Novel Magnetoelectronic Materials and Devices, 1999-2000

Preface

This is a compilation of the notes of a lecture series on Novel Magnetoelectronic Materials and Devices, that I presented at the Applied Physics Department of the Eindhoven University of Technology in the period September 1999 to June 2000. The lecture series will be continued in the new season, starting in September 2000. The tentative plan (version September 1999) of the full lecture series is given on the next pages. In the 1999-2000 season this scheme was followed quite closely, although the numbering is different. E.g., the original section 2.1 has been split in sections 2.1-2.3.

The lecture series is about novel magneto-electronic effects in nanostructured magnetic materials and devices. Often, in physics novel effects occur upon decreasing (at least) one of the structural dimensions of a system to values smaller than a relevant physical length scale. By decreasing the external and internal structural dimension(s) of magnetic materials and devices to nanometer scale values several exciting novel effects have been found during the last decade. Examples are the discovery of the giant magnetoresistance effect and the tunnel magnetoresistance effect. As the progress in the field of nanotechnology, which has enabled these discoveries, continues, it is likely that during the coming years other novel effects will be observed. The first driving force of the still expanding field of magnetoelectronics is therefore scientific curiosity. The second driving force is the prospect for applications of some of these effects in economically important areas. E.g. magnetic disk storage, nonvolatile solid state storage, magnetic sensors. However, I think that the importance of the field is in fact much wider. The dimensions of the key electronic components in the information, communication and sensor technology are now decreasing from the micrometer scale to the nanometer scale. In many cases these devices are based on non-magnetic metals, semiconductors, oxides, or in the future even on conducting polymers or biomolecules. In such materials the same transitions to new regimes in electronic transport are present, as observed for magnetic systems. However, when studying the electrical conduction of non-magnetic systems, the unique possibility to employ magnetic degrees of freedom for making reversible well controlled changes of the system is absent. Therefore, progress in magnetoelectronics will certainly have impact on progress in other fields of nanoelectronics.
The lecture series has been prepared for last-year pregraduate students, PhD students, postdocs, staff. The purposes are:

1. Bridging the gap between lectures on basic solid state physics and electronics, and advanced scientific and application oriented research on nanoscale magnetic devices.
2. Enabling participants to judge better which scientific and technological advances would really make a difference. Which effects, which devices are really interesting from an industrial point of view, and how can the product potential of new developments be assessed?

I have chosen to start with discussions of rather fundamental aspects of the magnetism of metals and compounds, and of transport (Chapter 2). This has the advantage of providing a broad framework and the required terminology for later discussions on new developments in the field of magnetoelectronics, in line with purpose (1) mentioned above. It has the disadvantage that it does not always immediately connect to the daily work. Helpful material on GMR, TMR and other magnetoelectronic devices can already be found in my lecture notes ‘New Magnetoelectronic Materials and Devices’, parts I and II, that I presented in the period 1996-1998 at the University of Amsterdam (available at the secretariat of the work group Physics of Nanostructures, or from the author). Also older lecture notes presented at the UvA (‘Giant Magnetoresistance’ and ‘Domain Wall Magnetoresistance’) can still be useful (available from the author). In order to enhance awareness of possible future developments (purpose (2)) I have included in the lectures discussions on special topics. Often, the subject was a recent paper or preprint. There are no formal lecture notes on these special topics. A subject title list and some references are included below, and copies of transparencies are available from the author.

Reinder Coehoorn
Eindhoven, September 2000

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Contact address: prof. dr. R. Coehoorn, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands. Email: reinder.coehoorn@philips.com.
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(provisional, lectures have/will not be presented necessarily precisely in this order, special hot topics may be discussed as an intermezzo)

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No lecture notes. Copies of transparancies available from the author.


- **Magnetoresistance of antiferromagnetic intermetallic compounds**.


- A new generation of magnetic hard disk media?
  See also www.research.ibm.com/news.

- Impressions from the NATO-ASI on Magnetic Storage Systems beyond the year 2000, Rhodes, June 2000.
1. Introduction

1.1. Mesoscopic magnetic systems

This is a series of lectures on magnetic materials and devices of which the electrical resistance is changed by a change of the internal magnetic structure on a nanometer scale. Such a change is usually the result of the application of a magnetic field. In the past ten years fascinating scientific and technological developments, real breakthroughs, have taken place in this field.

Using deposition in ultrahigh vacuum systems, it has become possible in the 1980s to fabricate in a well-controlled manner layered magnetic structures with layer thicknesses down to one atomic layer (one monolayer (ML)). This corresponds to a layer thickness of ≈0.2 nm (depending on the crystalline growth direction) for 3d-transition metal atoms such as Fe and Co. It is possible to create entirely new magnetic materials, by combining ferromagnetic (F), antiferromagnetic (AF) and non-magnetic (NM) metallic, oxidic and sometimes semiconducting layers. Their magnetic properties can often be tuned nicely by making use of various types of magnetic interactions which are related to the presence of interfaces and which are therefore particularly strong when the layer thicknesses are small (see chapter 14 and [1.1]).

Two magnetoresistive effects which already occur in macroscopic (bulk) materials are known for a long time, the ordinary magnetoresistance effect and the anisotropic magnetoresistance (AMR) effect. A discussion on an introductory level is given in sections 1.2 and 1.3. These effects occur already when all dimensions of the system are larger than the relevant physical length scales, such as the average electron mean free path, or the spin diffusion length (defined in chapters 2 and 3). That is our definition of the word ‘macroscopic’. The key point is that these length scales are, generally, in the nanometer range, and that magnetoresistive effects have been discovered which only occur for systems in which the magnetic structure can be varied on a scale that is smaller than the relevant physical length scale. Such systems are called ‘mesoscopic’. The conductivity of such systems is non-local, which means that Ohm’s law is not applicable. When the conductivity is local, Ohm’s law relates the current density \( j(r) \) at a point \( r \) to the electric field \( E(r) \) and the local conductivity, \( \sigma(r) \). It can be expressed as:

\[
\tilde{j}(\vec{r}) = \sigma(\vec{r}) \tilde{E}(\vec{r}) ,
\]

when the conductivity can be regarded as a scalar quantity. Most generally, the conductivity \( \sigma(r) \) is a tensor, viz. when an applied electric field in a certain direction leads to a current density in a direction perpendicular to that direction. The tensor has then non-diagonal elements. Instead, in a system for which the conductivity is non-local, the current density at a certain point \( r \) is determined by the conductivity of a region around \( r \) of which the size is
determined by the relevant physical length scale(s). Simple expressions for the resistance, such as the expressions $R = \frac{L}{A} \rho$ for the resistance of a wire with length $L$, cross-sectional area $A$ and resistivity $\rho = \sigma^{-1}$, are incorrect for mesoscopic systems. This is why the word ‘novel’ has been used in the title of this lecture series. The materials and devices discussed are not just ‘new’, not just based on gradual and evolutionary improvements. For those who were used to a macroscopic treatment of the electrical conductance, the understanding of the materials and devices discussed in these lectures requires a real mental switch. It is remarked that the term ‘microscopic’ is, within the terminology used here, reserved for effects which occur on an atomic scale. Of course, microscopic processes, such as scattering of electrons at an impurity atom, are of crucial importance to effects on larger length scales (mesoscopic and macroscopic).

