helium bath and above 4.2K in direct contact with He gas at 0.1bar to prevent thermal gradients between sample and resistor or along the sample. No hysteresis or self-heating effects were detected for temperatures as low as 1.4K. Voltage and current contacts were glued with conducting silver paint directly onto the sample (it was found that silver paint contacts are much less noisy than pressure contacts, if handled properly).

3.3.3 Thermometry

A carbon-glass resistor (CGR) manufactured by Lakeshore Cryotronics Inc. (Westerville, Ohio, USA) was used to measure the temperature in all experiments carried out at temperatures above 1.4K. The carbon-glass thermistor was chosen because of its very good reproducibility, sensitivity, and small magnetoconductivity. Its conductance was measured with a SHE Inc. (now Biomagnetic Technologies Inc., San Diego, California, USA) Model PCB 4-terminal a.c. potentiometric conductance bridge and was calibrated against Lakeshore Cryotronics Inc. calibrated Platinum (T>40K) and Ge (T<40) resistors. The conductance bridge can measure conductances from 20microMho to 200mMho to an accuracy better than 0.1% at a power dissipation of less than 18pWatt which prevents any self-heating of the thermistor. The accuracy of the temperature reading is only limited by the small magnetoresistance of the carbon-glass thermistor which causes a misreading of less than 2.5% at T=4.2K and B=6T. A differential analog voltage output of the PCB served as a driver to control the sample holder heater current described in section 3.3.1.



Figure 3.13 Diagram of the resistance probe sample holder (to scale).

1) thin-wall stainless steel tubes containing.

the sensor and heater leads

2) sample holder copper block

3) sensor and heater leads

4) solder on terminal for sensor and heater leads

5) sensing current and voltage leads

6) sample

7) resistive heater

8) carbon-glass thermometer embedded in the copper block

3.3.4 A.C. Resistance Bridge

The theories discussed in Chapter 2 predict that the magnetoresistance in Mg.Cu and Mg.Zn metallic glasses is at 6Tesla of the order of $\Delta R/R_{0} \approx 10^{-4}$ which is quite small. For this reason a sensitive 4-terminal a.c. resistance bridge designed by Cochrane, Kästner and Muir⁹³ was used to measure the resistance changes. A circuit diagram is given in Fig.3.14a. The important feature of this circuit is that sample and reference loop are driven by two identical driving transformers, T_1 , T_2 , powered by the same power supply, and coupled by the two transformers T_3 . As pointed out by the authors 9^3 this ensures that the current in the sample loop with respect to the current in the reference loop is stable against sample resistance changes. The circuit can easily detect changes of $5 \cdot 10^{-6} \Omega$ in a 1Ω resistor, however the absolute accuracy is somewhat less. Using an Ortec Brookdeal Ortholoc-SC 9505 two phase lock-in amplifier the in-phase and quadrature part of the signal, which is the difference between the voltage across the sample and the voltage across the Dekatran DT72A (ESI, Portland, Oregon, USA) inductive voltage divider, were measured simultaneously . The quadrature signal was - if necessary - adjusted tozero with a quadrature injector (V in Fig.3.14a). The output voltage of the lock-in amplifier was calibrated by changing the reference voltage across the inductive voltage divider which is proportional to a calibrated resistance change (see Fig.3.14a) AR and reading the resulting output voltage change ΔV , i.e. للمسكم

$$R_{sample} = R_{ref} + \frac{\Delta R}{\Delta V} \cdot V_{lock-in} \qquad (3.5)$$

The calibration was found to be linear over the entire sensitivity range of the lock-in amplifier. The noise on the output voltage of the bridge was reduced by using a time constant of 1 to 3 seconds. The stability of the cutput voltage was mainly determined by temperature fluctuation in the laboratory (air conditioning). On the time scale of a typical magnetoresistance measurement (20min) the resistance reading varied by $3 \times 10^{-6} \Omega$ for a 1 Ω sample. Fig.3.14b shows a block diagram of the entire system.

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Figure 3.14 a) Circuit diagram of the a.c. resistance bridge (taken from reference 93).

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S = sample	Rs = standard resistor
R = lead resistance	I = variable inductance
T = transformer	V = quadrature injector



Figure 3.14 b) Schematic diagram of the a.c resistance bridge and data aquisition system.

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3.3.5 Data Acquisition

All signal voltages - PCB analog output voltage, voltage across standard resistor (proportional to the applied magnetic field), and a.c. resistance bridge output voltage - were sensed with Keithley Instruments Model 175 autoranging digital multimeter (DVM) as is shown schematically in Fig.3.14b. An Apple 2e personal computer read the voltages on all 3 digital voltmeters through IEEE-488 standard interfaces. The time lapse between the readings of the individual multimeters was about 0.7sec which is smaller than the time constant of 1 to 3sec used on the PCB and the a.c. resistance bridge and hence hegligible. From the Apple 2e personal computer the data were transferred to a SUN computer for further processing.

3.3.6 Dilution Refrigerator

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Resistance measurements from 10K to 80mK were carried out on the superconducting Mg.Zn samples in a SHE mini dilution refrigerator. The actual experiment, a copper block with calibrated Ge (1-10K) and SPEER carbon (0.06-1K) resistive thermometers and sample holder screwed onto the block tightly, is attached to the bottom of the refrigeration stage, see Fig.3.15. The refrigeration stage is contained in an evacuated can which is immersed in a ⁴He bath. The top part of the refrigeration stage has a chamber which draws and evaporates ⁴He from the bath and is thus kept at 1K. The cooling of the sample is achieved by continuously (endothermally) diluting ³He in a ⁴He rich liquid in the mixing chamber. For further details refer to Lounasmaa 94 . A major problem in measuring the resistance at low temperatures is to avoid self-heating effects of the sample. Self-heating comes about when the energy dissipated in the sample by the sensing current of the resistance bridge can not be conducted at the same rate into the sample holder (mixing chamber) because of poor thermal conductivity at low. temperatures (the decoupling of the electron gas in the metal from its atomic matrix is comparatively of minor importance for $T \ge 10$ mK). Because the Mg-Zn and particularly Mg.Cu samples are much more brittle than for example Y.Al alloys it was not possible to glue them onto the sample holder using only a very thin

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GE-varnish layer. Instead the samples were stuck with a very thin layer of vacuum grease onto a thin electrically insulating mylar sheet which itself was glued to the sample holder with a thin layer of GE-varnish. Obviously, this way of mounting the samples reduces the thermal conductance between sample and holder so that the a.c. bridge power dissipation had to be kept below 70pWatt which caused an unfortunate reduction of sensitivity. Even with this method there was too much strain on all of the Mg-Cu samples and the $Mg_{70}Zn_{27}Ag_3$ sample so that they broke upon cooling from room temperature to 4.2K. (Note: for the measurements of the magnetoresistance above 1.5K it was not necessary to mount the samples as tightly as they were either immersed directly in the liquid He or in direct contact with the exchange gas). Self-heating effects of the thermometers were avoided by using the SHE potentiometric conductance bridge described in section 3.3.3.

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Figure 3.15 Schematic diagram of the dilution refrigerator.

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4. Results and Analysis

4.1 Introductory Remarks

The temperature and magnetic field dependence of the resistivity of high-purity Mg-Cu and Mg-Zn metallic glasses containing up to 15 atomic percent of Ag and Au was measured between 1.5K and 20K and in fields of up to 5.6T. In two cases, $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$, the resistivity was measured down to 0.1K and 0.08K respectively. Whereas the temperature dependence of the resistivity shows only very little variation from alloy to alloy, the magnetoresistance exhibits a wide range of behavior.

The magnetoresistance measurements, which are to be considered the main topic of the thesis, are presented and discussed in section 4.2. For the sake of clarity, the section is divided into several parts. First, all the magnetoresistance data are presented, and commented on qualitatively, in 4.2.1. This allows the reader to follow the detailed and quantitative discussion of the results on the non-superconducting Mg-Cu glasses in section 4.2.2 and the superconducting Mg-Zn glasses in section 4.2.3. The discussion of the dephasing field B_{d} and the spinorbit scattering field B resulting from the quantitative comparison of the theories of quantum corrections to the conductivity and measured magnetoresistance follows in section 4.2.4. Section 4.2 also contains some comments on magnetoresistance in icosahedral Mg-Zn-Al alloys (section 4.2.6) and in samples doped with magnetic impurities, i.e Mg70^{Zn}29^{Gd}1 and Mg70^{Cu}30(170ppm Mn) (section 4.2.5). The chapter is completed by a section (4.3) on the temperature dependence of the resistivity below 20K in Mg-based metallic glasses.

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4.2 Magnetoresistance

4.2.1 Experimental Data

The main experimental results of this thesis, the measurements of the magnetoresistance up to 5.6T in eleven $Mg_{70}Cu_{30}$ and $Mg_{70}Zn_{30}$ metallic glasses with Cu and Zn partially substituted by Ag and Au, are shown in Fig.4.1a-k. Each set of measurements was taken at 9 different temperatures ranging between 1.5K and 20K, with the exception of $Mg_{70}Cu_{29.9}Au_{0.1}$ and $Mg_{70}Cu_{24}Ag_6$, for which no measurements were taken below 4.2K.

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The figures exhibit several prominent characteristics. First the absolute size of the magnetoresistance, i.e $\Delta\rho/\rho \approx 10^{-4}$, which is many orders of magnitude larger than the normal, orbital magnetoresistance resulting from the Lorentz force on electrons.

The size of the magnetoresistance decays with increasing temperature in all alloys studied. This is consistent with the progressive destruction of quantum interference by the increase of inelastic electron-phonon (and to lesser extent electron-electron) scattering with temperature. Comparison of Fig.4.1a-k with Fig.2.6 shows that the measured magnetoresistance curves are qualitatively the same as the theoretical weak localization magnetoresistance. An approximate value of the dephasing field B_{ϕ} (defined in eq.2.24) may be found by direct comparison of the low field ($\hat{\mathfrak{A}} \leq 0.4T$) behavior of the data in Fig.4.1 and the theoretical curves in Fig.2.6a (specifically compare Fig.4.1a,b with Fig.2.6a and Fig.4.1g,h with Fig.2.6b).

The sign and size of the magnetoresistance curves in Fig.4.1a-k depend strongly on the Ag or Au concentration in the alloy. The magnetoresistance becomes more positive as the heavy metal concentration is increased. This is shown more clearly in Fig.4.2, where the magnetoresistance of several different alloys at one temperature (6K) is plotted. As expected from the discussion of weak localization in Chapter 2.2, the magnetoresistance is positive in all alloys at small fields ($B \approx 0.4T$). This is due to a finite spin-orbit scattering even in those alloys without Ag and Au. An approximate value for B_{so} may be found by

direct comparison of Fig4.2 with Fig.2.6c. In the alloys with weak spin-orbit scattering the magnetoresistance eventually changes sign at larger fields, e.g. at 0.8T for $Mg_{70}Cu_{30}$ as shown in Fig.4.2, and approaches an approximately $-\sqrt{B}$ high field asymptotic behavior, as was anticipated from the discussion of the form of f_3 at large fields (eq.2.27 in Chapter 2.2). The asymptotic regime is not reached in stronger spin-orbit scattering alloys in the accessible field range. With increasing Ag and Au content, the size of the magnetoresistance maximum observed at about 0.4T in $Mg_{70}Cu_{30}$ and $Mg_{70}Zn_{30}$ increases, and its position shifts to larger fields, again reflecting the increase of spin-orbit scattering[†].

At first sight the magnetoresistance of Mg-Zn glasses looks very similar to the magnetoresistance observed in Mg-Cu glasses. However, as will be shown later, there are in fact significant differences between the two,resulting from superconductivity.

Having seen from Fig.4.1 and Fig.4.2 that the characteristics of the measured magnetoresistance agree qualitatively with the predictions for weak localization, we can now compare theory and experiment quantitatively. We begin by analysing the data from Mg-Cu based glasses because they are not superconducting.

†) Bieri et al.³² measure a magnetoresistance maximum in $Mg_{80}Cu_{20}$ a factor of 20 smaller than observed in $Mg_{70}Cu_{30}$ here. We attribute this (see section 4.2.5) to magnetic impurities, which underscores the importance of using high purity materials.

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Figure 4.1 a) Normalized magnetoresistance of Mg₇₀Cu₃₀. The scale and the temperatures (in Kelvin) are indicated in the figure. The (solid and dashed) lines are the best fits to the weak localization theory as explained in the text.



Figure 4.1 b) Normalized magnetoresistance of Mg70^{Cu}27^{Ag}3. The scale and the temperatures (in Kelvin) are indicated in the figure. The (solid and dashed) lines are the best fits to the weak localization theory as explained in the text.

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 1 d) Normalized magnetoresistance of Mg₇₀Cu₁₅Ag₁₅. The scale and the temperatures (in Kelvin) are indicated in the figure. The (solid and dashed)
lines are the best fits to the weak localization theory as explained in the text.











Figure 4.1 g) Normalized magnetoresistance of Mg₇₀Cu₂₇Au₃. The scale and the temperatures (in Kelvin) are indicated in the figure. The (solid and dashed) lines are the best fits to the weak localization theory as explained in the text.





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Figure 4.1 i) Normalized magnetoresistance of Mg₇₀^{Zn}₃₀ fitted to the weak localization theory (line). The scale and the temperatures (in Kelvin) are indicated in the figure.

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Figure 4.1 j) Normalized magnetoresistance of Mg₇₀Zn₂₇Ag₃ fitted to the weak localization theory (line). The scale and the temperatures (in Kelvin) are indicated in the figure.

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Figure 4.1 k) Normalized magnetoresistance of Mg₇₀Zn₂₇Au₃ fitted to the weak localization theory (line). The scale and the temperatures (in Kelvin) are indicated in the figure.



Figure 4.2 Normalized magnetoresistance of several Mg-Cu based glasses at 6K. The scale and the alloy compositions are indicated in the figure. The (solid and dashed) lines are the best fits to the weak localization theory as explained in the text.

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4.2.2 Mg-Cu Metallic Glasses

(a) Low Field Range

We begin the discussion of the magnetoresistance by restricting the analysis to the low field behavior. Low field here means $B/T \le 0.4TK^{-1}$. In this range the contribution to the magnetoresistance from enhanced electron-electron interactions is very small as may be seen from Fig.2.11 (less than $\Delta p/p \approx 2 \cdot 10^{-5}$) so that, in Mg-Cu, the experimental magnetoresistance may be analysed by considering only the contribution from weak localization. This simplification allows us to test the validity of the weak localization theory separately from complicating contributions of enhanced electron-electron interactions[†].

The fitting procedure is as follows: First the data are fitted by a least-squares method, with both B_{SO} and B_{ϕ} treated as the <u>only</u> adjustable parameters (all other parameters are known, as was discussed earlier in Chapter 2.6). The resulting values for the temperature independent spin-orbit scattering field B_{SO} had a scatter of less than 10% in the weak and less than 20% in the strong spin-orbit scattering system over the 9 measured temperatures. The average of B_{SO} is listed in Table 4.1. Since the spin-orbit scattering is known to be temperature independent, we then carried out a second least-squares fit, fixing B_{SO} at the average of the values obtained in the first fits and allowing only B_{ϕ} to vary with temperature. Thus, in this second fit B_{ϕ} is the <u>only</u> adjustable parameter. The resulting values for B_{ϕ} and B_{SO} will be discussed in section 4.2.4.

†) A similar approach has been taken by Bergmann to examine the validity of the weak localization theory in two dimensional thin Mg,Cu,Ag,Au films ^{24,95,122}. In fact Bergmann restricted the field range at lower temperatures even more severely, using a limit $B/T^2 \leq 0.008TK^{-2}$ (which is equivalent in those systems to $B/B_1 \leq \text{const}$). This restriction is too severe in bulk Mg-Cu glasses; it would prevent a meaningful fit since the overall magnetoresistance is too small to allow a precise determination of the parameters B_{\pm} and B_{\pm} .

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This fitting procedure was adopted because it eliminates small correlation effects between the two parameters B_{ϕ} and B_{so}^{\dagger} .

The fits resulting from the least-squares analysis described above are shown as solid lines in Fig.4.1a-k (the extrapolation of the curves beyond the fitted field regime, $B/T \leq 0.4TK^{-1}$, is shown as dashed lines). For clearer demonstration of the quality of the fits, some representative graphs are plotted again in Fig.4.3a-c where the ordinate has been changed to B/T. Generally the theoretical solid line agrees very well with the measured data in the fitted regime. At higher temperatures, $T \geq 10K$, especially in alloys with larger spin-orbit scattering, the fit slightly overestimates the data at low fields ($B \approx 1T$) and underestimates it at higher fields ($B \approx 5T$). This is partly due to the neglect of the electron-electron interaction effects and may be partially removed if the Cooper and diffusion channel terms are included. At lower temperatures, $T \leq 6K$, the fit falls fight onto the data for the fitted regime (solid line).