The first important development has been the discovery, in 1988, and the subsequent technological development of materials and devices showing the giant magnetoresistance (GMR) effect. The realization of reliable fabrication processes of magnetic tunnel junctions showing the tunnel magnetoresistance (TMR) effect (in 1995) has been a second major breakthrough. Materials showing a change of the resistance of tens of percents at room temperature and in very small magnetic fields have been found. An introduction to these effects is given in sections 1.3 and 1.4. These developments have stimulated research on a variety of other novel materials and device structures. An overview is given in section 1.5.

The GMR effect has already since the end of 1997 been introduced in magnetic read heads by IBM, Fujitsu and other companies in the most advanced hard disk drive systems. The present growth of the bit densities on a hard disk is unthinkable without GMR read heads. See section 1.6.

The possible application of the GMR or TMR effect in so-called Magnetic Random Access Memories is now a subject of intensive research at many universities, institutes and a number of large industries, including IBM, Motorola, Honeywell, Toshiba and Siemens. Such memories are non-volatile: no electrical power is required to maintain the stored information. This is a clear advantage over volatile semiconductor DRAM (Dynamic RAM) and SRAM (Static RAM) memories used today in fast electronic systems such as PC’s. If successful, the impact on the performance of electronic systems, such as PCs, may be revolutionary.

Magnetic field sensors based on the GMR effect, with a combination of properties which makes them excellently suitable for automotive applications (temperatures up to 200 °C) have been recently been developed by Philips, while Siemens and Non-Volatile Electronics (NVE) have already commercialized GMR sensors suitable for application under for less difficult conditions.

This lecture series is focussed on the physics and materials science of nanostructured magnetic materials that are or might become suitable for device applications. In view of our interest in applications much attention will be paid to the stability of the magnetic domain structure (chapter 14), electronic noise (chapter 15), long term structural stability (chapter 16) and the frequency dependence of the magnetic response (chapter 17). The overall performance of a sensor, read head or memory device is never determined exclusively by the properties of the magnetoelectronic component itself. Other functional or structural elements do always play a certain role. One obvious example is the electronic noise due to contact leads and the amplifier. It is one of the aims of this lecture series to elucidate the role of at least some of the non-magnetic performance-determining aspects. These are often neglected in assessments on the application potential of a novel material or device. A simple consideration of the heat flow from a sensor to the surroundings (appendix 1A) already provides a first example.
1.2. The ordinary magnetoresistance effect

The seemingly simplest MR effect is the ordinary MR effect [1.2]. It is the increase of the resistance of a metal (which does not have to be ferromagnetic), a semimetal or a semiconductor as a result of the change of the electron trajectories due to the Lorentz force

\[ \vec{F} = -e \vec{v} \times \vec{B} \]  

(1.2)

by the induction \( \vec{B} \). See fig. 1.1. When \( \vec{B} \) is perpendicular to the applied electric field the MR ratio is for many materials to a good approximation proportional to \( B^2 \). This may seem a simple effect. However, theory shows that the effect would be absent when the electronic structure could be described in terms of the simple free-electron theory. Details of the electronic (band) structure beyond the free-electron approximation turn out to be crucial. See chapter 2. Note that the induction, not the magnetization, determines the Lorentz force. This is a fundamental difference with the MR effects that will be discussed below (including AMR, GMR and TMR).

At room temperature the ordinary MR effect is generally weak, less than 1 % for \( B= 1 \) T, which is already a relatively large induction. The induction in vacuum due to the earth magnetic field is much smaller, viz. approximately \( 5 \times 10^{-5} \) T. As the effect is quadratic in \( B \) the sensitivity (\( \partial \rho / \partial B \)) at zero field is zero, and the resistance change is independent of the sign of the induction. These drawbacks strongly restrict the practical use of the ordinary MR effect.

The ordinary MR effect is a galvanometric effect: it results from the Lorentz force that acts on the electrons. Another galvanometric effect is the Hall effect. In a system such as shown in fig. 1.1 an electric field arises parallel to the y-direction. The corresponding Hall voltage is to a first approximation a linear function of B. This is a desirable property for sensor applications. Hall sensors (based on semiconductor films) are used for a wide variety of applications.
1.3. The anisotropic magnetoresistance (AMR) effect

A second, and often more useful MR effect is the anisotropic MR (AMR) effect, which is observed for ferromagnetic metals. It is the change of the resistance upon a change of the angle between the current direction and the magnetization direction. See fig. 1.2.

![Diagram of anisotropic magnetoresistance effect](image)

*Fig. 1.2. The anisotropic magnetoresistance effect. The resistance is \( R(\theta) = R(\theta=0^\circ) - \Delta R_{\text{AMR}} \sin^2 \theta \).*

The AMR effect has already been discovered in 1857 by William Thomson, the later Lord Kelvin. It is a subtle relativistic effect, which has not been explained until the 1950s. See chapter 3. At low temperatures and at room temperature the Fe, Co or Ni based materials that show the largest relative resistance change (\( \Delta R_{\text{AMR}} / R(\theta=90^\circ) \)) ratio are the bulk random alloys \( \text{Ni}_{25}\text{Co}_{75} \) and \( \text{Ni}_{80}\text{Fe}_{20} \), viz. 25 % and 17 %, respectively at 4.2 K, and approximately 6.5 and 4 %, respectively, at room temperature [1.3]. Ni-Fe alloys with a composition close to \( \text{Ni}_{80}\text{Fe}_{20} \) are called permalloy, because their magnetic permeability is very high. It is possible to change the direction of the magnetization of permalloy in very small magnetic fields, of the order of 0.2-1.0 kA/m.

The AMR effect is used in magnetic field sensors and in read heads for magnetic disk and tape recording. However, the AMR effect is not large enough for large-scale applications of non-volatile magnetic solid state memories (there is a small aerospace niche market). And AMR materials are also not suitable for magnetic hard disk recording at bit densities larger than approximately 15 bit/\( \mu \text{m}^2 \) (10 Gbit/inch\(^2 \)) at a data rate of more than approximately 500 Mbit/s, which are the specifications of systems that are to appear on the market in 1999. The breakthroughs that make recording at such specifications feasible and that are providing the prospect of the large-scale application of non-volatile solid state memories are discussed in the next section.

1.4. The giant magnetoresistance (GMR) effect

The breakthrough that stimulated a world wide effort on the realization of magnetoelectronic devices was the discovery, in 1988, of the giant magnetoresistance (GMR) effect in magnetic
multilayers. The effect was discovered independently by Albert Fert and coworkers at the University of Paris-Sud [1.4] and Peter Grünberg and coworkers at the Forschungszentrum Jülich [1.5].

First some history. In 1986 Grünberg discovered that the ferromagnetic Fe layers in materials that consisted of a layer of Fe, a layer of Cr and again a layer of Fe, which were deposited on a flat carrier layer (‘substrate’) were strongly coupled antiferromagnetically when the Cr layer thickness was around 0.8 nm. See fig. 1.1.

Chromium is an antiferromagnetic (AF) metal with an ordering temperature $T_N = 308$ K (Néel temperature). The coupling between the Fe layers is called ‘indirect interlayer exchange coupling’ (direct exchange coupling is the exchange coupling between two neighbouring atoms which both carry a magnetic moment in magnetic materials). We return to this intriguing phenomenon in chapter 14. A magnetic field is required to overcome the coupling between the magnetic layers. In a large magnetic field, their magnetizations are parallel. In 1988 Grünberg discovered that this change if the magnetic structure is accompanied by a change of the resistance. See figure 1.4.