We conclude that the weak localization theory describes the magnetoresistance in Mg-Cu based glasses very well in the regime where it alone contributes (B/T ≤ 0.4 TK⁻¹). Bieri and coworkers³² reported a similar agreement in Cu₅₀Y₅₀; however their result is not valid since they had to assume a value for the resistivity prefactor (see eq.2.23 and eq.2.24) 50% larger than the measured resistivity. It has to be stressed that the analysis here employed essentially only one adjustable parameter (B₀) and only the measured value of ρ without any scale factors. Our work is therefore the first rigorous test of the validity of the weak localization theory in bulk metallic glasses.

+) Our method of determining B is different from Bergmann's 24,95,122 . In the bulk Mg-Cu glasses studied here, the relative sizes of B and B so are such that his method is not appropriate for all alloys. 0



Figure 4.3 a) Normalized magnetoresistance of Mg₇₀Cu₃₀ against B/T fitted to the weak localization theory (line). The scale and the temperatures (in Kelvin) are indicated in the figure.

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Figure 4.3 b) Normalized magnetoresistance of Mg₇₀Cu₁₅Ag₁₅ against B/T fitted to the weak localization theory (line). The scale and the temperatures (in Kelvin) are indicated in the figure.

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Figure 4.3 c) Normalized magnetoresistance of $Mg_{70}Cu_{27}^{4}Au_{3}$ against B/T fitted to the weak localization theory (line). The scale and the temperatures (in Kelvin) are indicated in the figure.

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(b) Full Field Range

We now turn our attention to the magnetoresistance data over the full field range. Since the two unknown parameters, B_{ϕ} and B_{so} , were uniquely determined by the low field fit discussed above (section 4.2.2a), we can use them to extrapolate the magnetoresistance contribution of the weak localization effect beyond the field limit $B/T = 0.4TK^{-1}$. The extrapolations are shown as dashed lines in the figures Fig.4.1a-k, Fig.4.2 and Fig.4.3a-c. One can see at once that the weak localization theory overestimates the measured data below 6K and that the difference increases as the temperature decreases. (Small temperature variations due to the small magnetoresistance of the carbon-glass thermometer cannot be the cause of this difference; the resistivity temperature dependence is so small that they cause a variation of the magnetoresistance signal smaller than the noise level of the resistance bridge.) At first glance it might be supposed that this difference could be made up by including the contributions from enhanced electron-electron interactions. That this is not the case however is shown by the fact that these contributions are all positive in Mg-Cu alloys (see eq.2.29 and eq.2.32). With a total contribution of $\Delta \rho / \rho \approx 4 \cdot 10^{-5}$ at full field and 1.5K (about 30% of the total magnetoresistance), they would significantly increase the deviation between theory and experimental data.

If, as an alternative procedure, we fit the data over the entire measured field range simultaneously to <u>all</u> quantum corrections to the magnetoresistance, one finds that the high field deviation is reduced but that this reduction is achieved at the expense of a poor fit at low fields. An example of such a fit is shown in Fig.4.4 for $Mg_{70}Cu_{30}$. Again, the dots are the measured data and the solid line the calculated fit. Though reproducing the data above T=6K equally well as the previous method (as expected), the fit completely misses the low field experimental data at temperatures below 6K, and this discrepancy is outside the acceptable range.

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^{Mg}70^{Cu}30 ι 10⁻⁴ 1.5 ∆ P/P 2.Q 3.0 3.6 6.0 10 WL + EEI 15 full field fit 20 2 3 σ 5 ý 1 4 6 B (T)

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It should also be stressed that the deviations cannot be explained by including magnetic impurity effects. Taking a conduction-electron local-moment exchange of $J = -0.25 \text{eV}^{56,57}$ the concentration of Mn in the alloys is too small to make a significant contribution to the magnetoresistance (eq.2.39), although such a combination would be of the right sign.

We therefore conclude that, even in the simplest bulk amorphous alloys, the observed magnetoresistance can not be accounted for quantitatively over the entire field and temperature range by current theories of quantum corrections to the conductivity.

Observations similar to ours have been reported by other workers for more complicated amorphous alloys; Olivier et al.²⁷ for Y-Al alloys, Bieri et al.³² in $Cu_{50}^{9}Y_{50}$ and other alloys, and Schulte²⁹ in the system Cu-Zr. Although these authors cannot definitively ascribe the discrepancies to a failure of the quantum correction theories, their observations lend support to this conclusion^{†)}.

Exactly where the theories of quantum corrections to the conductivity fail is not clear but one important point to consider is that at very large magnetic fields, where the magnetic dephasing time $\tau_{\rm H}$ (see Chapter 2.2) becomes comparable to the elastic scattering time (B \approx 400T), the quantum correction magnetoresistances must saturate, because the the constructive quantum interference is then destroyed^{††}).

†) Deviations between the weak localization and the measured magnetoresistance have also been found in a 2D system; in one report on thin Cu films²⁴ Bergmann shows fit and data outside the restricted field regime, $B/T^2 \leq 0.008TK^{-2}$, and some discrepancies are apparent. It is not clear if they can be explained by the enhanced electron-electron interaction contributions to the magnetoresistance and the author does not comment on this aspect.

††) The Aronov-Bohm effect²⁰ has shown that quantum corrections to the conductivity cause an oscillatory magnetoresistance in thin metal rings. In bulk amorphous metals one averages however over many such rings (Fig.2.2) so that the magnetoresistance assumes a mean value. None of the expressions given in Chapter 2 reflect this constraint, but we do not know whether the influence of this saturation should be felt in the magnetic field range used here.

A further point, made by Isawa⁹⁶, is that at large fields the weak localization magnetoresistance is overestimated by eq.2.23 and 2.24 because the diffusion cut-off, q_0 , was set to infinity to facilitate their derivation. However, on examining Isawa's calculation in detail, generalising it to finite spin-orbit scattering, we find only a negligible difference in the weak localization magnetoresistance (<0.1%) between the two extreme cases $q_0 = \infty$ and $q_0 = 1/\sqrt{D\tau_e}$.

Some of the discrepancies at large fields may be caused by expression, eq.2.32, for the Cooper channel magnetoresistance. It was mentioned in Chapter 2.3 that the exact magnetic field dependence of the electron coupling, g(B,T), is not known exactly. The expression given for g(B,T) in Chapter 2.3 is only, what Altshuler and Aronov call, "logarithmically correct"²⁰; higher order terms in B/T have been neglected. It is not known to what extent they alter the Cooper channel magnetoresistance in the field and temperature range considered here. Unfortunately the Cooper channel magnetoresistance cannot be experimentally isolated to reveal any possible inaccuracies.

The diffusion channel magnetoresistance is an unlikely source of, the discrepancies observed at large fields. It was shown recently by Trudeau and Cochrane⁵⁸ that the diffusion channel and weak localization expressions (eq.2.29 and eq.2.23) give an excellent description of the magnetoresistance (for B < 5T and 4K <T <77K) in the paramagnetic composition range of amorphous Fe-Zr alloys where their contributions are unusually large due to the Stoner enhancement of the Zeeman splitting (i.e 2.3 < $(1-\bar{I})^{-1}$ < 9.1. The Cooper channel magnetoresistance is negligible in these alloys, it contributes less than 5%). Therefore, the diffusion channel magnetoresistance is presumably also well described by eq.2.29 in the present Mg-based alloys where it is not enhanced $((1-\bar{I})^{-1} = 0)$. Whether this is also true at temperatures below 4.2K is not known, but we note that even at 1.5K its contribution is very small (according to eq.2.29 $\Delta \rho/\rho \approx 2 \times 10^{-5}$).

Whether the quantum correction expressions given in Chapter 2 have limitations other than those discussed above, is beyond our present knowledge.

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4.2.3 Mg-Zn Metallic Glasses

(a) Magnetoresistance due to Superconducting Fluctuation

The failure of the theories of quantum corrections to the conductivity in Mg-Cu complicates the interpretation of the magnetoresistance of Mg-Zn, where there are the additional contributions due to superconductivity. We therefore adopt a different approach to these data and begin by isolating the influence of superconductivity.

We do this by analysing the <u>difference</u> between the alloys Mg₇₀Cu₃₀ and Mg₇₀Zn₃₀, Mg₇₀Cu₂₇Ag₃ and Mg₇₀Zn₂₇Ag₃, and Mg₇₀Cu₂₇Au₃ and Mg₇₀Zn₂₇Au₃. We assume, and later justify (see section 4.2.4 and Table 4.1), that the dephasing field, B_φ, and the spin-orbit scattering field, B_{so}, have the same behavior in the two alloy systems Mg-Cu and Mg-Zn. Therefore, the difference in the magnetoresistance between the respective alloys reflects <u>only</u> contributions from the Cooper channel and the Maki-Thompson superconducting fluctuation magnetoresistance (eq.2.34). The weak localization and diffusion channel magnetoresistance cancels. Symbolically this can be written as

$$\left(\frac{\delta\rho}{\rho}\right)_{Mg-Zn} - \left(\frac{\delta\rho}{\rho}\right)_{Mg-Cu} = \left(\frac{\delta\rho}{\rho}\right)_{Mg-Zn}^{M-T} + \left(\frac{\delta\rho}{\rho}\right)_{Mg-Zn}^{CC} - \left(\frac{\delta\rho}{\rho}\right)_{Mg-Cu}^{CC}$$
(4.1)

The differences are plotted in Fig.4.5a-c. The data show immediately that there are indeed contributions from both superconducting fluctuations and the Cooper channel. At low temperatures and at low fields (B \leq 0.5), where the Cooper channel contributions vanish, there is still a substantial positive difference in the magnetoresistance, which we attribute to the positive magnetoresistance due to superconducting fluctuations. At higher fields the slope of the magnetoresistance changes sign (see Fig.4.5a). This cannot result from superconducting fluctuations but is consistent with contributions of the Cooper channel whose difference we expect, from the stronger attractive electron coupling (g(B,T) in eq.2.30) in Mg-Zn, to be negative. We therefore fit the data in Fig.4.5a-c to contributions from the Cooper

channel (eq.2.32) and superconducting fluctuations (eq.2.35). To calculate the latter contribution we use (i) the values of B_{ϕ} found earlier for Mg-Cu alloys (see eq.4.2 in section 4.2.4) and (ii) values for the Maki-Thompson parameter, β , given in the appendix A.4 (see also Fig.2.13). The fits are shown as solid lines in Fig.4.5a·c in the regime of validity of eq.2.35, i.e $B \leq (k_BT/4eD)\ln(T/T_C) \approx 0.2TK^{-1}$, and as dashed lines beyond. For clearer demonstration of the superconducting fluctuation magnetoresistance we have subtracted in Fig.4.6a·c the calculated Cooper channel part from the difference curves in Fig.4.5a-c and compared it directly to eq.2.35. Considering the fact that <u>no</u> adjustable parameters were used to generate the theoretical curves and considering the limited range of validity of eq.2.35, i.e B/T = 0.2T/K the figures Fig.4.5 and Fig.4.6 demonstrate a remarkable agreement between experiment and theory.

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We thus conclude that Larkin's expression for the Maki-Thompson superconducting fluctuation magnetoresistance in eq.2.35 is correct within its quoted limits, i.e $B_{,B_{\phi}} \leq (k_{B}T/4eD)\ln(T/T_{c}) \approx 0.2TK^{-1}$. Beyond this limit we can only say that the negative slope of the difference curves at 1.5K and B > 3T in Fig.4.5a,b indicates that the Cooper channel is indeed negative in Mg-Zn and positive in Mg-Cu provided that there are no additional magnetoresistance contibutions other than considered here. Unless the limitation on the superconducting fluctuation magnetoresistance expression is removed no further definite conclusions on the the validity of the Cooper channel expression in eq.2.32 can be made. The origin of the discrepancies between theory and experiment observed in Mg-Cu glasses still remains unsolved.



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and Mg₇₀Cu₂₇Au₃. The scale and the temperatures (in Kelvin) are indicated in the figure. The meaning of the solid line is explained in the text (see eq.4.1).

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The scale and the temperatures (in Kelvin) are indicated in the figure. The meaning of the solid line is explained in the text (see eq.4.1).

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Figure 4.5 c) Difference of the magnetoresistance in $Mg_{70}^{2n}27^{Ag}$ and $Mg_{70}^{Cu}27^{Ag}3$.

The scale and the temperatures (in Kelvin) are indicated in the figure. The meaning of the solid line is explained in the text (see eq.4.1).

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Figure 4.6 a) The superconducting fluctuation magnetoresistance

in $Mg_{70}Zn_{27}Au_3$. The scale and the temperatures (in Kelvin) are indicated in the figure. The solid line is calculated according to eq.2.35.



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Figure 4.6 b) The superconducting fluctuation magnetoresistance in $Mg_{70}Zn_{30}$. The scale and the temperatures (in Kelvin) are indicated in the figure. The solid line is calculated according to eq.2.35.

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Figure 4.6 c) The superconducting fluctuation magnetoresistance in $Mg_{70}Zn_{27}Ag_3$.

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The scale and the temperatures (in Kelvin) are indicated in the figure. The solid line is calculated according to eq.2.35.

(b) Low Field Range

With the validity of the Maki-Thompson magnetoresistance in eq.2.35 established at low field, we can now analyse the magnetoresistance data of the Mg-Zn alloys in the same way as in the Mg-Cu alloys. The result is shown in Fig.4.7a-c (the ordinate has been changed to B/T for better comparison of theory and experiment). Over the fitted range, $B/T \leq 0.2TK^{-1}$, the agreement is excellent, with the possible exception of the measurements at 20K in $Mg_{70}Zn_{27}Au_3$. The values of B_{ϕ} and B_{so} found for Mg-Zn glasses will be discussed with those obtained for Mg-Cu in the following section 4.2.4. Beyond the field range considered, the experimental data are severely overestimated by the weak localization and Maki-Thomson terms. The negative Cooper channel magnetoresistance cannot account for the gap. Thus, once again, we find that at high fields the quantum correction theories break down.

There is another aspect of the magnetoresiatance in Mg-Cu and Mg-Zn glasses worth noting. On the scale of the figures Fig.4.1a-k the low field ($B << B_{\phi}$) B^2 regime is not resolved. To investigate this regime we have carried out very high resolved. To investigate this regime Mg₇₀Zn₂₇Ag₃, at 1.5K and 4.2K up to 40mT only. The results are shown in Fig.4.8a,b. Also shown in the figures are the corresponding data and fits from Fig.4.7b. They compare well. The value of B_{ϕ} is indicated in the Fig.4.8a,b and we conclude that the experimental resolution is not high enough to resolve B^2 variation at temperatures this low.

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1.5 • 2.0 3.0 •3.6 ∆P/P 4.2 • •6.0 • 10 15 -4 20 10 Mg₇₀Zn₃₀ 0.3 0.4 0.2 0.1 0.5 0.0 0 B/T (T/K)

> Figure 4.7 a) The normalized magnetoresistance in $Mg_{70}^{2n}_{30}$ against B/T, fitted to the weak localization and superconducting fluctuation theory (line). The scale and temperatures (in Kelvin) are indicated in the figure.

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1.5 2.0 •3.0 •3.6 Δ P/P 4.2 6.0 10 15 20 10⁻⁴ Mg₇₀Zn₂₇Ag₃ 0.4 0.1 0.2 0.3 0.0 0.5 B/T (T/K)

Figure 4.7 b) The normalized magnetoresistance in Mg₇₀Zn₂₇Ag₃ against B/T, fitted to the weak localization and superconducting fluctuation theory (line). The scale and temperatures (in Kelvin) are indicated in the figure.

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Figure 4.7 c) The normalized magnetoresistance in Mg₇₀²ⁿ₂₇^{Au}₃ against B/T, fitted to the weak localization and superconducting fluctuation theory (line). The scale and temperatures (in Kelvin) are indicated in the figure.

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Figure 4.8 a) The low field magnetoresistance in Mg₇₀Zn₂₇Ag₃ (o) at 4.22. The scale is indicated in the figure. The solid line is the best fit to eq.2.23 and eq.2.35 as explained in the text. The closed circles (•) are the data of Fig.4.7b.

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Figure 4.8 b) The low field magnetoresistance in $Mg_{70}Zn_{27}Ag_3$ (o) at 1.5K. The scale is indicated in the figure. The solid line is the best fit to eq.2.23 and eq.2.35 as explained in the text. The closed circles (•) are the data of Fig.4.7b.

4.2.4 The Spin-Orbit Scattering Field B and the Dephasing Field B

In the previous two sections it was shown that for $B/T \le 0.4TK^{-1}$ the weak localization quantum interference theory (and, to the extent they contribute, the enhanced electron electron interaction theory) give an excellent description of the experimental magnetoresistance in the Mg-Cu metallic glasses and also in Mg-Zn metallic glasses if the superconducting fluctuation magnetoresistance is included. We now turn our attention to the two parameters, the spin-orbit scattering field B so and the dephasing field B which resulted from the analysis in the previous two sections.

(a) The Spin-Orbit Scattering Field B

The values for B_{SO} which resulted from the analysis in the previous two sections are listed in Table 4.1. As was expected the spin-orbit scattering fields in corresponding Mg-Cu and Mg-Zn alloys are identical within the quoted errors (10% in the weak and 20% in the strong spin-orbit scattering regime). This reinforces the consistency of our analysis. One can also see from Table 4.1 that B_{SO} increases with increasing Ag and Au content, and that the rate of increase with Au is much greater than for Ag, as expected.

In Fig.4.9 spin-orbit scattering rate, $1/\tau_{so} = 4eDB_{so}/h$, is plotted against Au and Ag concentration. The background spin-orbit scattering rate of the Mg₇₀Cu₃₀ matrix (0.32×10¹² sec⁻¹) has been subtracted. The solid line is a guide to the eye. From the linear dependence of the spin-orbit scattering Hamiltonian in Z, Z being the atomic number, we expect $1/\tau_{so}$ to scale as 2^8 if atomic orbital wave functions are assumed^{97,55}. However the slopes of the lines connecting the points in Fig.4.9 differ by a factor of 19 for small concentrations which is close to 2^6 , i.e $(Z_{Au}/Z_{Ag})^6 = 23$. We have no explanation for this weaker dependence on Z, except to say that it probably reflects the screening of the ionic charge. Shown in the insert of Fig.4.9 are results for $1/\tau_{so}$ obtained by Bergmann⁹⁵ on thin Mg films covered with

Table 4.1

Alloy	B _{so}	'so	L _{so}	те	1 _e
Mg ₇₀ ^{Cu} 30	77	3.1	46	0.81	1.3
Mg ₇₀ Cu ₂₇ Ag ₃	166	1.5	32	0.81	1.3
Mg ₇₀ Cu ₂₄ Ag ₆	242	1.1	26	0.77	1 [.] .2
$Mg_{70}Cu_{15}Ag_{15}$	409	0.69	20	0.69	1.1
$Mg_{70}Cu_{29.9}Au_{0.1}$	145	1.8	34	0.71	1.2
Mg ₇₀ ^{Cu} 28.5 ^{Au} 1.5	851	0.32	14	0.81	1.1
$Mg_{70}Cu_{27}Au_{3}$	1190	0.23	12	0.69	1.1
$Mg_{70}Cu_{21}Au_{9}$	1710	0.18	10	0.62	1.0
Mg ₇₀ ^{Zn} 30	75	3.7	47	0.65	1.1
$Mg_{70}Zn_{27}Ag_3$	151	2.0	33	0.58	1.0
$Mg_{70}Zn_{27}Au_{3}$	1030	0.30	13	0.57	1.0
$Mg_{70}Zn_{20}Gd_1$	110	2.7	39	0.61	1.0
$Mg_{40}Al_{30}Zn_{30}$	110				
$Mg_{A0}Al_{10}Zn_{A2}$	170				

Note : $\tau_{so} = \hbar/4eDB_{so}$, $L_{so} = \sqrt{D\tau_{so}}$, $l_e = v_F \tau_e$ Units: B_{so} in mT, τ_{so} in $10^{-12}sec$, L_{so} in $10^{-9}m$ τ_e in $10^{-15}sec$, l_e in $10^{-9}m$

Error: follows from those quoted for B and ρ in the text so

The dephasing fields, times and lengths can be calculated for all amorphous Mg-based alloys by eq.4.2 with the coefficients given in the text. For $Mg_{70}Cu_{30}$ this yields at 4.2K:

 $B_{\phi} = (4 \pm 2)mT$, $\tau_{\phi} = (75 \pm 35) \times 10^{-12} sec and L_{\phi} = (0.21 \pm 0.07) \mu m$.

fractional layers of Au. For the purpose of comparison the Au layer fractions have been converted into atomic concentrations assuming perfect dense packing of the Mg host. The value of $1/\tau_{so}$ for the alloy $Mg_{70}Cu_{29.9}Au_{0.1}$ is within the quoted error margins of Bergmann's data once the background spin-orbit scattering rate of the Mg-Cu matrix is subtracted.

We can also see in Fig.4.9 that $1/\tau_{so}(x)$ deviates at larger concentrations from the linear dependence observed for small concentrations; the values fall below the linear extrapolation. The cause of this deviation is not clear but the behavior is consistent with observations of Peters and coworkers⁹⁸ who quote a spin-orbit scattering rate of $1.2 \times 10^{13} \text{sec}^{-1}$ (B_{so} = 1.4T) for thin pure Au films, which implies that the strictly linear dependence of $1/\tau_{so}$ in Au covered Mg films (shown in the insert of Fig.4.9) would have to show the same deviations as the present Mg-Cu-Au system at higher concentrations (the slope of $1/\tau_{so}$ in the insert is $2.6 \times 10^{12} \text{sec}^{-1}$ per atomic percent Au). Also, in the derivation of the weak localization magnetoresistance for three dimensional conductors, Fukuyama and Hoshino⁴⁹ explicitly assume that the characteristic spin-orbit scattering time, τ_{so} , is much longer than the elastic scattering time, τ_e . Even though this condition is fulfilled, $\tau_{so} \approx (5/x) \times 10^{-13} \text{ sec}$ (x is the Au concentration in atomic percent) and $\tau_{a} \approx 7 \times 10^{-16}$ sec, it is not clear where the perturbation expansion in $\tau_e^{\tau_{so}}$ breaks down. In the $Mg_{70}Cu_{21}Au_9$ sample there is an Au atom in essentially every second nearest neighbor shell and correlations between the spin-orbit scatterings cannot be ruled out. As a consequence of the non-linearity of $1/\tau_{so}(x)$ one has to be very careful when one compares specific spin-orbit scattering rates of a particular elements since the spin-orbit scattering rate at large concentrations is an effective scattering rate which can no longer be normalized by the concentration. Thus, comparisons between specific spin-orbit scattering rates of elements are only meaningful if they are measured at the same dilution in a weak spin-orbit scattering matrix.

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Figure 4.9 The spin-orbit scattering rate in $Mg_{70}Cu_{30-x}Y_x$, Y = Ag, Au, as a function of concentration x. The solid lines are guides to the eye. The insert compares data in $Mg_{70}Cu_{29.9}Au_{0.1}$ (•) and in Au covered Mg films (o) by Bergmann⁹⁵.

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(b) The dephasing strength B_{\star}

Fig.4.10 shows the values of B_{ϕ} for $Mg_{70}Cu_{30}$, $Mg_{70}Cu_{27}Ag_{3}$ and $Mg_{70}Cu_{27}Au_{3}$, and $Mg_{70}Zn_{30}$ as representatives for the Mg-Cu and Mg-Zn glasses. Other samples show essentially the same behavior but for clarity are not included in the figure. Their magnitudes agree within the scatter of the data and demonstrate again the internal consistency of the analysis.

The scatter of the data is a result of small variations in the a.c. resistance bridge gain and signal (due to e.g temperature changes in the electronics) and the error on the absolute sample resistivity at 4.2K. They cause a mismatch between the true magnetoresistance signal and the resistivity prefactor ρ (common to all expressions of quantum corrections to the conductivity) of up to 7%. In the least-squares fits the mismatch is compensated by changes in B_{ϕ} which become larger with decreasing temperature where the weak localization magnetoresistance expression is less sensitive (see Fig.2.6a,b). In two dimensional systems or transition metal alloys the curves of B_{ϕ} against T are usually much smoother because the size of the measured magnetoresistance signal is at least a factor 3, and in some cases two orders of magnitude, larger (see Fig.1.5b).

For all alloys B_{ϕ} decreases sharply with temperature between 20K and 4.2K but then saturates at lower temperatures. The data of Fig.4.10 are well described[†]) by an expression of the form

$$B_{\phi} = B_{\phi}^{0} + A \cdot T^{n}$$
(4.2)

where $B_{d}^{0} = (2.7 \pm 0.4) \text{ mT}$, $n = (3 \pm 0.5)$ and $\ln(A) = (-11.3 \pm 1.3)$

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†) To provide equal weight to all the fitted points, their logarithm was fitted by the logarithm of the above equation. These values were used in section 4.2.3 when the superconducting fluctuation magnetoresistance was compared to the magnetoresistance difference in Mg-Cu and Mg-Zn alloys.

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Figure 4.10 The dephasing field B_{ϕ} against temperature. The solid line is the best fit to eq.4.2.

The strong dependence of B_{ϕ} on temperature is in essential agreement with previous studies, although the exponent n=3, however, is somewhat larger. Bergmann finds n=2 for Mg thin films¹⁹, as do Abraham and Rosenbaum⁹⁹ in thin Cu films, and Olivier et al.²⁷ in Y-AL glasses. Bieri et al.^{25,32} find a T² variation in $Cu_{50}Y_{50}$ and $Cu_{57}Zr_{43}$, in $Cu_{50}Lu_{50}$ however they report T³. Also Hickey and coworkers¹⁰⁰ find a T³ law in Cu-Ti-Au glasses above 8K over a wide range of composition. Schulte and Fritsch¹⁰¹ point out that the exponent can vary between 2 and 3 in Cu-Ti glasses depending on the value of B_{so} assumed in the fit. Theoretically there is also some confusion about the correct value of n. Takayama⁵¹ has calculated that the dephasing rate due to inelastic electron-phonon scattering should vary as T^2 (eq.2.19). Chakravartry and Schmid⁴⁵ recently presented another detailed calculation on the electron-phonon dephasing rate and find that the power law can range between T^2 and T^4 , depending on the transverse and longitudinal velocity of sound and the electron mean free path. In fact, using their expression and values estimated by Hafner¹⁰² for the velocity of sound for Mg₇₀Zn₃₀, one calculates dephasing rates of the right order of magnitude. Unfortunately, exact measurements of the velocity of sound in Mg-Cu and Mg-Zn alloys have not been made so that a more precise comparison is not possible. The temperature dependence of the dephasing rate due to electron-electron scattering is predicted to be T² or weaker (see eq.2.20), its magnitude is however two orders of magnitude smaller than the rates we find here. We can conclude that in the glasses studied here the dephasing of the quantum interference effects above 4.2K is presumably caused by inelastic electron-phonon scattering (as has been generally assumed).

On the other hand, the saturation of B_{ϕ} at lower temperatures is unexpected. Though such a saturation has been observed in many other systems, authors have invariably ascribed it to extraneous causes such as scattering by residual magnetic impurities¹⁰³, decoupling of the electron gas from the thermal bath¹⁰⁴, or scattering by paramagnetic surface states¹⁰⁵. In our alloys none of these explanations is valid.

It was already mentioned before that the inclusion of magnetic ,

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impurities into the analysis leaves the quality of the fit unaltered. We know from measurements by Bergmann¹⁰⁶ that the spin scattering rate $1/\tau$ of Fe impurities buried in bulk amorphous Mg is approximately $6 \times 10^7 \text{ sec}^{-1}$ per ppm. The dephasing field $B_{\phi}^0 = 2B_g$ (see eq.2.24) due to the 3ppm of Fe our alloys may contain (see Chapter 3.2.5) is therefore expected not to exceed 0.12mT which is 20 times smaller than observed saturation value of B_{ϕ} . Possible Fe impurities on the surface are of little importance since the thickness of the samples is several times the inelastic diffusion lengths. Also, from the measured Mn impurity concentration in our samples (see Table 3.4) one would expect \Re dephasing field of 2.2mT in the dirtiest sample but only of 0.08mT in the cleanest sample which is more than an order of magnitude smaller than what is observed (a value of J = -0.25eV was assumed for the spin exchange integral, see Chapter 2.5 and references 56,57).

Thermal decoupling of the electron gas from the thermal bath (lattice or sample holder) at temperatures higher than 1.5K has to be ruled out as well. Bergmann¹⁰⁷ has shown that the electron gas can only be overheated in Au films when the current densities exceed $1.7 \times 10^{+9} \text{A/m}^2$ at 4.2K. In the present measurements of the magnetoresistance above 1.5K the current densities were always smaller than $2.5 \times 10^{+5} \text{A/m}^2$, besides, the samples were immersed directly in the liquid He for measurements below 4.2K. Also, any scattering by paramagnetic surface states can be ruled out; it is difficult to imagine that surface effects in samples several inelastic diffusion lengths thick (see Table 4.1 and Chapter 3.1) can influence the bulk transport properties so drastically. We conclude that the saturation of B₀ observed in Mg-Cu and Mg-Zn glasses here is intrinsic.

A universal explanation for the low temperature saturation of the dephasing was proposed recently by Kumar, Baxter, Richter and Strom-Olsen¹⁰⁸. It is based on the idea that virtual phonon exchange could lead to dephasing by independently changing the phase of the two complementary electron paths (see Fig.2.2) even though the final energy of the electrons is unchanged. Using a semi-classical picture a qualitative estimate for the effect was given¹⁰⁸. The point of the argument is as follows: weak localization arises from two electrons traversing the diffusion loop in Fig.2.2 (redrawn in Fig.4.11a) in opposite directions and interfering in the region of the point 0.

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Figure 4.11 a) Coherent backscattering from a pair of time-reversed complementary paths, shown as Boltzmannian trajectories. Each scatterer is assumed to be executing zero-point motion leading to positional dispersion as indicated at one site in the figure.



Figure 4.11 b) Path length difference due to motion of one of the scatterers in Fig.4.11a.

- It was commonly assumed that a dephasing of the interference can only be achieved by thermal vibrations of the ions and subsequent inelastic electron-phonon scattering (or by magnetic impurity scattering). However, even at T=0, the ions vibrate about their equilibrium positions. The oscillation rate at T=O, if approximated by the Debye frequency, $\omega_{n} \approx 4.10^{13} \text{sec}^{-1}$, is comparable in size to other relevant time scales in the solid, i.e. $1/\tau_1$, $1/\tau_{so}$ etc. (see Table 4.1). Since the two electrons visit a given ionic scattering site at different times, they will find the ion at <u>different</u>, effectively) random, positions. This is demonstrated in Fig.4.11b where one of the scattering sites is drawn enlarged. The path length between complementary scatterings therefore differs by small random amounts which lead to an accumulated phase difference at the interference point 0. It is possible to quantify this phase difference using the Feynman path integral approach developed by Chakravartry and Schmid⁴⁵. This semi-classical approach is rigorous to the extent that all of the results of the strict quantum mechanical derivations (given in Chapter 2.2) may be reproduced.