Independently, Fert and coworkers observed even larger relative resistance changes for Fe/Cr multilayers. The magnetoresistance (MR) ratio is usually defined as

$$\frac{\Delta R}{R} = \frac{R_{AP} - R_P}{R_P}, \quad (1.3)$$

where $R_{AP}$ and $R_p$ are the resistances of the system in the state in which the magnetization of neighbour layers is perfectly antiparallel and parallel. An MR ratio as large as 90 % was found at 4.2 K. See figure 1.5. Later work revealed that the MR ratio of Fe/Cr multilayers with thinner Fe layers could be as large as 220 % at 1.5 K [1.6]. Also at room temperature the effect can be several tens of percents. The effect was called giant magnetoresistance because it was much larger than the already known magnetoresistance effects, the ordinary MR effect and the AMR effect.

Detailed studies of the GMR effect showed that the resistance change is related to the change of the angle between the magnetization directions of neighbour magnetic layers. The resistance does not depend on the direction of the current, as long as it is in the plane of the layers. This geometry, with the Current In the Plane of the layers, is called the CIP-geometry. Experiments with the Current Perpendicular to the Plane of the layers (CPP-geometry) have revealed even larger GMR ratios for Fe/Cr multilayers.

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The magnetic fields at which the full resistance change is obtained are for the Fe/Cr/Fe bilayers and the Fe/Cr multilayers discussed above quite high, viz. 80 and 1600 kA/m, respectively (see figures 1.4 and 1.5). These fields are proportional to the interlayer exchange coupling energy. Applications in read heads for disk recording, or as an electronic compass, e.g., require that the relative orientation of the magnetic layers can be changed in much smaller fields. The earth magnetic field \( H \) is only (approximately) 40 A/m (which, as already mentioned, corresponds in vacuum to \( B = 5 \times 10^{-5} \) T). GMR systems have been developed within which full rotation of the layers already takes place in fields as small 500 A/m. Large GMR ratios (several tens of percents) are not only observed for Fe/Cr multilayers, but also for Co/Cu multilayers.

The origin of the GMR effect in magnetic multilayers can be understood within the two-current model for the electrical conductivity in metals. As the spin quantum number of a conduction electron is conserved in the vast majority of scattering processes, at least at low temperatures, the total conductivity can be expressed as the sum of separate contributions from spin-up and spin-down electrons. In the CIP geometry the GMR effect then arises:

1. if the electron scattering probability is spin-dependent,
2. if for at least one spin direction the electron mean free path is much larger than the thickness of the nonmagnetic spacer layers, and
3. if it is possible to change the magnetic structure in a magnetic field.

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**Fig. 1.4.**
Magnetoresistance of a GaAs[110]/12 nm Fe/1.0 nm Cr/ 12 nm Fe bilayer [1.2]. The MR ratio is 1.7 %. The current is parallel to the plane of the layers. 1000 Oe (cgs units) corresponds to 125 kA/m. The experiment has been carried out with the applied field perpendicular to the current direction. An experiment with the applied field parallel to the current direction gives rise to a slightly larger resistance in saturation, which has been taken as the the reference resistance, \( R_{ref} \). The difference between the parallel and perpendicular resistances is due to the small anisotropic magnetoresistance of the Fe layers.
In fig. 1.6 the electrical conduction through a cobalt/copper/cobalt bilayer system is shown schematically. In the cobalt layers and at the cobalt/copper interfaces scattering is weak for the so-called majority spin electrons, the electrons with spin parallel to the magnetization direction of the cobalt layer where the scattering takes place, and strong for electrons with the opposite spin (minority spin electrons). Each magnetic layer acts as a spin-selective valve: its magnetization direction determines whether it most easily transmits spin up or spin down electrons. In the case of parallel aligned magnetic layers the resistivity for one spin-channel is very low, leading to a low total resistance. However, antiparallel alignment of the magnetization directions results in appreciable scattering for electrons in both magnetic layers, and hence in a larger resistance.

The origin of the spin-dependence of scattering in materials such as Fe or Co and at interfaces such as the Fe/Cr and Co/Cu interfaces is discussed in chapters 2 and 4. A quantitative model of the effect is given in chapter 4. Fig. 1.6 makes clear why the GMR effect is a mesoscopic effect: it would be absent if the non-magnetic spacer layer (Cu) would be much thicker than the electron mean free path, or if the magnetic layers would be much thicker than the majority spin mean free in those layers. Mean free paths in many metals are of the order of several nanometers at room temperature, and in thin films also at low magnetic fields.

Fig. 1.5. Magnetoresistance of (Fe/Cr)<sub>N</sub> multilayers, with <i>N</i> the number of repetitions, measured at 4.2 K (Baibich et al., 1988). The current is parallel to the plane of the layers. 10 kOe (cgs units) corresponds with 800 kA/m (an induction in vacuum of 1 T).
temperatures (due to scattering at structural defects). The GMR effect therefore only occurs in magnetic structures which are compositionally inhomogeneous on a nanometer scale (magnetic nanostructures).

As simple as the explanation of the GMR effect might appear, it was never predicted. Its discovery was a big surprise! A semipopular paper on the GMR effect, its discoverers and its applications is [1.7].

Fig. 1.6. Electron scattering in a cobalt/copper/cobalt bilayer with parallel and antiparallel magnetization directions of the cobalt layers, according to the two-current model. The electric field is parallel to the plane of the layers. The red (blue) lines are typical trajectories of an electron with spin up spin up (down), where up (down) are defined as majority (minority) spin directions when the magnetization direction is to the right.

1.5. Tunnel magnetoresistance (TMR)

Magnetic tunneljunctions consist of two magnetic layers, separated by a non-magnetic (often) oxidic barrier (spacer) layer, with a thickness of only 0.5 to 3 nm. The barrier layer consists of an electrically insulating material, often aluminium oxide (Al₂O₃). However, it is so thin that when a voltage is applied across the barrier layer conduction takes place between the electrode layers due to quantum-mechanical tunneling. A schematic picture of such a structure is shown in fig. 1.7. It shows a tunnel junction that is made by deposition of stripe-shaped electrode layers through shadow-masks, in a ultra-high vacuum deposition system. The electrical conduction between the two layers takes place in the overlap area between the two stripes. The tunnel current is proportional to the overlap area (in fact, the picture shows a device that is current driven, not voltage driven).
When the electrode layers are made of a ferromagnetic material the tunnel current depends on the angle between the magnetization directions of the two electrode layers. This tunnel magnetoresistance (TMR) effect (sometimes also called ‘junction magnetoresistance (JMR) effect’) is due to the dependence of the tunnel probability of electrons on their spin direction.

The TMR effect has been discovered already in 1975 [1.8]. However, only in 1995 a process was developed which led to junctions that showed a high TMR ratio at room temperature [1.9]. Nowadays magnetoresistance ratios of typically 40 % are obtained for systems such as Co/Al$_2$O$_3$/Co. Magnetic tunnel junctions are considered as candidates for applications in MRAMs, and maybe in magnetic read heads. Ref. [1.10] is an overview article (in Dutch).

1.6. Overview of novel magnetoelectronic devices

A wide variety of structures of magnetoelectronic devices has been proposed and in part realized. Below a selection is given on the basic elements of such devices are given. Only schematic pictures are given, and only the ‘active part’ of the device is shown. Current leads are indicated only schematically, although in actual devices their geometry is sometimes important. For the color scheme used: see overview chapter.

(Although the devices discussed in this lecture series are based on continuous layers, it should be remarked that in some cases interesting effects have been observed for systems with discontinuous layers (layers which are not uniform in the direction parallel to the film plane, but consist e.g. of ‘clusters’ or ‘islands’)).
1. **CIP-GMR element.** Device based on a magnetic metallic layered material, with the current parallel to the plane of the layers. Length scales: (spin-dependent) mean free paths.