The argument starts with the definition

$$K(\vec{r}_f, \vec{r}_i, t_f, t_i) = \sum_{\vec{r}_t} A[\vec{r}_t] \exp(\frac{i}{\hbar}S[\vec{r}_t])$$
(4.3)

as the (probability) amplitude of electron wave propagating from \vec{r}_i to \vec{r}_f during the time t_i to t_f (in principle this applies to any kind of wave propagation). The points \vec{r}_i and \vec{r}_f correspond to e.g. A and B in Fig.2.1. The summation is taken over all possible paths connecting the two end points with a suitable weight factor $A[\vec{r}_t]$. The action S is defined as

$$S[\vec{r}_t] = \int_{t_1}^{t_f} dt \ L(\dot{\vec{r}}_t, \vec{r}_t)$$
(4.4)

where the Lagrangian L can be written as

$$L = \frac{m}{2} \dot{\vec{r}}_{t}^{2} - \dot{V}(\vec{r}_{t} - \vec{u}(\vec{r}_{t}, t)) - e\Phi(\vec{r}_{t}, t) + L_{i}$$
(4.5)

V is the random impurity potential which is here the potential of the

randomly positioned ions in the amorphous metal. The ionic displacements due to the quantum oscillations and thermal lattice vibrations is considered by the displacement field \vec{u} . L_i is a Lagrangian describing time symmetry breaking processes such as the magnetic field dependence of the Lagrangian or magnetic spin-scattering and $e\Phi$ is the deformation potential due to the displacement \vec{u} . In the present discussion these last two terms are ignored. Using eq.4.3 the probability $W = K^2$ that an electron is found at point \vec{r}_f and time t_f , which had started to propagate from point \vec{r}_i a time $\tau_{\phi} = (t_f - t_i)$ earlier, is:

$$\mathbb{V}\left(\vec{r}_{t}, \vec{r}_{1}, \tau_{\phi}\right) = \frac{1}{2N(\epsilon_{F})} \sum_{\vec{r}_{t}} \sum_{\vec{r}_{t}'} \mathbb{A}\left[\vec{r}_{t}\right] \mathbb{A}^{*}\left[\vec{r}_{t}'\right]$$

$$\times \left\{\delta\left(\epsilon\left[\vec{r}_{t}\right] - \epsilon_{F}\right) + \delta\left(\epsilon\left[\vec{r}_{t}'\right] - \epsilon_{F}\right)\right\} \times \exp\left(\frac{1}{\hbar}\left(S\left[\vec{r}_{t}\right] - S\left[\vec{r}_{t}'\right]\right)\right)$$

$$(4.6)$$

Again the summations are carried out over all possible paths \vec{r}_t and \vec{r}_t' . The δ -functions ensure that the electrons propagate with the Fermi velocity. Unless the paths \vec{r}_t and \vec{r}_t' are equal, the phase factor in eq.4.6 will average to zero over the length of the paths. For the paths $\vec{r}_t = \vec{r}_t'$ it follows that

$$\mathbb{W}\left(\vec{r}_{f},\vec{r}_{i},\tau_{\phi}\right) = \frac{1}{\mathbb{N}(\epsilon_{F})} \sum_{\vec{r}_{t}} |A[\vec{r}_{t}]|^{2} \delta\left(\epsilon[\vec{r}_{t}] - \epsilon_{F}\right)$$
(4.7)

Similarly one can define a quasi-probability, \tilde{W} , which describes the interference probability of two electrons traversing the paths from \vec{r}_i to \vec{r}_f in opposite directions during time τ_{ϕ} . \tilde{W} can be deduced from W in eq.4.6 by reversing the time index on the second path vector, i.e. $\vec{r}_t' - \vec{r}_{-t}'$. Again all terms in the double summation but those with $\vec{r}_t = \vec{r}_{-t}'$ vanish so that

$$\tilde{\mathbb{V}}(\vec{r}_{f}, \vec{r}_{i}, \tau_{\phi}) \stackrel{\simeq}{=} \frac{1}{N(\epsilon_{F})} \sum_{\vec{r}_{t}} |A[\vec{r}_{t}]|^{2}$$

$$\times \delta(\epsilon[\vec{r}_{t}] - \epsilon_{F}) \times \exp(i\Delta\Phi[\vec{r}_{t}])$$
(4.8)

where

$$\hbar \Delta \Phi[\vec{r}_{+}] = S[\vec{r}_{+}] - S[\vec{r}_{-+}]$$

$$= \int_{-\tau_{\phi}/2}^{+\tau_{\phi}/2} dt \left[L\left(\dot{\vec{r}}_{t}, \vec{\vec{r}}_{t}\right) - L\left(\dot{\vec{r}}_{-t}, \vec{r}_{-t}\right) \right]$$

(The weight factor A does not depend on the direction of propagation.) Here, where we are discussing the propagation of electrons, the endpoints of the paths have to be less than an electronic wave length apart (see Fig.4.11a), and τ_{ϕ} is the time over which phase coherence in the interference region of the path end-points is maintained. If the displacement field \vec{u} were zero, only the time-reversal symmetry-breaking part of the Lagrangian, L_i , would lead to a finite phase difference $\Delta \Phi$ at the path end-points. To calculate the phase difference due to a finite displacement field consider the first two terms of the Lagrangian in eq.4.5. Transforming $\vec{r} \rightarrow \vec{r} - \vec{u}$ and using

$$\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} - \frac{\mathrm{d}\vec{r}}{\mathrm{d}t} + \frac{\partial\vec{u}}{\partial t} + \left(\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} \cdot \vec{\nabla}_{r}\right)\vec{u}$$

gives to first order in the displacement u that L transforms to

$$L \rightarrow L_{\vec{u}=0} + m\left(\frac{d\vec{r}}{dt} \cdot \left(\frac{\partial \vec{u}}{\partial t}\right) + m\left(\frac{d\vec{r}}{dt} \cdot \left(\frac{d\vec{r}}{dt} \cdot \vec{\nabla}_{r}\right)\vec{u}\right)$$
(4.9)

 $L_{\vec{u}=0}$ is the time-reversal symmetric part of the Lagrangian, which does not yield a phase difference $\Delta \Phi$. The last term on the right-hand-side in eq.4.9 has been calculated by Chakravartry and Schmid⁴⁵ and shown to lead to dephasing by inelastic electron-phonon scattering dephasing. The second term on the right-hand-side, which deals with the uncorrelated zero-point motion of the ions, was neglected by Chakravartry and Schmid. It leads to a phase difference

$$\Delta \Phi[\vec{r}_t] = \frac{m}{\hbar} \int_{-\tau_{\phi}/2}^{+\tau_{\phi}/2} dt \left(\frac{d\vec{r}_t}{dt} \cdot \frac{\partial \vec{u}(\vec{r}_t, t)}{\partial t} - \frac{d\vec{r}_{-t}}{dt} \cdot \frac{\partial \vec{u}(\vec{r}_{-t}, -t)}{\partial t} \right)$$
(4.10)

The precise general evaluation of this integral is quite difficult, if

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(4.8)

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not impossible, but one can find an approximate solution if one assumes that the ions oscillate in an uncorrelated manner and fast enough for the phase shifts due to the single ions to be calculated individually. In this case

$$\Delta \Phi_{i}[\vec{r}_{t}] = \int_{-\tau_{\phi}/2}^{+\tau_{\phi}/2} dt \left(\frac{\vec{k}_{t}}{dt} \cdot \frac{\partial \vec{u}_{t}}{\partial t} - \frac{\vec{k}_{-t}}{dt} \cdot \frac{\partial \vec{u}_{-t}}{\partial t} \right)$$
(4.11)
where $\vec{k} = \frac{m}{h} \frac{d\vec{r}}{dt}$

Assuming that the change of momentum at the scattering site \mathbf{R}_{i} is instantaneous, gives

$$\Delta \Phi_{i} = \left(\vec{k} - \vec{k}'\right) \cdot \delta \vec{R}_{i} = 2k_{F} \delta R_{i} \sin(\theta/2) \qquad (4.12)$$

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Here, θ is the scattering angle between the incident and outgoing wave vectors \vec{k} and \vec{k} ' as indicated in Fig.4.11b, and

 $\mathbf{R}_{1} = \int_{-\tau_{\phi}/2}^{+\tau_{\phi}/2} dt \left(\frac{\partial \vec{u}_{-t}}{\partial dt}\right)$

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Since there are τ_{ϕ}/τ_{0} scattering events along the loop, where τ_{0} is the time between collisions, the mean-squared average accumulated phase shift between the two electron trajectories at the interference point in Fig.4.11a is

$$\langle \Delta \Phi^2 \rangle = \left(\tau_{\phi} / \tau_{o} \right) 8 k_F^2 \langle \delta R^2 \rangle \langle \sin^2(\theta/2) \rangle$$
(4.13)

A factor of two arises because there are two complementary trajectories. The collision time and the geometrical factor may be combined to the elastic scattering transport time τ_e (the momentum relaxation time), i.e $\tau_e = \tau_o / \langle \sin^2(\theta/2) \rangle$. In the case of isolated and localized ionic scattering, as may be expected to hold for transition metal alloys, the

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zero-point displacement $\delta \vec{R}_i$ can be written in terms of its normal modes

$$\delta \vec{R}_{i} = \sum_{\vec{q}} \vec{a}(\vec{q}) e^{i\vec{q}\cdot\vec{R}_{i}}$$
(4.14)

If one replaces the phonon spectrum by a δ -function at the Debye frequency, ω_D , it follows that the mean-squared average displacement of the oscillating ions of mass M is given by

$$\langle \delta R^2 \rangle = \frac{3\hbar}{2M\omega_{\rm D}} \tag{4.15}$$

The assumption of isolated and localized ionic scattering does not necessarily hold in every metal. In the weak scattering simple Mg-based alloys studied here, the electron momentum decays over many ionic scattering events. Consequently the electron wave function and the ionic oscillations will be correlated over a distance ξ , which is the lesser of the phonon coherence length and the Debye length $\sqrt{D/\omega_D}$, the distance electrons diffuse during one oscillation of the ion. To account for the correlation over the distance ξ , which attenuates the dephasing due to the ibnic zero-point motion, one has to replace $\langle \delta R^2 \rangle$ by a coarse-grain averaged displacement, i.e one has to introduce an attenuation factor

$$E(\vec{q}) = \frac{3}{4\pi\xi^3} \int_{r<\xi} d\vec{r} \ e^{i\vec{q}\cdot\vec{r}}$$
(4.16)

in the normal mode expansion of $\delta \vec{R}_i$. Evaluating $f(\vec{q})$ at the Debye wave vector, q_D , which is approximated by π/a , a is the average interatomic spacing, gives

$$\langle \delta R_1^2 \rangle_{cga} = \frac{3\hbar}{2M\omega_D} |f(q_D)|^2 \approx \frac{3\hbar}{2M\omega_D} \frac{9}{2} (\frac{a}{\pi \xi})^4$$
 (4.17)

where $q_D \xi >> 1$ was assumed. Collecting the terms gives for the meansquared phase difference

$$\langle \Delta \Phi^2 \rangle = \frac{108}{\pi^4} \left(\frac{\tau_{\Phi}}{\tau_{e}} \right) \left(\frac{m}{H} \right) \left(\frac{T_F}{\theta_D} \right) \left(\frac{a}{\xi} \right)^4 \approx \left(\frac{\tau_{\Phi}}{\tau_{e}} \right) \left(\frac{m}{H} \right) \left(\frac{T_F}{\theta_D} \right) \left(\frac{a}{\xi} \right)^4$$

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The coherence between the two complementary trajectories at the interference point 0 is destroyed when their total phase difference is of the order 1. Provided that all other dephasing time scales are longer and thus irrelevant, this defines a saturation dephasing cut-off, τ_A^0 , due to ionic zero-point motion as

$$\mathbf{r}_{\phi}^{o} \approx \left(\frac{\mathbf{M}}{\mathbf{m}}\right) \left(\frac{\theta}{\mathbf{D}_{p}}\right) \left(\frac{\mathbf{D}}{\mathbf{D}_{o}}\right) \left(\frac{\mathbf{h}}{\boldsymbol{\epsilon}_{p}}\right) \left(\frac{\boldsymbol{\epsilon}}{\mathbf{a}}\right)^{4}$$
(4.18)

where the elastic scattering time, τ_e , was expressed in terms of the electron diffusivity, D, and $D_a = \hbar/m$. Using the relation

$$B_{\phi}^{O} = \frac{\hbar}{4eD\tau_{\phi}^{O}}$$

equation eq.4.18 defines a lower bound on the dephasing strength B_{ϕ} . It is stressed that this dephasing does <u>not</u> involve any inelastic processes[†].

For a typical metal, $M/m_e \approx 10^5$, $\theta_D/T_P \approx 3 \times 10^{-3}$, $\epsilon_F \approx 8 \text{eV}$, eq.4.18 predicts a saturation, τ_{ϕ}^0 , of $0.5 \times 10^{-12} \text{ sec}$ in the strong scattering limit (D $\approx 0.1 \text{ cm}^2/\text{sec}$ and $\xi/a=1$) and up to $50 \times 10^{-12} \text{ sec}$ in the weak scattering limit. This range encloses all observed values. In the case of Mg-Cu and Mg-Zn glasses we find with $\epsilon_F = 7.3 \text{eV}$, $M/m_e = 6.7 \times 10^4$, $T_F \approx 85000$ k, D= $6.5 \text{cm}^2/\text{sec}$, a= 3.1Å and $\theta_D = 315$ K that eq.4.18 reproduces our measured value of τ_{ϕ}^0 (90psec) if we assume for ξ a value of 16Å. This length corresponds to 5 interatomic spacings. It is much shorter

t) A small temperature dependence arises though from excitations of the ionic oscillators. It is identical to the temperature dependence of the Debye-Waller factor, W, calculated by $2iman^{42}\sqrt{1.e}$.

$$\frac{B_{\phi}^{0}(T)}{B_{\phi}^{0}(T=0)} = \frac{\langle \delta R^{2} \rangle_{T}}{\langle \delta R^{2} \rangle_{T=0}} = \frac{W(T)}{W(T=0)} = 1 + \frac{2\pi^{2}}{3} \left(\frac{T}{\theta_{D}}\right)^{2}.$$
(4.19)

This correction is less than 0.2% at T=4.2K and thus negligible. It becomes important only at T $\geq \theta_{\rm D}/2$.

than the Debye length $(\sqrt{D/\omega_D} = 40 \text{\AA})$ but consistent with the phonon coherence length on expects in metallic glasses. Theoretical calculations by von Heimendahl¹⁰⁹ and inelastic neutron scattering measurements by Suck et al.¹¹⁰ have shown that the dynamical structure factor in Mg₇₀Zn₃₀ has a large spread in (\vec{q}, ω) -space. Their results indicate that phonons are very localized excitations in Mg₇₀Zn₃₀ (probably most metallic glasses) and decay over distances of about 2 to 10 interatomic spacings. For Y₆₀Al₄₀ one finds, using $\epsilon_{\rm F}$ = 8eV, M/m_e = 1.2×10^5 , T_F = 91000K, D = 1cm²/sec, a = 3.2\AA , $\theta_{\rm D}$ = 300K and again with $\xi = 16 \text{\AA}$ (which coincides here with $\sqrt{D/\omega_{\rm D}} = 15.8 \text{\AA}$), that $\tau_{\phi}^{\circ} = 18$ psec compared to the measured²⁷ value of 26psec. The larger value of τ_{ϕ}° in Y₈₀Al₂₀ is consistent with eq.4.18 but inconsistent with magnetic impurities. Y is the part of the alloy which contains almost all of the magnetic, mostly rare earth oxide, impurities. We therefore expect τ_{ϕ}° to decrease with increased Y concentration if its saturation were caused by magnetic impurities.

We can extend the above model to two dimensional systems to investigate saturations of B₀ observed in thin metal films and semiconductors. In metallic thin films the bulk electrical resistivity is dominated by the resistivity arising from surface scattering as is reflected by the strong dependence of the sheet resistance on the film thickness^{99,111}. One can take account of the surface scattering in the zero-point motion dephasing calculation by noting that there are approximately v_p/d surface scatterings per unit time (d is the thickness of the film). In the time τ_0^0 these give an additional meansquared phase shift of $(\tau_0^0 v_p/d)(2k_p \delta R)^2$, where the scattering angle, θ , has been set to π . It has to be added to the phase shift due to bulk scattering calculated above, and hence one finds for two dimensional conductors

$$\left(\frac{1}{\tau_{\phi}^{0}}\right)_{\text{film}} \approx \left(\frac{1}{\tau_{\phi}^{0}}\right)_{\text{bulk}} + 12\left(\frac{v_{F}}{d}\right)\left(\frac{T_{F}}{\theta_{D}}\right)\left(\frac{m}{M}\right)$$
(4.20)

This relation predicts that $1/\tau_{\phi}^{0}$ and equivalently $\mathbb{B}_{\phi}^{0}/\rho$ should vary as 1/d in thin metallic films. This is exactly what was observed by Abraham

and Rosenbaum⁹⁹ in thin Cu-films as is shown in Fig.4.12. This behavior is not consistent with the constant, or at least thickness independent, magnetic impurity concentrations in the samples. In fact the value of B_{ϕ}^{O}/ρ is the smallest in the sample which contains the most impurities according to the authors.





Peters and coworkers⁹⁸ observe a saturation of B_{ϕ} even in very high purity (< lppm Fe) Au films for which they give no explanation. Unfortunately, the authors did not study samples of equal purity and varying thickness so that the scaling of $1/\tau_{d}^{0}$ as 1/d can not be

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confirmed here. However, we shall take their observation as another confirmation that a saturation of B_{d} can not always be linked to extraneous causes. Bishop and coworkers 104 studied the saturation of the dephasing field at low temperatures in Si MOSFETs (They find that it depends in both low and high mobility samples on the applied gate voltage. They argue that the saturation is a consequence of decoupling of the electron gas from the lattice (phonons) which occurs when the inelastic diffusion length, $\sqrt{D\tau_i}$, becomes comparable to the sample size. With eq.4.18 and eq.4.20 we can give a different explanation: The gate voltage, V_g , changes the carrier density but not, to first order, the density of states. Therefore D varies linerly with V_{σ} . Consequently, since D is the only quantity in eq.4.18 which depends on the gate voltage, τ_{ϕ}^{o} should increase with V_{g} which is exactly what Bishop et al. observed in both, high and low mobility samples. Furthermore, the absolute value of τ_{d}^{0} is larger in the high mobility sample which is also consistent with eq.4.18. The reader should also note that the temperature at which the saturation of τ_{d} begins in the MOSFETs is approximately independent of the gate voltage which it should not be according to the explanation by Bishop and coworkers.