![CIP-GMR element diagram](image)

2. **CPP-GMR element.** Device based on a magnetic metallic layered material, with the current perpendicular to the plane of the layers. Length scale: spin diffusion length (for 5-50 nm thick films at 4.2 K typically \( \approx 5 \) nm for Ni\(_{80}\)Fe\(_{20}\), \( \approx 50 \) nm for Co, and \( \approx 500 \) nm for Cu).

![CPP-GMR element diagram](image)

3. **Magnetic tunnel junction.** Device in which two magnetic electrode layers are separated by a 0.5-3 nm barrier layer across which conduction takes place as a result of electron tunneling. Double junctions (with two barrier layers, and in the center of the structure an additional magnetic or non-magnetic metallic layer) have also been proposed. In schematic pictures of layer structures the width of the non-metallic barrier layers will be larger than the width of the metallic layers, in order to discriminate such layers from metallic spacer layers.

![Magnetic tunnel junction diagram](image)

4. **“Johnson spin switch” (“all metal spin transistor”).** In contrast to the structures 1-3 this is a three-terminal device (fig. 1.11). A ferromagnetic ‘emitter layer’ and a ferromagnetic ‘collector layer’ are separated by a metallic non-ferromagnetic layer. When
the system is connected as shown in the figure, a change of the relative magnetization directions of the emitter and collector layers gives rise to a change of the voltage $V$. The arrows drawn (magnetization directions) give only one possible example of the magnetic functioning of the device. An interesting variant is the lateral structure (two electrodes on a metallic substrate), see fig. 1.12.

1. 
2. 
3. 
4. "Monsma spin transistor". This is a so-called metal-base transistor, consisting of two semiconductor electrode layers (‘emitter’ and ‘collector’), separated by a metallic base layer which contains a GMR layer stack. For its functioning, the presence of Schottky barriers at the two semiconductor-metal interfaces, through which transport takes place by electron tunneling, is crucial. A change of the magnetic structure of the base layer gives rise to a change of the collector current. Variants have been proposed in which one or two oxidic barriers are present, instead of a Schottky barrier.
6. **Metallic magnetic point contacts.** Point contacts are systems in which the current flows through a narrow constriction. Point contacts can be made with nanometer-scale constriction dimensions. Conceptually, an idealized point contact could be viewed as a system in which two metallic half-spaces of a certain metal are separated by a thin insulating layer which contains a very small hole. In practice, point contacts are made by e.g. making contact between two sharp metallic tips (fig. 1.14(a)), or by depositing a metallic layer on the two sides of a thin membrane which contains a hole (fig. 1.14(b)). Magnetic point contacts, in their simplest form consisting of a single ferromagnetic metal, could provide an interesting magnetoelectronic device, e.g. if a change of the alignment of the magnetization of the two parts of the structure could be changed so that a domain wall is created in the constriction, giving rise to a change of the resistance. An MR ratio of 280% at room temperature has recently been observed for a Ni>Ni point contact. Theoretical understanding of magnetotransport at the nanometer scale (which requires, at least, understanding of the crystal and magnetic structure at that scale, is only at its infancy. Depending on the conditions transport is classical (diffusive or ballistic, when the contact radius is much larger or much smaller than the electron mean free path, respectively), or quantized.

This overview is not complete. Ferromagnetic / semiconductor hybrid devices with ferromagnetic electrodes on a semiconductor layer (like the structure shown in fig. 1.12) are attracting considerable attention. It turns out that in semiconductors the spin polarization of a current is sometimes preserved over remarkably long distances [1.11]. The focus in this lecture series will not be on semiconductor based systems, although interesting developments may be discussed as a special topic.

A related field is that of spin polarized tunneling across vacuum, such as used in spin polarized scanning tunneling microscopy (SP-STM). The tunnel current is measured between a ferromagnetic tip and a magnetic material. The technique has been used to study e.g. spin polarized surface states, changes of magnetization at step edges of antiferromagnets such as Cr, magnetic domain structure. The scanning mode makes it possible to obtain spatial resolution. For the purpose of this lecture series SP-STM will not be considered as a magnetoelectronic device (although the use of massively parallel scanning probe systems is sometimes regarded as a potential route towards data recording at densities beyond $10^3$-$10^4$ bits/$\mu$m$^2$). However, it will be shown that the physical understanding that has emerged from SP-STM studies is very relevant to the understanding of solid state devices within which spin-polarized tunneling takes place.
1.7. Applications: magnetic disk recording, Magnetic Random Access Memories (MRAMs) and magnetic field sensors

Simple considerations on the signal and the electronic noise show that the signal-to-noise ratio (SNR) of magnetoelectronic devices decreases in many cases (but there are exceptions) upon miniaturization of the device (see chapter 15). This provides, of course, a strong motivation for the search of novel magnetoelectronic materials and devices which show a higher relative resistance change, already in smaller magnetic fields. Whereas these are maybe the most obvious requirements, the SNR depends for actual devices on many different device properties. See e.g. appendix 1-A. It is one of the purposes of this lecture series to explain this in more detail for a number of important devices. Three applications will be discussed most extensively throughout these lectures: read heads for magnetic disk recording, MRAMs and magnetic field sensors.

Magnetic hard disk recording is used as a means of non-removable data storage as a peripheral to computer systems, including main frame systems as well as PC’s. It is expected that hard disks will soon be applied in consumer products for the storage of digital video signals (settop boxes, TVs, video recorders). Fig. 1.15 shows the development of areal density for commercial systems, and the development of the areal density realized in laboratory systems. The growth of the areal density has been 60 % per year since 1991. The highest density for which recording has been successfully demonstrated in the laboratory was 26 Gbit/inch$^2$ in August 1999 (the US-dominated hard disk industry refuses use SI units; 26 Gbit/inch$^2$ corresponds to 40 bit/µm$^2$). Commercial systems with this density are expected to be available within 1-2 years, and to operate at a data rate of approximately 800 Mbit/s. The data rate grows with 40 % per year.

Fig. 1.16 shows a written track on a hard disk, from a publication in 1997 [1.12]. The track width and bit length are 3 µm and 0.2 µm, respectively, corresponding to an areal density of 1.5 Gb/inch$^2$, the density for commercial systems at that time. The dimensions of bits decrease with increasing areal density according (approximately) to the green arrow shown in fig. 1.17. The bit aspect ratio (BAR), the ratio between the track pitch (center-to-center distance between the tracks) and the user bit length (approximately equal to the shortest distance between two magnetic transitions) decreases from approximately 15 (around 1 Gbit/inch$^2$) to 4 (expected around 100 Gbit/inch$^2$). This turns out to improve the signal-to-noise ratio due to the granular medium, although it makes track following even more difficult than for an increase of the density at constant BAR.

Fig. 1.18 shows schematically the structure of a read head containing a magnetoresistive element, a stripe shaped thin magnetic AMR or (in present systems) GMR film. Its resistance is sensitive to the flux from the transitions in the (longitudinally magnetized) medium over a width that is determined by the distance between two thick metallic contact leads. This read width is slightly smaller than the track pitch. The MR element (MRE) is sandwiched in between two thick soft magnetic shields (only shown partly in fig. 1.18), due to which the sensitivity of the MRE to the flux from more distant transitions is reduced. Introductions to magnetic disk recording are [1.13] and [1.14].
Fig. 1.15. Areal density of commercial IBM hard disk systems and of laboratory demos (from IBM web-page. September 2000: the most recent laboratory demo (56 Gbit/inch$^2$, Seagate) has been included.