To end this discussion of the saturation of B_{ϕ} we conclude: The saturation of B_{ϕ} in Mg-Cu based alloys is not due to external circumstances. Specifically, it is not induced by thermal decoupling of the electron gas from the thermal bath, it is not caused by finite size effects as the sample dimensions are much larger than all relevant electron transport length scales (see Table 4.1), and it is inconsistent with the measured magnetic impurity concentrations. A new temperature independent dephasing mechanism of the weak localization effect due to ionic zero-point motion is presented. It is intrinsic to <u>all</u> conductors and capable of explaining many of the dephasing field saturation phenomena reported in the literature. For Mg-Cu and Mg-Zn metallic glasses the model gives a correct value for the observed saturation field B_{ϕ}^{0} if a short phonon coherence length is assumed. A suitable system and experiment to specifically study the zero-point motion dephasing effect has yet to be devised.

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4.2.5 Magnetic Impurities

In Chapter 2 it was pointed out that magnetic impurities destroy the quantum coherence effects. To underline the importance of using high purity materials for studies of the quantum correction theories, magnetoresistance measurements were carried out on a Mg₇₀Cu₃₀ sample containing (170 ± 10) ppm of Mn and a Mg₇₀Zn₃₀ sample containing (7600 ± 200) ppm of Gd. Both Gd and Mn carry a moment in the these alloys. Gd has a moment of $7\mu_{\rm B}$ which is independent of the particular bandstructure of the host metal as its ${}^{8}S_{7/2}$ ground state configuration is extremely stable. The spin-exchange integral is most likely quite small, Cochrane et al.⁷¹ have reported J = 0.057eV for Gd in Lu. The Gd concentration (7600ppm) is sufficient to quench superconductivity 112 in $Mg_{70}Zn_{30}$ and the alloy should thus be comparable to $Mg_{70}Cu_{30}$ containing Mn as a magnetic impurity. Mn holds a moment of about $4.5\mu_{\rm p}$ in many metals. The spin-exchange integral however is negative and larger than that of Gd. Values of J = -0.25eV have been reported 56,57. Fig.4.13 shows the magnetoresistance at 4.2K of both magnetic impurity samples in comparison to high purity Mg70Cu30 (same data as in Fig.4.1a). One can clearly see that the most striking characteristic of the weak localization effect at finite spin-orbit scattering, the positive magnetoresistance at small magnetic fields, is suppressed by the magnetic impurity scattering. Similarly, the large negative magnetoresistance at higher fields, typical of the high purity $Mg_{70}Cu_{30}$ and $Mg_{70}Zn_{30}$ samples, should be suppressed as well because the damping $1/\tau_{c}$ enters both parts of the Cooperon in eq.2.18. Comparing the data in Fig.4.13 one finds that the magnetoresistance at 3T in Mg70Cu30(170ppm Mn) and Mg70Zn29Gd1 is actually larger than in high parity $Mg_{70}Cu_{30}$. This demonstrates the importance of the negative magnetoresistance term due to magnetic impurities discussed in Chapter 2 (eq.2.39). Included in Fig.4.13 is a measurement by Bieri and coworkers 3^{22} on amorphous Mg₈₀Cu₂₀. Even though this alloy is expected to have a lower spin-orbit scattering rate than our Mg-Cu alloys because the Cu content is 30% smaller, the magnetoresistance should be positive at low fields as well. The dashed line in Fig.4.13 is an estimate of the

magnetoresistance Bieri et al. should have observed, had they used high purity materials (it is calculated with $B_{so} = 0.052T$, i.e 2/3 of the value in $Mg_{70}Cu_{30}$, and B_{ϕ} according to eq.4.2). We conclude that their alloy contained a very high level of magnetic impurities. This explains why the authors had to scale the weak localization magnetoresistance in eq.2.24 by a factor of 1.23 to fit the data. It also underlines the importance of the minimal adjustable parameter analysis we have carried out.

The magnetoresistance in $Mg_{70}Zn_{30}$ (7600ppm Gd) was also measured at other temperatures. Fig.4.14 shows the resulting data, which turned out to be quite difficult to analyse. Even though the superconductivity observed in $Mg_{70}Zn_{30}$, as well as the diffusion channel magnetoresistance will be quenched to zero, it is not quite clear what sign and size the coupling constant, g, of the Cooper channel should have. Also, in this regime of strong magnetic impurity scattering, the expression in eq.2.22 for the scattering dephasing time, τ_s , should be modified to take into account its field and temperature dependence. The dephasing due to magnetic scattering is expected to be smaller at large magnetic fields. Nevertheless bearing these complications in mind, we attempted to fit the data to the weak localization and magnetic impurity magnetoresistance (eq.2.24 and eq.2.38). The solid curves in Fig.4.14 were calculated with $B_{so} = 0.11T$, J = 0.035eV and B_{d} according to eq.4.2. Considering the crudeness of this approach the agreement is quite acceptable.

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Figure 4.13 Comparison of the magnetoresistance at 4.2K in several Mg-based glasses containing magnetic impurities. The compositions are indicated in the figure. The data for Mg₈₀Cu₂₀ are taken from reference 32. The solid line is an estimate of the magnetoresistance in high purity Mg₈₀Cu₂₀ as explained in the text. The scale is indicated in the figure.





4.2.6 Using Weak Localization to Measure Resistivity

There is one important detail of the analysis of the magnetoresistance in simple metallic glasses that has not yet been pointed out. One can use magnetoresistance measurements to determine the resistivity of disordered simple metal samples, whose irregular geometry does not allow a meaningful determination of the cross-section area (see section 3.2.6). This is simply done by fitting the measured magnetoresistance data to the weak localization expression in eq.2.23 or eq.2.24 with ρ as an additional adjustable parameter (here too, only in the field regime $B/T \le 0.4TK^{-1}$). In a few tests on the weak spin-orbit scattering glasses $Mg_{70}Cu_{30}$ and $Mg_{70}Cu_{27}Ag_3$ it was found that one does in fact recover the correct estimate of the resistivity to better than 10%. A reasonable estimate for ρ is also found in Mg₇₀Zn₃₀, even if the Maki-Thompson superconducting fluctuation magnetoresistance is neglected $(\beta = 0)$. In a least-squares fit, the positive fluctuation magnetoresistance is compensated by a slightly underestimated value of B_{\pm} . In strong spin-orbit scattering alloys, however, the correlation between ρ and B_{μ} is large enough to lead to a considerable underestimation of the resistivity (about 40%). The measured and normalized magnetoresistance signal, $\Delta R/R = \Delta \rho/\rho$, is independent of the geometry of the sample. i.e it does not depend on variations of the thickness or width. The reason why this method works is that that the absolute size of the weak localization effect is a material constant and can not be disputed. It is the consequence of a quantum interference effect and the correction it contributes to transport properties is exclusively[†]) determined by the resistivity ρ and coherence cut-offs, i.e τ_e , τ_b , τ_s and τ_{so} .

t) The small error which was probably introduced into the expression for the weak localization magnetoresistance, eq.2.23 and eq.2.24, by setting τ_e to zero, see section 4.2.2 and reference 96, can be neglected for the purpose of the present discussion.

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The above method was applied¹¹³ to measure the resistivity in icosahedral $Mg_{40}Al_{30}Zn_{30}$ and $Mg_{40}Al_{18}Zn_{42}$. These icosahedral alloys can be produced by melt-spinning. The resulting ribbons are usually very short (< 5mm long), extremely brittle, have rough edges and a very irregular surface. The measured magnetoresistance data are shown in Fig.4.15a,b; they have the same characteristics as those in Fig.4.1. The resulting values for the resistivity were $(70 \pm 7)\mu\Omega cm$ in Mg₄₀Al₃₀Zn₃₀ and $(105 \pm 10)\mu\Omega cm$ in Mg₄₀Al₁₈Zn₄₂ with spin-orbit scattering fields of $B_{so} = (0.10 \pm 0.01)T$ and $(0.17 \pm 0.02)T$, respectively[†]). The resistivities are larger than in $Mg_{70}Zn_{30}$, but the spin-orbit fields are are comparable to those in Mg₇₀Zn₃₀ and Mg₇₀Cu₃₀, see Table 4.1 and 114 Table 3.5. Within the error the values of B_{a} are the same as in Fig.4.10. The magnetoresistance curves in Fig.4.15a,b show very clearly that icosahedral Mg-Al-Zn alloys are disordered conductors from an electron transport point of view even though their atomic structure exhibits a five-fold rotational symmetry with long range order as has been shown by X-ray and electron diffraction experiments¹¹³. This subtle difference, which is not investigated further in this thesis, should be investigated in more detail.

t) The values given by Baxter, Richter and Strom-Olsen¹¹³ are slightly different because the data were fitted over the enire field range.



Figure 4.15 a) Normalized magnetoresistance in icosahedral Mg₄₀Al₃₀Zn₃₀. The scale and the temperatures (in Kelvin) are indicated in the figure. The solid line is the best fit to the weak localization theory as explained in the text.

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Figure 4.15 b) Normalized magnetoresistance in icosahedral Mg₄₀Al₃₀Zn₃₀. The scale and the temperatures (in Kelvin) are indicated in the figure. The solid line is the best fit to the weak localization theory as explained in the text.

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4.3 The Resistivity Temperature Dependence

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Measurements of the resistivity down to 0.08K were carried out on several samples in a dilution refrigerator. The measurements are complicated by problems with the brittleness of the samples, the thermal contact to the sample holder and the small size of the signal. To resolve resistance changes of the order $5 \times 10^{-5} \Omega$ in an approximately 1Ω sample requires, with the a.c. resistance bridge used here, a considerable sensing current which can cause self-heating effects of the electron gas. For the two alloys $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$ it was possible to circumvent these difficulties. The data are shown in Fig.4.16. Mg₇₀Zn₃₀ has a superconducting transition at 0.12K with a width of 6mK which is in good agreement with the value of 0.11K reported by Van den Berg et al.³⁷. The difference is not significant as the absolute value of T_c is very sensitive to small concentrations of magnetic impurities in the alloy. Kästner and Wassermann¹¹² reported that T_c decreases by about 0.04 T_c per 1 ppm Mn. The materials Van den Berg et al. used, were distilled Mg but only 99.999% pure Zn. This easily explains the slightly lower transition temperature. The Mg70Zn27Au3 sample was cooled to the limit of the refrigerators ability, 0.08K, but a superconducting transition was not reached. However, Fig.4.16 shows a substantial decrease of the resistance due to superconducting fluctuations⁶⁵, the precursers of a superconducting transition at lower temperatures. Rather than fitting the data on Mg70Zn27Au3 to any theoretical expression of the resistivity one can use an easier method to estimate T_c in this alloy. $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$, differ in their fluctuation induced conductivity because of their different transition temperatures. Johnson et al. 66 found in amorphous La₇₅Au₁₅Cu₁₅ and $Mo_{30}Re_{70}$ that this fluctuation conductivity decays as $exp(-\gamma\sqrt{t})$ for $T > 0.4T_c$, $t = (T - T_c)/T_c$ is the reduced temperature (\sqrt{T} is the order parameter of the superconducting transition and γ_{\circ} is a measure of the free energy difference between the normal and superconducting state). A plot of $\ln(\Delta \sigma_{fl}/\sigma_0)$ against \sqrt{t} as shown in the insert of Fig.4.17 yields a straight line.

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The normalized resistivity change in $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$ from 0.08K to 6K. The scale is indicated in the figure.



Figure 4.17

The (negative) normalized superconducting fluctuation, conductivity in $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$ against the square root of the reduced temperature. The scale is indicated in the figure.

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Ami and Maki⁶⁵ showed that this decaying conductivity can be attributed to the Maki-Thompson type contribution to the conductivity. The Aslamasov-Larkin type contribution is important only very close to the transition temperature, i.e. t<0.05. They cause the deviations from linearity close to T_e seen in Fig.4.17. The important fact Johnson and coworkers report is that the quantity γ is constant in all of their samples studied (i.e $\gamma = 4.5$). This should also be true for the two very similar alloys $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$. One can isolate the superconducting fluctuation related conductivity of the two Mg-Zn alloys by fitting the curves in Fig.4.16 far above T_c (T) 10T; to a background function, $\Delta R(T)/R_{o} = a\sqrt{T} + const.$, extrapolating this background to lower temperatures and subtracting it from the measured resistance change. Fig.4.17 shows the resulting curves and we find that in Mg-Zn glasses too the superconducting fluctuation conductivity decays according to the above function. For $Mg_{70}Zn_{30}$ the decay constant γ is 0.76. With a T_c of (40 ± 15) mK the same value results for Mg₇₀Zn₂₇Au₃. This estimate of T was used in section 4.2.3 for the analysis of the magnetoresistance in $Mg_{70}Zn_{27}Au_3$ and $Mg_{70}Zn_{27}Ag_3$.

The resistivity change in the four amorphous alloys $Mg_{70}Cu_{30}$, $Mg_{70}Cu_{27}Au_3$, $Mg_{70}Zn_{30}$, $Mg_{70}Zn_{29}Gd_1$ between 1.5K and 6K is compared in Fig.4.18. For better comparison it is plotted as the negative conductivity change against the square root of temperature. Between these four alloys some of the most important parameters of the theories of quantum corrections to the conductivity are altered. It was shown in the previous section 4.1 that the magnetoresistance in these four alloys is distinctly different. This is not the case for the resistivity temperature dependence. In all alloys investigated the resistivity changes as $\Delta \rho / \rho^2 \approx -\alpha \sqrt{T}$ between 1.5K and 6K with $\alpha = (135 \pm 25) \times 10^{-5} (\Omega m K^2)^{-1/2}$. Within its error α is not correlated with the spin-orbit scattering strength or any other property. Icosahedral $Mg_{40}Al_{30}Zn_{30}$ also shows a similar temperature dependence. One comes therefore to the following conclusions: As predicted, the weak localization effect contributes only very little to the overall



Figure 4.18 Comparison of the (negative) conductivity temperature dependence in several Mg-based glasses. The alloy composition and scale are indicated in the figure. The solid line is the diffusion channel contribution according to eq.2.33.

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resistivity between 1.5K and 6K. Similarly, the Cooper channel contribution to the resistivity temperature dependence is very small as no significant difference in α is observed between Mg-Cu and Mg-Zn glasses. Eq.2.34 describing the temperature dependence of the Maki-Thompson superconducting fluctuation resistivity correction must be incorrect; in conjunction with the other contributions (weak localization, Cooper and diffusion channel) it predicts a maximum of the resistivity at around 2K for $Mg_{70}2n_{30}$ which is not observed. This conclusion is supported by the analysis of the fluctuation conductivity earlier in this section. The residual fluctuation conductivity at 1.5K, as shown in Fig.4.17, is negligible. The only quantum correction to the resistivity which is supposed to be the same in all alloys studied here, is the diffusion channel contribution given in eq.2.34 (to what extent it is altered by strong spin-orbit scattering or by the magnetic scattering due to 7600ppm of Gd is not known). It depends only on the electron screening parameter $ilde{ extsf{F}}_{\sigma}$ which is 0.5 in all of the alloys studied here (see Tab.2.1). Comparing the magnitude of the diffusion channel term, the solid line in Fig.4.18, with the measured data, one finds that it is about a factor of 2 too small^{†)}. The data can only be fitted to the quantum correction theories if \tilde{F}_{σ} is allowed to assume unphysical negative values ranging between -0.1 and -0.6. Similar observations have been reported by Poon et al.¹¹⁴ and Hickey et al.¹⁰⁰. At the moment we do not know how to interpret these results. It is surprising that the magnetoresistance is so well described at low fields by the quantum correction theories but not the temperature dependence of the resistance. We note however that our analysis of the magnetoresistance has only proven the validity of the weak localization effect and the expression for the

t) Newson and coworkers¹¹⁵ have reported recently that the ratio between the temperature coefficients of the Hall effect coefficient and the resistivity in some doped three dimensional GaAs MESPETs is a factor of two smaller than predicted by Altshuler and Aronov²⁰.



superconducting fluctuation magnetoresistance (at low fields). This does not allow us to make any statement about the validity of the expressions describing the resistivity temperature dependence due to enhanced electron-electron interaction (eq.2.33). The above results shall therefore be taken as an indication that the expressions describing the temperature dependence of the quantum corrections to the conductivity need to be improved.