Figure 1. Areal density perspective.

Fig. 1.16. Recorded track on a Co-Cr-Ta-Pt thin film hard disk medium, made visible using magnetic force microscopy [1.12].
Fig. 1.17. Contours or equal areal density as a function of the user bit length and the track distance (=track pitch), in Gbit/inch$^2$. The green arrow indicates the actual (expected) evolution of the bit dimensions.

Fig. 1.18. Schematic structure of a read head for hard disk recording. The head is part of a ‘slider’, which ‘flies’ at a $\approx 20$-$30$ nm height above the disk.
Research on Magnetic Random Access Memories (MRAMs) began by the end of the 80s, and has led to 16 kbit memory ICs (Honeywell) based on AMR elements. These low-capacity products are mainly made for the aero-space market, where the radiation hardness of magnetic materials provides an advantage over non-volatile memories based on semiconductor storage elements. Recent work has focussed on MRAMs based on GMR [1.15] and TMR [1.16] elements. The structure of TMR-based MRAMs is shown schematically in fig. 1.19. Each MRE is positioned at the cross point of two metallic lines. Read out is accomplished by selecting the element of interest by measuring the resistance between the these two lines. Currents through the other elements are avoided by integration of a diode or a transistor in series with each of the MR elements. The magnetic structure of the MR elements is switched by the combination of currents through the two crossing metallic lines, which are chosen such that a current through only one of the lines is not sufficient for switching.

GMR materials can be used for fabricating magnetic field sensors which are more sensitive than AMR-based magnetic field sensors. For many applications the robustness of the sensor material with respect to the application of a high magnetic field or in a hot environment is an important issue. The possibility to ‘design’ a GMR layer stack which help fulfil these criteria (e.g. for applications in cars for measuring the rotation of the wheels for an ABS system) has recently led to the realization of a pair of two GMR rotation sensors with (together) better than 0.5° accuracy over the entire 360° range [1.17]. Note that two (or more) AMR-based sensors can never be used for measuring the angles over the entire 360° range, due to their \( \sin^2 \theta \) signal form (caption of fig. 1.2). This benefit of two GMR over AMR sensors is depicted schematically in fig. 1.20. How AMR and GMR sensors work precisely will be discussed in section 9.2.

Fig. 1.19. Schematic matrix structure of a Magnetic Random Access Memory. The highlighted element shows one possible layer structure, within which one of the magnetic layers is fixed, and the magnetization of the other magnetic layer can be changed by the write field (‘0’ and ‘1’).
Fig. 1.20. Schematic view of analog angle sensing by means of two mutually rotated AMR (top) and GMR (bottom) sensors. From [1.17]. The 4-legged sensor chips depicted are Wheatstone bridge structures which are designed to sense fields parallel to the direction of the legs. See section 9.2.
Appendix 1A.
Some remarks on effect of the temperature rise of magneto-electronic devices on the output signal

The thermal conductivity of the environment of a magnetoelectronic device can be a factor which ultimately limits its performance. Let us consider a read head. The signal voltage $V_S(t)$, i.e. the signal-related a.c. part of the voltage across the MRE (i.e. the total voltage across the MRE minus the random noise voltage across the MRE, is equal to

$$V_S(t) = I_{\text{sense}} \left( R_S(t) - R_{\text{av}} \right),$$

where $R_S(t)$ is the signal-related part of the time dependent resistance, $R_{\text{av}}$ is the time-average of the resistance, and $I_{\text{sense}}$ is the sense current through the MRE. The factors that determine the time dependence of the resistance (including the magnetoresistance ratio, the flux from the medium and the flux efficiency of the head) are discussed in Ch. 9. These factors may be improved by improvements of the properties of the MR material, the medium material (and the write heads which should be able to write the signal at the required density), and the mechanics (making a low stable flying height and good track following possible).

In addition, the signal voltage is also proportional to the sense current. Limitations of the maximum allowable sense current ultimately limit the performance of a given head-medium system. In the first place, the sense current leads to dissipation of power in the MRE. For battery powered portable systems this contribution to the overall power consumption may already limit the allowable sense current. Secondly, the sense current gives rise to a magnetic field, which acts on the magnetic layers and may influence the flux dependence of the resistance. The focus will be on a third issue, viz. the resulting temperature rise of the MRE leads, which leads to a maximum of the allowed sense current. Heating of the MRE can lead to long term degradation due to thermally activated electromigration, due to degradation of the layer structure due to diffusion across the interfaces, or due to an irreversible change of the exchange biasing interaction. In addition, the MR ratio of magnetoelectronic devices decreases generally with increasing temperature, leading to an optimum of the signal voltage as a function of the sense current, instead of a monotonic increase. Let us, as a simple example, calculate the temperature rise of a thin film MRE in between two shields, each at a distance $g$ (the read gap length) from the MRE, separated from the MRE by an insulating gap oxide with a thermal conductivity $\kappa_{\text{ox}}$. Nowadays, $\text{Al}_2\text{O}_3$ is used, with for thin films $\kappa_{\text{ox}} \approx 1 \text{ Wm}^{-1}\text{K}^{-1}$. The shields are assumed to be perfect heat sinks, and the heat flow problem is assumed to be one-dimensional (no heat flow to the current leads). This latter approximation is in fact not quite correct, but for the purpose of the present discussion that does not present a problem. Setting the power dissipated in the MRE per unit area equal to the heat flux to the shield leads to the following expression for the maximum allowable sense current when the temperature rise should not exceed a value $\Delta T$ (verify this yourselves):

$$I_s = \sqrt{\frac{\Delta T \kappa_{\text{ox}}}{R_{\text{sh}} g}} \times h,$$

where $h$ is the MRE height (i.e. the dimension of the MRE stripe in the direction perpendicular to the disk surface). Eq. (1A.5) reveals the importance of improvements of the thermal conductivity of the gap material. Use of e.g. AlN, with for thin films $\kappa_{\text{ox}} \approx 3 \text{ Wm}^{-1}\text{K}^{-1}$. 

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instead of $\text{Al}_2\text{O}_3$, can improve the performance of MR heads by a factor $\sqrt{3}$. Secondly, as $g$ decreases with decreasing user bit length, cooling to the shields becomes more efficient. Part of the ever increasing sensitivity (in terms of output voltage) of read heads, is due to the possibility to use ever increasing current densities. The current density in GMR elements in read heads used for laboratory demonstrations is nowadays typically $5\times10^{11}$ A/m$^2$, one order of magnitude larger than the current densities typically used in interconnect lines on semiconductor Integrated Circuits (ICs). However, due to the efficient cooling, the resulting temperature rise in such heads can be limited to +50 K.
References Chapter 1

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1.9 M. Julliere, Phys. Lett. 54, 225 (1975).