Above 6K, the resistivity of all Mg-based glasses studied has a positive T^2 temperature dependence. This is demonstrated in Fig.4.19 where the resistivity change in Mg₇₀Cu₃₀, normalized in the same way as in Fig.4.18, is plotted against T^2 . According to Matsuda, Mizutani and Yoshino^{34,36,116}, who studied the resistivity temperature dependence above 6K of simple metallic glasses in great detail, this regime extends up to $T_{max} \approx 40$ K and the resistivity decreases with increasing temperature roughly as $-T^2$ above T_{max} . This behavior is in agreement with the generalized Faber-Ziman theorys¹¹⁷ describing the uncorrelated intense scattering contributions to the resistivity; it is not of interest in the present context.

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Figure 4.19



5. CONCLUSIONS

From the results presented in this thesis we are able to draw the following conclusions:

At low fields, where enhanced electron-electron interactions are negligible, the weak localization theory gives an excellent description of the magnetoresistance in amorphous Mg-Cu, both in the low and high spin-orbit scattering regime. An equally good description of the magnetoresistance in amorphous Mg-Zn is achieved if the additional contribution from superconducting fluctuations is included. In particular the size of the effect is given accurately by the theoretical expression by Fukuyama and Hoshino, without the need for an arbitrary scaling factor, as has been used by other authors.

At high fields, the theories of quantum corrections to the conductivity do not account for the measured magnetoresistance. In the superconducting Mg.Zn alloys some of the discrepancies between theory and experiment are caused by an incomplete evaluation of the superconducting fluctuation magnetoresistance. We speculate that further discrepancies are caused by an incorrect description of the high field weak localization magnetoresistance by the theory of Fukuyama and Hoshino.

From the comparison of the experimental magnetoresistance with the quantum corrections theories at low fields the dephasing and spin-orbit scattering rates are deduced.

Above 4K the dephasing rate varies approximately as T³, which is consistent with the dephasing of the quantum interference by inelastic electron-phonon scattering, but below 4K it saturates to a common value in all samples. The saturation cannot be attributed consistently to residual magnetic impurity scattering or other extraneous causes. To explain the saturation of the dephasing rate a model has been proposed. It is based on the dephasing of the quantum backscattering interference by ionic zero-point motion. For the Mg-based metallic glasses studied here, the model gives a consistent value for the dephasing saturation rate if a phonon coherence length of five interatomic spacings is assumed. Equally applicable to other disordered conductors, the model is capable of explaining many of the dephasing rate saturation systematics observed by other workers.

The spin-orbit scattering rate increases in Mg-Cu and Mg-Zn glasses when Cu and Zn are replaced by the heavier elements Ag or Au. As expected, the increase is linear in concentration, x, but only if x < 3atX. In this regime the increase on adding Au is much stronger than on adding Ag which is expected from the dependence of the spinorbit scattering Hamiltonian on Z. At larger concentrations the increase of the spin-orbit scattering rate is weaker; for Au it falls drastically below the linear extrapolation. This may reflect the limitation of the expansion in τ_e/τ_{so} used in the derivation of the weak localization magnetoresistance expression. The values of $1/\tau_{so}$ compare well to those found by other authors.

The <u>difference</u> between the magnetoresistance in Mg-Cu and Mg-Zn is explained quantitatively (with no adjustable parameters) by a combination of the Cooper Channel interaction and Maki-Thompson superconducting fluctuation magnetoresistance. At low fields where the Cooper channel is negligible, this difference is the <u>first</u> direct measurement of the superconducting fluctuation magnetoresistance in bulk metallic glasses. It is well described by the theory of Larkin.

As a consequence of its quantitative accuracy at low fields, the weak localization magnetoresistance may be used to measure directly the resistivity of bulk disordered metals. The method was applied to "icosahedral Mg-Al-Zn alloys whose irregular geometry precluded resistivity measurements by conventional means.

By deliberate doping of two Mg-Cu and Mg-Zn alloys with small amounts of Mn and Gd we have also demonstrated the extreme importance of using samples free of magnetic impurities if reliable values of the dephasing and spin-orbit scattering rates are to be deduced.

In the absence of a magnetic field the resistivity varies approximately as $-\alpha\sqrt{T}$ between 1.5K and 6K as expected from the quantum correction theories. The value of α is approximately the same in all Mg-Cu and Mg-Zn glasses. Its magnitude is not consistent with the predictions of the quantum correction theories. We have no explanation

for this observation. Above 6K the resistivity changes with temperature as predicted by the Faber-Ziman theory. The superconducting fluctuation conductivity in $Mg_{70}Zn_{30}$ and $Mg_{70}Zn_{27}Au_3$ is isolated. It decays as $exp(-\gamma\sqrt{t})$ with the reduced temperature $t = (T-T_c)/T_c$ which is in agreement with the theory of Ami and Maki.

To complete this chapter the following suggestions for further research on quantum corrections to the conductivity are made:

To understand the high field magnetoresistance in nonsuperconducting amorphous metals it is necessary to investigate the limitations of the weak localization theory and to improve it for large fields. Also, a more precise expression for the Cooper channel magnetoresistance with a better than approximate expression for the electron coupling g(B,T) is needed. Once the magnetoresistance is fully understood in non-superconductors, Larkin's expression for the Maki-Thompson superconducting fluctuation magnetoresistance has to be improved to give a correct description at all accessible magnetic fields.

Given that the weak localization theory is successful in simple weak scattering metallic glasses ($(k_{\rm F}l_{\rm e})^{-1} << 1$), its validity should be tested in systems at the strong scattering limit ($(k_{\rm F}l_{\rm e})^{-1} \approx 1$). A possible system for such a study is $Ca_{70}Mg_{30-x}Al_x$, where $(k_{\rm F}l_{\rm e})^{-1}$ varies between 0.05 and 0.4 (for x=0 and 30 respectively) while other material characteristics remain unchanged.

The non-linear behavior of the spin-orbit scattering rate at larger concentrations of spin-orbit scattering centers deserves further attention. In particular the point at which the spin-orbit scattering rate deviates from linear dependence in concentration should be examined in detail, in particular its dependence on the atomic number.

The proposed model for the dephasing of the weak localization quantum interference by ionic zero-point motion has to be put onto a solid theoretical footing. A more precise evaluation of the dephasing effectiveness is needed. Furthermore, experiments have to be devised to give a strict quantitative proof of the existence of the zero-point motion dephasing effect. The magnetoresistance measurements on the 0

simple metallic glasses presented in this thesis cannot be considered as such, as the total signal is very small. The experiments by Abraham and Rosenbaum on Cu-films with varying thickness, and by Bishop and coworkers on Si MOSFETs could be repeated in more detail to concentrate specifically on the saturation aspect.

APPENDICES

The expressions given in Chapter 2 for the temperature dependence of the quantum corrections to the resistivity in the absence of an applied field are quite easy to evaluate numerically. They involve only logarithms or square roots. This is not true of the expressions describing the magnetoresistance; they are presented in terms of either difficult infinite series or complicated integrals. For the sake of clearity their numerical evaluation was left out of Chapter 2 and will follow in appendix A. The development of efficient numerical algorithms is an important part of this thesis since there were approximately 120 data curves to analyze and some calculations had to be carried out many times with varying parameters. The calculation times involved are quite long (days) even with the fast SUN Microsystems workstation available. The numerical evaluation of Larkin's β -function is also given in appendix A. In appendix B the least squares fitting algorithm employed for the fitting is presented. The detailed listing of the program is omitted because it would just fill another 50 or more pages. In appendix C the kernel program containing the magnetoresistance equations is shown as a subroutine which is called by the least squares fitting program. It could in principle be used by any other fitting algorithm if details of the calling sequence are adjusted.

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Appendix A: Numerical Recipes

A.1 The f_3 -function

The weak localization magnetoresistance expression eq.2.23 by Fukuyama and Hoshino⁴⁹ and eq.2.24 by Altshuler and Aronov²⁰ as well as eq.2.35 by Larkin⁶⁸ describing the Maki-Thompson magnetoresistance due to superconducting fluctuations involve the function $f_2(x)$

$$f_{3}(x) = \sum_{n=0}^{\infty} a_{n}(x)$$

where
$$a_n(x) = 2\left(n+1+\frac{1}{x}\right)^{1/2} - 2\left(n+\frac{1}{x}\right)^{1/2} - \left(n+\frac{1}{2}+\frac{1}{x}\right)^{-1/2}$$

For large x this series converges only as $(1/n)^{3/2}$. This is so slow that one would have to sum more than 10^5 terms to achieve an accuracy better than 1%. Ousset and coworkers¹¹⁸ have presented an approximation that can be derived by truncating the Euler-MacLaurin asymptotic expansion of this series. Although many times faster than direct summation it is still quite cumbersome and a faster form would be handy since f_3 is likely to be called several times in some data fits. (The reader should note that the expression given by Ousset contains a typographical error, the exponent -3/2 on their last term should be -1/2.) A faster form for f_3 can be found⁶⁴ by explicitly summing the first two terms which gives $f_3(x) = 2\left[\left(2+\frac{1}{x}\right)^{1/2} - \left(\frac{1}{x}\right)^{1/2}\right] - \left[\left(\frac{1}{2}+\frac{1}{x}\right)^{-1/2} + \left(\frac{3}{2}+\frac{1}{x}\right)^{-1/2}\right] + R(x)$ (A.1.1)

with the remainder as

$$R(x) = \sum_{n=2}^{\infty} y^{1/2} \left\{ 2 \left[(1 + \frac{1}{2y})^{1/2} - (1 - \frac{1}{2y})^{1/2} \right] - \frac{1}{y} \right\}$$

where $y = n + \frac{1}{2} + \frac{1}{x}$

The remainder can be expanded in terms of 1/2y in a Taylor series yielding

$$R(x) = \sum_{N=2}^{\infty} \sqrt{y} \left[2\sqrt{1+1/2y} - 2\sqrt{1+1/2y} - 1/y \right]$$

Converting the summation into an integral and disregarding higher order terms gives

$$R(x) \approx \frac{(2.5 + 1/x)^{-3/2}}{48} + \frac{(2.5 + 1/x)^{-7/2}}{1024} + \cdots$$
 (A.1.2)

An accuracy of better than 0.1% is achieved if only the first term of R(x) is retained and the value of 2.5 in this term is replaced by 2.015 to give the proper asymptotic behavior, i.e $f_3(x \rightarrow \infty) = 0.6049$.

In the parameter range considered it is possible for γ in eq.2.23 to become larger than 1 for large fields B. This does not impose a serious problem. Examining the integral expression from which Maekawa and Fukuyama¹⁸ have calculated the conductivity in two dimensional conductors and which • Fukuyama and Hoshino⁴⁹ have extended for bulk conductors in eq.2.23, one finds that it is well defined for all applied fields. It is therefore legitimate to analytically continue equation eq.2.23. The imaginary terms cancel out. To do this one has to interchange analytical continuation with the series summation of the function f₃, which can still be approximated with the above expression A.1.1 and A.1.2. Exploiting the fact that B₊ and t₊ are the complex conjugates of B₋ and t₋ respectively, eq.2.23 turns into a lengthy expression involving terms of the form

$$\frac{2}{2i\sqrt{\gamma-1}} \left[(a + ib)^{p} - (a - ib)^{p} \right]$$
 (A.1.3)

such as $\frac{1}{2i\sqrt{v-1}}\left[\sqrt{t_+} - \sqrt{t_-}\right]$

$$=\frac{1}{2i\sqrt{\gamma-1}}\left[\left((t-1/2)+i\sqrt{\gamma-1}\right)^{1/2}-\left((t-1/2)-i\sqrt{\gamma-1}\right)^{1/2}\right]$$

which can be rewritten as

$$\frac{1}{\sqrt{\gamma-1}} \left[a^2 + b^2 \right] \sin \frac{\alpha}{2}$$

where $\alpha = \arctan \left(\frac{b}{a} \right)$

The exact details of this analytical continuation can be found in the program kernel rfit.c listed in appendix C. The calculation is easily checked; for large values of D eq.2.23 falls onto eq.2.24 given by Altshuler and Aronov²⁰ and no discontinuity was observed at $\gamma=1$.

A.2 The g_3 -function

The diffusion channel magnetoresistance expression in eq.2.29 derived by Lee & Ramakrishnan²¹ contains the integral

$$g_{3}(x) = \int_{0}^{\infty} d\omega \left[\frac{d^{2}}{d\omega^{2}} \left(\frac{\omega}{e^{\omega} - 1} \right) \right] \left[\sqrt{\omega + x} + \sqrt{|\omega - x|} - 2\sqrt{\omega} \right]$$
(A.2.1)

Ousset and coworkers¹¹⁸ presented a very useful approximation for $g_3(x)$, which was used for the data analysis in this thesis. It has an accuracy of better than 0.25%. For small x one can expand the square roots in eq.A.2.1 which yields a series

$$g_{3}(x) = \sum_{p=1}^{\infty} a_{p} x^{2p}$$

The coefficients a_p are determined by the integral. Ousset et al. have evaluated the function g_3 numerically in the range, x < 3, and fitted the result to a series of the above form. This gives

$$g_{3}(x) \approx 5.6464 \times 10^{-2} x^{2}$$

$$- 1.4759 \times 10^{-3} x^{4} + 4.2747 \times 10^{-5} x^{6}$$

$$- 1.5351 \times 10^{-6} x^{8} + 6 \times 10^{-8} x^{10}$$
(A.2.2)

Similarly they expanded the roots for large x in terms of ω/x . Evaluating the resulting series of integral they find that $g_3(x)$ can be approximated for $x \ge 8$ by

$$g_3(x) \approx x^{1/2} - 1.2942 - \frac{\pi^2}{12x^{3/2}}$$

$$-\frac{\pi^4}{16x^{7/2}} - \frac{5\pi^6}{32x^{11/2}}$$
(A.2.3)

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In the intermediate range, $3 \le h \le 8$ with u = h - 4, the authors fitted the numerically integrated function g_3 to a polynomial in u

which gives

$$g_3(\mathbf{x}) \approx 0.64548 + 0.235u - 7.45 \times 10^{-4}u^2$$

- 2.94 × 10^{-3}u^3 + 6.32 × 10^{-4}u^4
- 5.22 × 10^{-5}u^5

As a test we have integrated the function g₃ numerically at a few points using the integration routine "varint()" listed in appendix C. We found agreement with the above approximations by Ousset and coworkers within the quoted accuracy.

A.3 The Φ_3 and Φ_p functions

There are three different forms for the Cooper channel magnetoresistance. The expression given by Altshuler and Aronov⁶¹ involves the integral

$$\Phi_{3}(\mathbf{x}) = \left(\frac{\pi}{2\mathbf{x}}\right)^{1/2} \int_{0}^{\infty} dt \frac{t^{1/2}}{\sinh^{2} t} \left(1 - \frac{\mathbf{x}t}{\sinh(\mathbf{x}t)}\right)$$
(A.3.1)

For x << 1 one can exploit the fact that the asymptotic form of the integrand is governed by the $t^{1/2}/\sinh^2 t$ term and hence expand the bracket in terms of xt. Calculating the first few terms of the resulting series of integrals exactly and adjusting the 4th order term Ousset and coworkers¹¹⁸ find for x < 0.7

$$P_3(\mathbf{x}) \approx 0.3295 \ \mathbf{x}^{3/2} \stackrel{\frac{5}{2}}{-} 0.11894 \ \mathbf{x}^{7/2}$$
 (A.3.2)
+ 0.10753 $\mathbf{x}^{11/2} - 0.0636 \ \mathbf{x}^{6.63}$

A similar analysis for the limit $x \gg 1$ yields for x > 2.4

$$\Phi_3(\mathbf{x}) \approx 1.900344 - 2.29392 \mathbf{x}^{-1/2}$$

+ 1.2266h⁻² - 0.826h^{-3.5}
(A.3.3)

In the intermediate range,
$$0.7 \le x \le 2.4$$
,

$$\Phi_3(x) \approx -0.03043 + 0.22616 x + 0.14104 x^2$$
. (A.3.4)
- 0.10293 x³ + 0.02759 x⁴ - 0.0028 x⁵

According to Ousset et al. the accuracy of the above approximations is better than 0.025%. The reader should note that in their article the last coefficient is mistyped as 0.00028.

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(A.2.4)

The second Cooper channel magnetoresistance expression in eq.2.31 involves an integral $\mathbf{F}_{-1}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$. This integral differs from Φ_3 given above essentially only by a factor

$$\cos\left(\frac{g\mu_{B}^{B}}{\pi k_{B}^{T}} \cdot t\right) \exp\left(-\frac{4eDB_{S}}{\pi k_{B}^{T}} \cdot t\right)$$

which accounts for the Zeeman bandsplitting and the attenuation of the magnetoresistance due to magnetic spin scattering. In this case it is not possible to use the approximations for Φ_3 given above since the integrand is now a three parameter integral. Instead one has to integrate F_{-1} numerically for every set of parameters B, B_s , T individually. Because the term 1/sinh in the integrand causes a numerical integration to fail, the integral in eq.2.31 has to be split into two parts

$$\int_{0}^{\infty} dt f(B,B_s,T,t) = \int_{0}^{\epsilon} dt f(B,B_s,T,t) + \int_{\epsilon}^{\infty} dt f(B,B_s,T,t) \quad (A.3.5)$$

The first integral on the right hand side can be calculated explicitly for $\epsilon \ll 1$, i.e.

$$e^{3/2} \frac{x_1^2}{9} \left(1 - e^{\left(\frac{3x_3}{5} + \frac{e}{20}\right) \left(\frac{30(x_3^2 - x_2^2) - (7x_1^2 + 20)}{7} + x_3^2 + \frac{10(3x_2^2 - x_3^2) - (7x_1^2 + 20)}{9} + \cdots \right)}{10(3x_2^2 - x_3^2) - (7x_1^2 + 20)} + \cdots \right)$$

(A.3.6)

and the second integral is calculated by the routine "varint()" given in appendix C. For more details of the calculation the reader is refered to the relevant program parts in appendix C. It is found that the exponetial term describing magnetic impurity scattering effects is not important for magnetic impurity levels of less than 3ppm Mn and can therefore be neglected in our samples. Similarly it is found that the Zeeman splitting term is small (see Fig.2.11) if the electron diffusivity is as large as in the Mg-based metallic glasses studied here. The above approximation for Φ_3 given by Ousset et al. is therefore good enough for our purposes (if the missing factor of $1/\pi$ in eq.2.30 is taken into account). Isawa and Fukuyama²² have derived yet another form of the Cooper channel magnetoresistance (eq.2.32). It is expressed in terms of the series

$$\Phi_{\mathbf{F}}(\mathbf{B},\mathbf{B}_{\mathbf{i}},\mathbf{T}) = \sum_{k=1}^{\infty} k \left[\zeta \left(\frac{5}{2}, \frac{1}{2} + \frac{k+\gamma}{\gamma h} \right) - \frac{2}{3} \left(\frac{\gamma h}{k+\gamma} \right)^{3/2} \right]$$
(A.3.7)
where $\gamma = \frac{2 \text{DeB}_{\mathbf{i}}}{\pi k_{\text{B}} T}$ and $h = B/B_{\mathbf{i}}$

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ζ(s,z) stands for the generalized Riemann Zeta-function,

i.e.
$$\zeta(s,z) = \sum_{n=0}^{\infty} (n+z)^{-s} d$$

Again, as the f_3 -function, Φ_F is a very slowly converging series. At first glance one is tempted to accelerate its convergence by using the Euler-MacLaurin summation formula:

$$F(n) = \sum_{k=0}^{n} f(k) = \sum_{k=0}^{N-1} f(k) + R(N,n)$$
 (A.3.8)

$$R(N,n) = \frac{1}{2}f(n) + \int_{0}^{n} f(N+t)dt + C + \sum_{j=1}^{\infty} (-1)^{j+1} \frac{B^{j+1}}{(j+1)N_{o}} f^{(j)}(N+n)$$

where $C = \lim_{m \to \infty} \left[\sum_{j=1}^{m} \frac{(-1)^{j} B_{j+1}}{(j+1)!} f^{(j)}(N) + \frac{1}{2} f(N) \right]$

+
$$\frac{(-1)^{m}}{(m+1)!} \int_{0}^{\infty} dt B_{m+1}(t-[t]) f^{(m+1)}(t) \bigg]$$

B are the Bernoulli numbers. Up to the 4^{th} order one can express the Euler MacLaurin expansion as

$$F(n) = \sum_{\substack{k=0\\n}}^{n} f(k)$$

= $\int_{0}^{n} dk f(k) - \frac{1}{2}[f(N) + f(0)]$
+ $[f'(N) - f'(0)] - \frac{1}{720}[f'''(N) - f'''(0)] + \cdots$

It turns out that the Euler-MacLaurin expansion cannot be applied directly to Φ_p because the integral of the second term in the brackets of eq.A.3.7 diverges. One can avoid this bothersome problem if one applies the Euler-MacLaurin expansion first to the ζ -function. This gives

$$\zeta(s,z) = \sum_{n=0}^{N-1} \frac{1}{(n+z)^{s}} + \frac{1}{(s-1)(N+z-1)^{s-1}} - \frac{1}{2(N+z-1)^{s}}$$
(A.3.9)
+ $\frac{B_{2}s}{(N+z-1)^{s+1}} + \frac{B_{4}s(s+1)(s+2)}{2(N+z-1)^{s+3}}$

For s = 5/2 with N = 10 the accuracy is better than one in 10^7 . Using this expression for the ζ -function one can rewrite Φ_p as

$$\begin{split} \mathfrak{Q}_{p}(\mathbf{B},\mathbf{B}_{1},\mathbf{T}) &= \sum_{k=1}^{\infty} f(k) \end{split} \qquad (A.3.10) \\ \text{with } f(k) &= k \left[\sum_{n=0}^{N-1} \left(n + \frac{1}{2} + \frac{1}{h} + \frac{k}{\gamma h} \right)^{-5/2} \\ &+ \frac{3}{2} \left[\left(N-1 + \frac{1}{2} + \frac{1}{h} + \frac{k}{\gamma h} \right)^{-3/2} - \left(\frac{1}{h} + \frac{k}{\gamma h} \right)^{-3/2} \right] \\ &- \frac{1}{2} \left(N-1 + \frac{1}{2} + \frac{1}{h} + \frac{k}{\gamma h} \right)^{-5/2} \\ &+ \frac{5}{12} \left(N-1 + \frac{1}{2} + \frac{1}{h} + \frac{k}{\gamma h} \right)^{-7/2} \\ &- \frac{21}{32} \left(N-1 + \frac{1}{2} + \frac{1}{h} + \frac{k}{\gamma h} \right)^{-11/2} \right] \end{split}$$

We carry out this summation explicitly to the M^{th} term and expand remaining sum over k in an Euler-MacLaurin series up to the third derivative in f(k). The integration of the term of power -3/2 in the second row is now well defined. Instead of explicitly presenting the results here, which would fill another three or four pages, the reader is referred for details to the source code of the program kernel listed

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in appendix C. It was found that the an accuracy of better than 0.1 with good speed is achieved with N=10-and-N=5.

The consistency of the various numerical evaluations of the Cooper channel magnetoresistance is best demonstrated by the fact that they give the same results for B<3T (if the same electron coupling g(B,T) is used and $\alpha = 1/\pi$ in eq.2.30).

A.4 Larkin's β -function

Larkin's β -function⁶⁸ describing the temperature dependence of the coupling between superconducting fluctuations and normal electrons, is defined as

$$\beta(T) = \frac{\pi^2}{4} \sum_{m=-\infty}^{\infty} (-1)^m \Gamma(|m|) - \sum_{m=0}^{\infty} \Gamma''(2m+1)$$

$$= \frac{\pi^2}{4} \Gamma(0) + \frac{\pi^2}{2} \sum_{m=1}^{\infty} \left[\Gamma(2m) - \Gamma(2m-1) \right] - \sum_{m=0}^{\infty} \Gamma''(2m+1)$$
(A.4.1)

with
$$\Gamma(m) = \left[\operatorname{sign} \cdot \left(\psi(m+1/2) - \psi(1/2) \right) + \ln(T/T_c) \right]^{-1}$$

 ψ is the digamma function. In Larkin's paper⁶⁸ the sign in the definition of the function Γ is negative (sign=-1). Since $\ln(T/T_c)$ is positive this implies an unphysical singularity at certain values of $T/T_c > 1$. Lopes Dos Santos and Abrahams⁶³ have rederived the β -function and in their definition Γ is written with a positive sign (in this definition m carries factor of 1/2 in the argument of ψ which is however a mistake⁶⁹). To check the table of values that Larkin published for the β -function we have calculated $\beta(T/T_c)$ using the following simple approximation. The first M-1 terms of the first series in eq.A.4.1 are added up explicitly. Using the Euler-MacLaurin expansion to first order, the remainder, R_1 , of the first series is estimated as

$$R_{1}(M) \approx \int_{M}^{\infty} dm \left(\Gamma(2m) - \Gamma(2M-1) \right) - \frac{1}{2} \left(\Gamma(2M) - \Gamma(2M-1) \right) + \cdots \qquad (A.4.2)$$

 $\approx -\frac{1}{2\left[\psi(2M)-\psi(1/2)+\ln(T/T_c)\right]} \left(1-\frac{1}{2M\left[\psi(2M)-\psi(1/2)+\ln(T/T_c)\right]}\right)$

The accuracy of the remainder depends critically on the size of 2M since only the first order asymptotic form of the digamma function (i.e. $\psi(m>>1) = \ln(m)$) was used to evaluate the integral in eq.A.4.2. This is the a crucial part of the approximation. Similarly one can sum the first M-1 terms of the second series in eq.A.4.1 and estimate the remainder, R₂, as

$$R_{2}(M) \approx \frac{(2M+1) + 1/2}{2[(2M+1)(\ln(2M+1) - \psi(1/2)) - 1/2]^{2}}$$
(A.4.3)

The second series has essentially converged for M=2000. To test the very bad convergence of the first series in eq.A.4.1 and the very approximate evaluation of the remainder β was calculated for several values of M ($M-1=10^{P}-1$, p=4, 5, 6). Since the convergence was still very poor, a Shank's transformation in p was used to compute the final result, i.e

$$\beta \approx \frac{\beta(p=4) \cdot \beta(p=6) - \beta^2(p=5)}{\beta(p=4) + \beta(p=6) - 2\beta(p=5)}$$
(A.4.4)

The results are the same within 3% as those calculated by an explicit numerical integration of the remainder⁶⁴ with the routine "varint()" listed in the appendix C. A plot of our results compared to Larkin's⁶⁸ is shown in Fig.2.13. They differ by about 30%. The source code beta.c for our calculation of the β -function is given in appendix C. Our calculation also includes the effects of inelastic electron-phonon scattering on β according to considerations by Lopes Dos Santos and Abrahams⁶³ (they are however negligible for the alloys discussed here).

Appendix B: Non-Linear Least-Squares Fitting

¹ For the comparison of the experimental magnetoresistance data presented in Chapter 4.1 with the theoretical expressions of the quantum corrections to the conductivity in Chapter 2 a non-linear least-squares fitting algorithm was used. The algorithm follows closely the procedures developed by Marquardt¹¹⁹. Some of its details are discussed in the following section, for further information the reader is referred to Bevington¹²⁰.

Suppose (x_i, y_i) is a set of experimental data (e.g. $(B, \Delta \rho / \rho)$) and y=f(x, \vec{a}) is a model function depending on a set of unknown parameters $\vec{a} = (a_1, \ldots, a_n)$. For a certain set of parameters the model function is supposed to reproduce the average data function $\langle y_i(x_i) \rangle$. As the parameters \vec{a} (e.g. (B_{ϕ}, B_{SO})) are not known one has to adjust (fit) them until an optimal correspondence between data and model is found. One can define a measure for the quality of the fit (giving the method its name) as

$$\chi^{2}(\vec{a}) = \sum_{i} \frac{1}{\sigma_{i}^{2}} (y_{i} - f(x_{i}, \vec{a}))^{2}$$

An optimal fit is reached for a set of parameters \sqrt{a} at which χ^2 is minimized, i.e.

$$\vec{\nabla}_a \chi^2(\vec{a}) = 0 \tag{B.2}$$

The minimization problem can be visualized by noting that eq.B.1 defines a hypersurface in the (χ^2, \vec{a}) space and eq.B.2 a local minimum (maximum) on the surface. There are three fundamental problems with non-linear least-squares fits: (i) The optimized parameters are meaningless if a model function is used that is in principle not capable of describing the full set of data because, for example, it neglects an essential part of the physical reality of the system investigated. The only cure for this problem is to optimize the model function or to truncate the data to the regime where the model function is in principle correct. (ii) The χ^2 surface may well have more than one minimum, and the absolute minimum 7:

(B.1)

may not necessarily correspond to a physically meaningful set of parameters. This problem is usually solved by constraining the parameters to a regime one considers physically meaningful and which contains only one minimum. Admittedly this introduces some bias. In the present case of fitting the magnetoresistance this problem fortunately does not appear as the χ^2 surface is well behaved. (iii) A time efficient search algorithm must be constructed which leads iteratively from an initial point in parameter space, \vec{a}_0 (the "educated guess"), to the point \vec{a} at which χ^2 has its minimum. There are several powerful algorithms listed in the literature.

The very efficient algorithm proposed by Marquardt combines the gradient search and linear expansion techniques 120^{120} . It starts at an initial set of parameters \vec{a}_0 and decreases χ^2 by incrementing the parameters by

$$B\vec{a} = B^{-1} \cdot \vec{\beta} \tag{B.3}$$

(B.4)

where $B = A - I\lambda$ with $\lambda > 0$.

I is the unit (identity) matrix. The matrix A (known as the curvature matrix) is defined as (with $f_0(x_i)=f(x_i, \vec{a}_0)$)

$$A_{ij} = \frac{1}{2} \frac{\partial^2 \chi^2(\vec{a}_0)}{\partial a_i \partial a_j}$$
(B.5)
$$= \sum_{i} \frac{1}{\sigma_i^2} \left[\frac{\partial f_0(x_i) \partial f_0(x_i)}{\partial a_j \partial a_k} - (y_i^{-i} f_0(x_i)) \frac{\partial^2 f_0(x_i)}{\partial a_j \partial a_k} \right]$$

The vector β which points in the direction of steepest descend of the χ^2 hypersurface is defined as

$$\beta_{k} = -\frac{1}{2} \frac{\partial \chi^{2}(\vec{a}_{o})}{\partial a_{k}}$$

$$= \sum_{i} \frac{1}{\sigma_{i}^{2}} \left(y_{i} - f(x_{i}, \vec{a}_{o}) \right) \frac{\partial f(x_{i}, \vec{a}_{o})}{\partial a_{k}}$$
(B.6)

The linear equation in eq.B.3 can be solved using numerical matrix

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inversion techniques listed in reference 121. To simplify and accelerate the computation of the matrix elements A_{jk} , one can make use of the fact that the parameters, a_j , are uncorrelated to a large degree so that the second order derivatives in eq.B.6 are negligible, i.e

$$A_{jk} \approx \sum_{i} \frac{1}{\sigma_{i}^{2}} \left(\frac{\partial f(x_{i}, \bar{a}_{0})}{\partial a_{j}} \frac{\partial f(x_{i}, \bar{a}_{0})}{\partial a_{k}} \right)$$
(B.7)

The partial derivatives of the model function, $f(x_1, \vec{a})$, are computed by

$$\frac{\partial f(x_{i}, \vec{a})}{\partial a_{j}} \approx \frac{f(x_{i}, a_{j} + \Delta a_{j}) - f(x_{i}, a_{j} - \Delta a_{j})}{2\Delta a_{j}}$$
(B.8)

(B.9)

The step sizes Δa_j are chosen so that the value for the partial derivative does not change by more then 10% if the step size is reduced by a factor of 10 and the numerator on the right hand side is larger than 0.01% of the value of $f_0(x_i)$.

For large λ , the diagonal terms of the matrix B in eq.B.4 are dominant and the components of the increment vector $\delta \vec{a}$ in eq.B.3 are therefore very close to

$$\delta a_{j} \approx \frac{\beta_{j}}{\lambda |A_{jj}|}$$

In this case the parameters are incremented along the steepest descent of χ^2 , which is the direction a gradient search routine would take. This path direction on the χ^2 surface is particularly efficient far away from the minimum of χ^2 , it is mpt optimal close to the minimum. For small λ the increment vector calculated with eq.B.3 does not point along the the direction of steepest descent any longer. In fact it points in a direction almost orthogonal to it. In this case the path direction on the χ^2 surface is the same as would be predicted by a linear expansion type algorithm. It is particularly efficient close to the χ^2 minimum. The obvious problem, the choice of the size of λ , is circumvented by adopting the iterative search procedure Marquardt proposed:

- i) calculate χ^2 at the starting point \vec{a}_0 first, set $\lambda = 0.001$,
- ii) calculate the inverse matrix B^{-1} in terms of λ , $\delta \vec{a}$ and $\chi^2(\vec{a}, +\delta \vec{a})$,
- iii) if $\chi^2(\vec{a}_0 + \delta \vec{a}) > \chi^2(\vec{a}_0)$
 - multiply λ by 10 and repeat ii'),
 - if $\chi^2(\vec{a}_0 + \delta \vec{a}) < \chi^2(\vec{a}_0)$
 - divide λ by a factor of 10, define $\vec{a} = \vec{a}_{A} + \delta \vec{a}$
 - as the new starting point and repeat ii).