Some overview papers:

- Several articles in a special issue of Physics Today 48 (April 1995) on ‘Magnetoelectronics’.
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(added in 2001):


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Novel Magnetoelectronic Materials and Devices – Reinder Coehoorn
2. Electrical conduction in magnetic metals

2.1. Electronic structure of magnetic metals

2.1.1. Itinerant versus localized electron states
The fundamental physics that underlies the properties of solids is well known (Maxwell equations, quantum mechanics and (special) relativity). However, first principles (\textit{ab initio}) calculations of the ground state, transport and other (e.g. optical) properties of many-electron systems are hampered by the impossibility to deal in an exact way with the correlated motion of the interacting electrons in the systems of interest. Electrons do not move independently, but interact with each other via the (repulsive) Coulomb force. The repulsive Coulomb interaction is, effectively, weaker between electrons of equal spin, due to the Pauli exclusion principle. This effectively attractive exchange interaction between electrons with the same spin leads for some solids to a (ferro)magnetic ground state, but not for all solids. Why are some solids (ferro)magnetic, and others not? Why is (bcc) iron ferromagnetic? More generally, can we predict the \textit{ground state properties} of a solid? These are the properties that only depend on the (crystal structure and lattice parameter dependent) total energy, and on the electron and spin density, such as:

- equilibrium crystal structure,
- equilibrium lattice parameters,
- elastic constants,
- magnetization (and its dependence on the lattice parameters),
- magnetic moments (i.e. the integrated magnetization within a certain well defined region around each of the atoms).

In the first part of this chapter a theoretical approach, \textit{band structure theory}, will be discussed \cite{2.1,2.2}. The ground state properties of magnetic metals based on the 3d-transition metal atoms such as Fe, Co and Ni can be explained well on the basis of this theory. In these metals the electrons which are responsible for the magnetism are \textit{itinerant}: their wavefunctions extend over the crystal. The 3d-electrons, which are responsible for the magnetism of transition metal (TM) atoms, spend only a finite time on an atom, before hopping to one of its neighbours. Band structure theory provides a reasonably successful, but not perfect description of the magnetic properties of these materials, because the correlated movement of electrons is only taken into account in an approximate way. In order to better clarify this point, some attention will be paid to the magnetism of rare-earth (RE) ions, for which band structure theory is not applicable. The 4f electrons, which are responsible for the magnetism of RE atoms, are localized, and their electronic structure is described in terms of concepts used in atomic theory.

Later in this chapter, band structure theory will be used as the basis of a discussion of the electrical conduction in magnetic metals.
2.1.2. Formation of energy bands
When a molecule or a solid is formed from isolated atoms the hopping of valence electrons through the solid leads to modifications of the atomic energy level structure (fig. 2.1). The splitting, $\Delta E$, between the states in a molecule and the band width, $W$, in a solid can be related to the time, $\Delta t$, which an itinerant electron on the average spends on an atom before hopping to one of its neighbours. According to Heisenberg’s uncertainty principle, $\Delta E$ is of the order $\hbar/\Delta t$.

If the atomic orbitals forming a band are not completely filled, only the lower part of the band, up to the Fermi level $E_F$, is occupied. In the case of a half-filled band, the contribution per electron to the heat of formation is of the order $W$. The decrease of the total energy is mainly due to the decrease of the kinetic energy of the electrons in the occupied lower part of the band due to the hopping process. Their wave functions have a larger amplitude in the region in between atoms than the wave functions of the states in the unoccupied upper part of the band, resulting in a less rapid spatial variation of their wavefunction and a lower kinetic energy.

In a crystal the potential $V(r)$ is periodic, which implies that with each eigenfunction $\psi$ a wavevector $k$ may be associated, which is confined to the first Brillouin zone. For a given $k$ the solutions of the Schrödinger equation can be labeled by the band index $j$ (usually defined such that $E_j(k) \leq E_{j+1}(k)$). The set of energy levels $E_j(k)$ with a certain value of $j$ is called an energy band.

![Fig. 2.1. Schematic representation of energy levels in an atom, a molecule and a solid.](image)

2.1.3. Band structure calculations
Ab initio band structure calculations are based on the density functional (DF) theory by Hohenberg, Kohn and Sham [2.3]. The first major result of DF theory is that the total energy $E$ of the system of interacting electrons is given by a unique (i.e. system independent)
functional of the spin-resolved electron density throughout the system. A functional is a function of a function. The energy functional is a function of the electron density, which is a function of the position. Secondly, DF theory shows that the ground state charge and spin density, which minimizes $E$, can be obtained by solving a set of one-electron Schrödinger equations (see below). Unfortunately, the complicated energy functional for the inhomogeneous electron gas is not known. Therefore the effective exchange-correlation contribution to the potential which enters the one-electron Schrödinger equations is not known. Most commonly, in practical calculations the following approximation is made. The total energy $E$, the electron density $n(\mathbf{r})$ and the spin density $m(\mathbf{r})$ are obtained by solving the Schrödinger equations

$$
\left(-\frac{\hbar^2}{2m} \nabla^2 + V^{s}(\mathbf{r})\right) \psi_{i,s}^\dagger(\mathbf{r}) = E_{i,s} \psi_{i,s}(\mathbf{r})
$$

(2.1)

for a single electron with spin $s$ (up or down (↑ or ↓)) in a local periodic potential which is given by

$$
V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}^{s}(n(\mathbf{r}), m(\mathbf{r})).
$$

(2.2)

The electron densities for spin up and spin down electrons are given by:

$$
n^{s}(\mathbf{r}) = \sum_{i=1}^{N} |\psi_{i,s}(\mathbf{r})|^2,
$$

(2.3)

where $N^\uparrow$ and $N^\downarrow$ are the number of spin up and spin down eigenstates with eigenvalues $E_{i,s} < E_F$. The Fermi energy, $E_F$, is found from the condition that $N^\uparrow + N^\downarrow = N$, the total number of electrons. The electron and spin densities are given by $n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r})$ and $m(\mathbf{r}) = m^\uparrow(\mathbf{r}) - m^\downarrow(\mathbf{r})$. The external potential $V_{\text{ext}}$ contains the attractive potential due to the nuclei, and (if present) a contribution due to the external magnetic field. The second term in eq. (2.2) represents the interaction of an electron at $\mathbf{r}$ with the average electrostatic field due to all other electrons. The exchange-correlation potential $V_{\text{xc}}^{s}$, which depends on the spin $s$, is a function of the local electron and spin density. This is an approximation, the local spin density approximation (LSDA), because as mentioned already in an exact treatment of the problem $V_{\text{xc}}^{s}(\mathbf{r})$ is a (unique) functional of the charge and spin density in the entire crystal.

Within the LSDA, $V_{\text{xc}}^{s}(\mathbf{r})$ is replaced by the exchange-correlation potential $V_{\text{xc}}(n(\mathbf{r}), m(\mathbf{r}))$ of the homogeneous electron gas, which is well known from numerical calculations. The exchange-correlation term takes into account that the actual electron density around a certain electron at a certain point is lower than the average electron density at that point, due to the direct Coulomb repulsion between electrons and the exchange interaction. The exchange interaction results from the Pauli exclusion principle, which states that the total wavefunction of interacting electrons (fermions) is antisymmetric for the exchange of two electrons. This leads to a reduction of the average Coulomb repulsion between two electrons with parallel spins, compared to two electrons in similar orbitals but with antiparallel spins (see e.g. [2.1]).