With this algorithm λ will always have the appropriate size, it will be large far away from the χ^2 minimum and small close to it. Even if the choice of λ and thus $\delta \vec{a}$ is not optimal at one particular iteration step, the χ^2 will decrease and the algorithm will compensate for it in the next step and keep no further memory. The iteration towards the χ^2 minimum is stopped if

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(B.10)

 $\frac{\chi^2(\vec{a}+\delta\vec{a}) - \chi^2(\vec{a})}{\chi^2(\vec{a})} < \epsilon$

e is usually chosen between 1% and 0.001%.

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13

1) P. Duwez, in "Glassy Metals I",

edited by H.-J. Güntherodt and H. Beck, Topics of Applied Physics Vol.46, Springer-Verlag, Berlin, 1981

2) T. Egami, in "Glassy Metals I" (see reference 1)

3) K. Suzuki, in "Amorphous Metallic Alloys", edited by F. E. Luborsky, Butterworths, London, 1983

4) a good overview is found in relevant sections of the proceedings of the 5th International Conference on Rapidly Quenched Metals, compiled in "Rapidly Quenched Metals",

edited by S. Steeb and H. Warlimont,

North-Holland, Amsterdam, 1985,

and the proceedings of the 6th International Conference on Rapidly Quenched Metals, to be published in Mat. Sci. Eng. 1988

- 5) U. Köster and U. Herold in "Glassy Metals I" (see reference 1)
- J. O. Strom-Olsen in the proceedings of the "Summer School on Amorphous Metals", Wilja, Poland, 1985, edited by H. Matyja and P. G. Zielinsky, World Scientific, Philadelphia, 1986

7) U. Mizutani, Prog. Mat. Sci. <u>28(2)</u>, 97 (1983)

8) J. H. Mooij, Phys. Stat. Solidi (a) <u>17</u>, 521 (1973)

- 9) R. Richter, D. V. Baxter, J. O. Strom-Olsen, to be published
- (0) M. Trudeau, Ph.D. Thesis, University of Montreal, Montreal, 1986
- 11) R. W. Cochrane, R. Harris, J. O. Strom-Olsen

and M. J. Zuckermann, Phys. Rev. Lett. <u>35(10)</u>, 676 (1975)

, •	-206-	
12)	R. Harris and J. O. Strom-Olsen in "Glassy Me	etals II",
	edited by H. Beck and HJ. Guntherodt,	, • , •
~ '	Topics in Applied Physics Vol.53,	• •
	Springer-Verlag, Berlin, 1983	· · · ·
13).	E. Abrahams, P. W. Anderson, D. C. Licciardel	10 2, 673 (1979)
14)	B. L. Altshuler and A. G. Aronov, Sov. Phys. JETP <u>50(</u> 5), 968 (1979)	•
15)	D. J. Thouless, Phys. Rev. <u>C13</u> , 93 (1973)	
.16)	J. S. [°] Langer and T. Neal, Phys. Rev. Lett. <u>16(22)</u> , 984 (1966)	ي يوسو المحمد
17)	P. W. Anderson, E. Abrahams and T. V. Ramakri Phys. Rev. Lett. <u>43</u> (10), 718 (1979)	shnan,
18)	S. Maekawa and H. Fukuyama, J. Phys.₂Soc. Japan <u>50</u> (8), 2516 (1981)	~ .
19)	G. Bergmann, Phys. Reports <u>107</u> (1), 1 (1984)	, , , , , , , , , , , , , , , , , , ,
20)	B. L. Altshuler and A. G. Aronov in	* . • • • • • • • •
-	edited by A. L. Efros and M .Pollak,	eu systems ,
21)	P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. <u>57</u> (2), 287 (1985)	ب م ع
22)	Y. Isawa and H. Fukuyama, J. Phys. Soc. Japan <u>53</u> (4), 1415 (1984)	• • • • • •
23)	"Electron-Electron Interaction in Disordered edited by A. L. Efros and M. Pollak,	Systems",
•		• • • • • • • • • • • • • • • • • • • •
24) _«	G. Bergmann, Z. Phys. B <u>48</u> , 5 (1982)	e
25)	J. B. Bieri, A. Fert and G. Fert, Sol. State Comm. <u>49</u> (9), 849 (1984)	، ، ، م ر م
	•	· · · · ·

- 26) S. J. Poon, E. J. Cotts and K. M. Wong, Sol. State Comm. <u>52(5)</u>,519 (1984)
- 27) M. Olivier, J. O. Strom-Olsen, Z. Altounian,
 R. W. Cochrane and M. Trudeau,
 Phys. Rev. B<u>33</u>(4),2799 (1986)
- 28) M. A. Howson, B. J. Hickey and C. Shearwood, J. Phys. F<u>16</u>,L175 (1986)
- 29) A. Schulte, Sol. State Comm. <u>60</u>(2),99 (1986)
- 30) M. Olivier, J. O. Strom-Olsen and Z. Altounian, Phys. Rev. B<u>35</u>(1),333 (1987)
- 31) F. Küss, A. Schulte, P. Löbl, E. Lüscher and G. Fritsch, Proceedings of Nato Advanced Summer Schoel on Liquid and Amorphous Materials, La Mandola, Italy, 1985
- 32) J. B. Bieri, A. Fert, G. Creuzet and A. Schuhl, J. Phys. F<u>16</u>,2099 (1986)
- 33) U. Mizutani and K. Yoshino, J. Phys. F<u>12</u>,2331 (1982)
- 34) U. Mizutani and K. Yoshino, J. Phys. F14,1179 (1984)
- 35) T. Matsuda, U. Mizutani and S. Sato, J. Phys. F<u>16</u>,1005 (1986)
- 36) T. Matsuda and U. Mizutani, J. Phys. F<u>12</u>,1877 (1982)
- 37) R. Van den Berg, S. Grondey, J. Kästner and H. v. Löhneysen Sol. State Comm. <u>47</u>(2),137 (1983)

{ ۱

- 38) N. W. Ashcroft and N. D. Mermin, "Solid State Physics", Saunders College, Philadelphia, 1976
- 39) G. D. Mahan, "Many-Particle Physics", Plenum Press, New York, 1981
- 40) D. K. C. MacDonald and K. Mendelsohn, Proc. Roy. Soc. A<u>202</u>, 103 (1950)
- 41) D. Gugen, Proc. Roy. Soc. A<u>325</u>, 223 (1971)

42)) (J. M. Ziman, "Principles of the Theory of Solids", Cambridge University Press, 1964
43)) J. O. Strom-Olsen, Proc. Roy. Soc. A <u>302</u> , 83 (1967)
44)	N. F. Mott and H. Jones,
	Dover Publications, New York, 1958
45)	S. Chakravartry and A. Schmid, Phys. Rep. <u>140</u> (4), 193 (1986)
46)	A. Kawabata, Sol. State Comm. <u>34</u> , 431 (1980)
47)	R. Berkowits and M. Kaveh, J. Phys. C <u>20</u> , L181 (1987)
48)	H. Fukuyama in
	"Electron-Electron Interaction in Disordered Systems", edited by A. L. Efros and M. Pollak, North-Holland, 1985
49)	H. Fukuyama and K. Hoshino, J. Phys. Soc. Japan <u>50</u> (7), 2131 (1981)
50)	S. Hikami, A. L. Larkin and Y. Nagaoka, Prog. Theor. Phys. <u>63(</u> 2), 707 (1980)
51)	H. Takayama, Z. Phys. <u>263</u> , 329 (1973)
52)	A. Schmid, Z. Phys. <u>271</u> , 251 (1974)
53)	N. R. Werthamer, E. Helfand and P. C. Hohenberg, Phys. Rev. <u>147</u> , 295 (1966)
54)	K. M. Wong, E. J. Cotts and S. J. Poon, Phys. Rev. B <u>30(</u> 3), 1253 (1984)
55)	B. J. Hickey, D. Greig and M. A. Howson, J. Phys. F <u>16</u> , L13 (1986)
56)	MT. Béal-Monod and R. A. Weiner, Phys. Rev. <u>170</u> (2), 552 (1968)
57)	K. Yosida, Phys. Rev. <u>407</u> (2), 396 (1957)
58)	M. Trudeau and R. W. Cochrane, to be published

- 208 -

ş

C

d

\$. 7

59)	G. Bergmann, Phys. Rev. B <u>35(9)</u> , 4205 (1986)
60)	P. A. Lee and T. V. Ramakrishnan, Phys. Rev. B <u>26(8)</u> , 4009 (1982)
61)	B. L. Altshuler, A. G.Aronov, A. I. Larkin and D. E. Khmelniskii, Sov. Phys. JETP <u>54(2)</u> , 411 (1981)
62)	W. L. McLean and T. Tsuzuki, Phys. Rev. B <u>29(1)</u> , 503 (1984)
63)	J. M. B. Lopes dos Santos and E. Abrahams, Phys. Rev. B <u>31(1), 172 (1985)</u>
64)	R. Richter, D. V. Baxter and M. Trudeau, to be published
65)	S. Ami and K. Maki, Phys. Rev. B <u>18</u> (9), 4714 (1978)
66)	W. L. Johnson and C. C. Tsuei, Phys. Rev. B <u>13(</u> 11), 4827 (1976)
67)	B. L. Altshuler, A. A. Varlamov and M. Y. Reizer, Sov. Phys. JETP <u>57</u> (6), 1329 (1983)
[.] 68)	A. I. Larkin, Sov. Phys. JETP Lett <u>31(</u> 4), 221 (1980)
69)	E. Abrahams, private communication
70)	J. Kondo, Prog. Theor. Phys. <u>32(</u> 1), 37 (1964)
71)	R. W. Cochrane, J. O. Strom-Olsen, G. Williams and S. C. Ho, Phys. Rev. B <u>17(1)</u> , 254 (1978)
72)	R. W. Cochrane, F. T. Hedgcock and J. O. Strom-Olsen, Phys. Rev. B <u>8</u> (9), 4262 (1973)
73)	Z. Altounian, E. Batalla, J. O. Strom-Olsen and J. L. Walter, J. Appl. Phys. <u>61(1)</u> , 149 (1987)
74)	Z. Altounian, Tu Guo-hua and J. O. Strom-Olsen, J. Appl. Phys. <u>54(6)</u> , 3111 (1983)
75)	G. Revel, J. L. Pastol, J. C. Rouchaud and R. Fromgeau Metall. Transactions B <u>9B</u> , 665 (1978)
76)	"CRC Handbook of Chemistry and Physics", edited by R. C. Weast, CRC Press, 1986
	∼ . "

۱

- 77) "Binary Alloy Phase Diagrams" Vol. 1 and 2, edited by T. B. Massalski, American Society for Metals, 1986
- 78) A. Calka, J. Phys. F<u>16</u>, 1577 (1986)
- 79) R. Richter, M.Sc. Thesis, McGill University, Montreal, 1984
- 80) G. Marshall, M.Sc. Thesis, McGill University, Montreal, 1984
- 81) U. Köster, U. Herold, H.-G. Hillenbrand, Script. Metall. <u>17</u>, 867 (1983)
- 82) H. E. Kissinger, Anal. Chem. <u>29</u> (11), 1702 (1957)
- 83) Z. Altounian, Tu Guo-Hua and J. O: Strom-Olsen, J. Mat. Sci. <u>17</u>, 3268 (1982).
- 84) JCPDS Powder Diffraction Files International Center for Diffraction Data, Pennsylvania, USA
- 85) L. N. Mulay, "Magnetic Susceptibilty", Interscience, New York, 1963
- 86) R. T. Lewis, Rev. Sci. Instrum. <u>42</u>, 31 (1971)
- 87) A. Cambron, M.Sc. Thesis, McGill University, Montreal, 1984
- 88) R. M. White, "Quantum Theory of Magnetism", Springer-Verlag, Berlin, 1983
- 89) R. Dupree and E. F. W. Seymour, in "Liquid Metals, Chemistry and Physics", edited by S.Z.Beer, Marcel Dekker Inc., New York, 1972
- 90) D. de Soete, R. Gijbels and J. Hoste, "Neutron Activation Analysis", John Wiley and Sons, New York, 1972
- 91) U. Mizutani, J. Hashizumi and T. Matsuda, J. Phys. Soc. Japan <u>55</u>, 3188 (1986)
- 92) H. S. Chen, Rep. Prog. Phys. <u>43</u>, **23** (1980)

- 93) R. W. Cochrane, B. J. Kästner and W. B. Muir, J. Phys. <u>E15</u>, 425 (1982).
- 94) O. V. Lounasmaa, "Experimental Principles and Methods below 1K" Academic Press, 1974
- 95) G. Bergmann, Phys. Rev. Lett. <u>48</u>(15),1046 (1982)
- 96) Y. Isawa, J. Phys. Soc. Jap. <u>53</u>, 37 (1984).
- 97) E. Merzbacher, "Quantum Mechanics" John Wiley and Sons, New York; 1970
- 98) R. P. Peters, G. Bergmann and R. M. Mueller, Phys. rev. Lett. <u>58(19)</u>, 1964 (1987)
- 99) D. Abraham and R. Rosenbaum, Phys. Rev. B<u>27(2)</u>, 1413 (1983)
- 100) B. J. Hickey, D. Greig and M. A. Howson, Phys. Rev. B<u>36</u>(6), 3074 (1987)
- 101) A. Schulte and G. Fritsch, J. Phys. F<u>16</u>,L55 (1986)
- 102) J. Hafner in "Glassy Metals I" (see reference 1)
- 103) J. J. Lin and N. Giordano, Phys. Rev. B<u>35(3)</u>, 1071 (1987)
- 105) C. Van Haesendonck, J. Vranken and Y. Bruynseraede, Phys. Rev. Lett. <u>58(19)</u>, 1968 (1987)
- 106) G. Bergmann, Phys. Rev. Lett. <u>57</u>(12), 1460 (1986)
- 107) G. Bergmann, Sol. State Comm. <u>46(4)</u>, 347 (1983)
- 108) N. Kumar, D. V. Baxter, R. Richter and J. O. Strom-Olsen, Phys.Rev.Lett. <u>59</u>, 1853 (1987).
- 109) L. von Heimendahl, J. Phys. F<u>9</u>(2), 161 (1979)
- 110) J.-B. Suck, H. Rudin, H.-J. Güntherodt and H. Beck J. Phys. C<u>13</u>, L1045 (1980)

-211 -

a

111) J. Kästner and R. Mölleken in proceedings of the International Conference on Localization, Interaction and Transport Phenomena in Impure Metals, edited by L. Schweitzer and B. Kramer, Suppl. PTB-PG-1 Physikalische Technische Bundesanstalt, Braunschweig Federal Republic of Germany, 1984 112) J. Kästner and E. F. Wassermann, J. Low Temp. Phys. 29(5/6), 411 (1977) 113) D. V. Baxter, R. Richter and J. O. Strom-Olsen, Phys. Rev. <u>B35(10)</u>, 4819 (1987), and references therein 114) S. J. Poon, K. M. Wong and A. J. Drehman Phys. Rev. B<u>31(3)</u>, 1668 (1985) 115) D. J. Newson, M. Pepper, E. Y. Hall and G. Hill, J. Phys. C20, 4369 (1987) 116) T. Matsuda and U. Mizutani, Sol. State Commun. <u>44(2)</u>, 145 (1982) Mg-Cu 117) L. V. Meisel and P. J. Cote, Phys. Rev. B27(8), 4617 (1983) 118) J. C. Ousset, S. Askenazy, H. Rakoto and J. M. Broto, J. Physique <u>46</u>, 2145 (1985) 119) D. W. Marquardt, J. Soc. Ind. Appl. Math. <u>11(2)</u>, 431 (1963) 120) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969 121) W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, "Numerical Receipes", Campridge University Press, 1986 122) G. Bergmann, Phys. Rev. B28(2), 515 (1983) 123) W. L. McMillan, Phys. Rev. <u>167</u>(2), 331 (1968)