The region around an electron in which the electron density is decreased as compared to the time-averaged value is called the exchange-correlation hole. The integrated amount of ‘missing’ charge corresponds to one electron charge. The radius of the exchange-correlation

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hole at position \( \mathbf{r} \) (taking for simplicity the case of a non-magnetic solid) is therefore of the order of the so-called Seitz-radius, which is the radius of a sphere whose volume is equal to the volume per conduction electron:

\[
    r_s = \left( \frac{3}{4\pi} \frac{1}{n(\mathbf{r})} \right)^{1/3}.
\]  

(2.4)

Note that the inverse proportionality with \( n^{1/3} \) follows already from a dimensional analysis. Similarly, the Fermi wavelength for a homogeneous electron gas with density \( n \) is inversely proportional with \( n^{1/3} \), viz. \( \lambda_F = (2\pi / [3\pi^2 n])^{1/3} \). The size of the exchange-correlation hole is therefore proportional with the Fermi wavelength, and of the same order of magnitude. A first (order-of-magnitude) estimate of the exchange-correlation potential is therefore

\[
    V_{xc} \propto \frac{1}{4\pi\varepsilon_0} \frac{e}{r_s} \propto n^{1/3}.
\]

(2.5)

Numerical calculations for the homogeneous electron gas have revealed that for relatively large electron densities \( V_{xc} \) is indeed inversely proportional to \( n^{1/3} \), with a proportionality constant that is close to the value indicated by eq. (2.5). For small densities \( V_{xc} \) is a more complicated function of the density.

The exchange-correlation term is different for spin-up and spin-down electrons. \( V_{xc}^{\uparrow}(n(\mathbf{r}),m(\mathbf{r})) \) and \( V_{xc}^{\downarrow}(n(\mathbf{r}),m(\mathbf{r})) \) become more negative with increasing charge density and become more negative and less negative, respectively, when increasing the spin polarization. In section 2.2 the circumstances which lead to the spontaneous formation of magnetic moments are discussed.

Band structure calculations are often carried out according to the scheme shown in fig. 2.2. One begins by assuming a certain trial charge and spin density, from which the potential is constructed. Then eq. (2.1) is solved for both spin directions and for a dense mesh of \( \mathbf{k} \) points in the Brillouin zone (technical detail: only the ‘irreducible part of the Brillouin zone (BZ)’ has to be considered, see books on space group theory). From the wave functions of the \( N \) states with the lowest eigenvalues \( E_i(\mathbf{k}) \) new charge and spin densities are constructed, using eq. (2.3). The procedure is repeated until selfconsistency is obtained. The old and new potential are mixed in order to damp oscillations, thereby accelerating the convergence of the iteration process.

Within state-of-the-art methods the selfconsistent potential can have any shape. One speaks about full potential calculations. However, such calculations are limited with respect to the size (number of atoms) of the unit cell. For densely packed metals a good balance between the computational effort and the reliability of the results is obtained when using the Atomic Spheres Approximation (ASA), developed by the end of the 1970s [2.4], within which the crystal is subdivided by overlapping spherical regions, centered around the atomic positions. The potential inside the spheres is taken to be spherically symmetric (but the resulting selfconsistent charge and spin density is not). The ASA is used within the frequently used ‘Linearized Muffin Tin Orbitals’ (LMTO) [2.5] and ‘Augmented Spherical Wave’ [2.6] methods.

The calculated ground state properties of transition metals and their compounds, obtained using the LSDA approximation, are often in a remarkably good agreement with experiment. However, in some cases the agreement with experiment is not fully satisfactory. For Fe, Co, and Ni, e.g., the calculated lattice parameters are a few percent too small. See
section 2.1.4. So far, the vast majority of advanced electronic structure calculations of (magnetic) solids has been carried our using the LSDA. However, around the beginning of the 1990s an improved treatment of the exchange-correlation potential has been developed, the **Generalized Gradient Approximation** (GGA). Within this approach the exchange correlation potential is not only a function of the local majority and minority spin electron density, but also of the local gradient of the minority and spin electron density. This correction is important at points $r$ at which the dimensionless scaled density gradient $s = (|\nabla n| / n)r_s$ is of the order of one or larger, i.e. when the electron density varies appreciably over the exchange correlation hole. The approach is not to modify $V_{xc}$ by adding just the first expansion term (second order term of the series $1 + A s^2 + B s^4 + \ldots$), but to apply a more general function of $s$. Hence ‘generalized’. The reader is referred to [2.7] and references therein for the technical details and for results on a wide variety of systems. For metals this approach leads to a significant further improvement of the agreement between theory and experiment, also for magnetic metals such as Fe and Ni, as discussed in the next section.

![Fig. 2.2. Schematic representation of steps in selfconsistent band structure calculations.](image)
2.1.4. Band structure calculations – ground state properties of Fe, Ni and some non-magnetic metals

The classical source book on results of band structure calculations of cubic elemental metals on the basis of the LSDA is ref. 2.8. It shows the successes of this approximation, and the remaining discrepancies (lattice parameters, bulk modulus, magnetic moments). In a very recent publication [2.9] a detailed comparison is made for Fe, Ni and some nonmagnetic metals between results obtained within the LSDA and results obtained with the GGA. Some results given in [2.9] will be discussed briefly in this section.

![Diagram showing calculated total energy versus the lattice parameter for Al, Fe, Ni, Cu, Rh, Pd and Ag, obtained by the LSDA and the GGA (full circles). The results of non-selfconsistent GGA calculations (open spheres) are not discussed in the text. From [2.9].](image)

Fig. 2.3 gives an overview of the calculated total energy per atom for a seven metals. For each metal typically eight separate calculations have been performed, at different lattice parameters, using the LSDA and the GGA (the curves ‘non-selfconsistent GGA’ will not be discussed here). The total energy \( E \) is the energy (per atom) required to assemble the atom from a nucleus and from the isolated electrons, \( E_{\text{at}} \), plus the binding energy of the solid (per atom), i.e. the energy required to assemble the solid from the isolated atoms, \( E_{\text{B,solid}} \). One rydberg (Ry) corresponds to 13.605 eV (the ionization energy of H), and one atomic unit (a.u.) corresponds to \( a_0 = 0.0529 \text{ nm} \) (the Bohr radius). As shown in fig. 2.4 the relative changes of the total energy with the (cubic) lattice parameter, within the range considered, are
small, of the order of 0.1 eV. The predicted lattice parameter is the value at which the total energy is minimal.

Figure 2.3 shows that the use of the GGA improves the agreement with experiment (lattice parameter in the limit \( T = 0 \) K, vertical lines in the figure) significantly. An overview is shown in fig. 2.4 (a). Fig. 2.4 (b) shows that also the predictions of the bulk modulus, \( B \), are improved. The bulk modulus is an elastic constant that characterized the stiffness when applying an isotropic pressure, \( P \). It is defined as

\[
B = -\frac{\Omega}{\partial} \frac{\partial P}{\partial \Omega} = -\frac{\partial^2 E}{\partial \Omega^2},
\]

where \( \Omega \) is the volume per atom.

Fig. 2.4. Calculated error of the equilibrium lattice constant \( a \) and the bulk modulus \( B \) with respect to experimental data. From [2.9].

Fig. 2.5 shows for Fe and Ni, in their experimental bcc and fcc crystal structures, respectively, the calculated magnetic moment and magnetic energy (the energy difference between the ferromagnetic state and the hypothetical non-magnetic state). It clearly makes a difference whether the atomic spheres approximation (ASA) or full potential (FP) theory is used. For Fe, the calculated spin magnetic moment at the calculated lattice parameter (5.34 a.u.) is within 0.01 \( \mu_B \) from the experimental spin-contribution to the magnetic moment at zero temperature (2.13 \( \mu_B \)), using the FP-GGA approach. For Ni, there is still a discrepancy (calc.: 0.66 \( \mu_B \); expt.: 0.57 \( \mu_B \)). The magnetic moment decreases with decreasing lattice parameter, i.e. with increasing pressure. It is of interest to compare the calculated magnetic energy with the thermal energy \( k_B T_C \) at the ferromagnetic Curie temperature, 144 meV and 87 meV for Fe and Ni, respectively. For Fe, the calculated magnetic energy is almost 600 meV, much larger than \( k_B T_C \). This is consistent with other, experimental and theoretical, evidence, that at the Curie temperature, Fe is not (close to) a nonmagnetic state, in which all magnetic moments are zero, but that local moments of a finite size still exist at \( T = T_C \). See e.g. [2.2] and references therein.
In transition metals and compounds based on Fe, Co and Ni, of which the magnetization is mainly due to a splitting of the band derived from the rather localized 3d atomic orbitals, large gradients exist in the charge and spin density. The degree of localization of the 3d orbitals in Fe can be judged from fig. 2.6(b), which shows the calculated majority spin contributions to the radial charge density of iron (bcc crystal structure), derived from the 4s, 4p and 3d valence atomic orbitals. The atomic radius is about 0.14 nm. For future reference, a similar analysis of the radial charge density of gadolinium (fig. 2.3(a)), within which the 4f orbitals are even more localized than the 3d orbitals in iron.

The non-uniformity of the spin-density in iron can be seen fig. 2.7. The spin density is highest near the maximum of the charge density due to 3d-electrons. It is much smaller in the interstitial region and near the nuclei, and even negative at the nucleus and in part of the interstitial region. The negative spin density at the nucleus is confirmed by measurements of the hyperfine splitting, using the Mössbauer effect.

Band structure calculations have been employed rather successfully for calculating magnetic moments in structurally complex systems such as 3d-compounds for permanent magnets and magnetic multilayers, work functions and surface free energies, the relative stability of compounds in various alternative crystal structures (although the issue whether Fe is expected to be fcc or bcc appears to be subtle, depending on details of the approximations chosen).
Fig. 2.6. Calculated radial charge density of majority spin valence orbitals in Fe(bcc) and Gd(hcp) [2.2]. The charge density of each orbital has been normalized, by dividing the actual charge density by the number per atom of electrons in that orbital.

Fig. 2.7. Contours of equal spin density in a (100) plane of Fe, as obtained from band structure calculations. Shaded areas: negative spin density. Subsequent contours differ by 0.1 $\mu_B$ per $a_0^3$ ($a_0 = 0.0529$ nm, the Bohr radius). The maximum spin density, at a distance of about 0.035 nm from the nucleus, is in between 0.5 and 0.6 $\mu_B a_0^{-3}$. From [2.10].

For calculating the magnetocrystalline anisotropy the inclusion of spin-orbit coupling is required. This is a relativistic effect that couples the spin magnetic moment to the angular magnetic moment, leading to a preferred orientation of the total magnetic moment with respect to the crystal axes. The spin-orbit Hamiltonian can be written as

$$H_{s.o.} = \lambda_{s.o.} \left( \frac{1}{2} (L^+ S^- + L^- S^+) + L_i S_i \right)$$ (2.5)
where $L^\pm$ and $S^\pm$ are the raising and lowering orbital and spin angular momentum operators, and where $\lambda_{s.o.}$ is the spin-orbit parameter. So the spin orbit interaction mixes majority and minority spin states. This implies in practice an increase in the calculational effort of approximately a factor of 4. In calculations for light elements such as Fe, Co and Ni, for which the spin orbit parameter is small as compared to the d-band width (of the order of 0.1 eV) spin-orbit interaction is often neglected (unless effects which originate from spin-orbit coupling are to be calculated). Spin orbit coupling also leads to a small orbital magnetic moment, in addition to the generally much larger spin-magnetic moment. For Fe, Co and Ni the experimental spin (orbital) magnetic moments are 2.13 (0.09), 1.57 (0.15) and 0.57 (0.05) $\mu_B$ per atom. ‘Standard’ band structure calculations (as discussed above) underestimate orbital moments often by some tens of percents. This is ascribed to the neglect within the LSDA of orbital correlation effects, as expressed within atomic physics by Hund’s second rule (it is also neglected in the GGA). Some references on this issue can be found in [2.11]. Relativistic effects which can be included simply as an additional term in the expression of the potential, without mixing majority and minority spin states, are the mass-velocity effect and the so-called Darwin correction (both not given in eq. (2.2)). These terms are nowadays almost always routinely taken into account.

### 2.1.5. Correlation effects

Band structure theory based on the LSDA takes the correlated movement of electrons into account, but only insofar as this is present in the homogeneous electron gas. Although the GGA provides an improvement with respect to the LSDA, it should still be emphasized that DF theory only guarantees that use of the exact (but unknown) exchange correlation potential would yield the correct ground state properties. It does not guarantee that the correct excited states are obtained. In addition, even the single-electron eigenvalue spectrum (band structure) obtained from eq. (2.1) with the exact exchange correlation potential would not predict the band gap of an insulator or a semiconductor, or the exact Fermi surface of a metal. Indeed, band gaps of semiconductors predicted by LSDA band structure calculations are typically 30-50 % smaller than the experimental values. Does this mean that the calculated band structures or density of states are useless when discussing transport properties, our present topic of interest, or when discussing e.g. the optical properties? Let us consider the situation in more detail.

**Charge fluctuations** are treated improperly within band structure theory. A decomposition of the total wave function of the system into terms which correspond to different occupation numbers, $p$, of a certain shell on a specific atom results in a rather broad distribution of the probability of each of the configurations. As an example, the probability distribution for the case of an average of 8 electrons in a d-shell is given in fig. 2.8(a). One of the effects of electron correlation is to suppress charge fluctuations, making large deviations from the average occupation number of the shell less probable (fig. 2.8(b)).

On the one hand, this leads to a decrease of the kinetic energy which is gained by the hopping of electrons. On the other hand, it leads to a decrease of the repulsive Coulomb interaction energy between electrons on the same atom. The competition between both effects has been studied by means of model calculations using the Hubbard Hamiltonian [2.12] or by more sophisticated versions of it [2.13]. These Hamiltonians contain a term which is equal to the **intraatomic correlation energy**, $U$, times the number of electron pairs on a certain atom. In the limit of a large value of $U$ charge fluctuations are suppressed completely. The electrons are localized and the number of electrons on each atom is fixed (fig. 2.8(c)). **The criterion**
For localization is that $U$ should be much larger than the band width $W$, as can be seen from the following quantitative discussion.

Let us consider the process of hopping of an electron between two atoms which are in the ground state, with $q$ electrons in the 3d shell:

$$2 \times (3d^q) \rightarrow 3d^{q+1} + 3d^{q-1} \quad (2.6)$$

Upon hopping $q$ electron pairs are broken and $(q+1)$ electron pairs are formed, and the increase of the total energy of the system is $U$. The band width $W$ is a good measure for the energy that is gained by hopping. So $U$ and $W$ are the quantities that have to be compared, in order to decide whether localization will take place.

Fig. 2.8. Schematic probability distribution of the number of d electrons on a transition metal atom. The average occupation number is 8. (a) Itinerant electrons, (b) Intermediate case, (c) Localized electrons.

The band width $W$ is related to the overlap between orbitals on nearest neighbour atoms. Fig. 2.6 shows the radial charge densities of different orbitals in Gd and Fe metals. The case of rare earth metals will be discussed in order to be able to more clearly elucidate the consequences of localization. The 4s and 4p orbitals of Fe, and the 6s, 6p and 5d orbitals of Gd have a large density at a distance from the nucleus that corresponds to the Wigner Seitz radius of the atom, i.e. the radius of a sphere with a volume equal to the volume per atom in the solid (about 0.14 and 0.20 nm for Fe and Gd, respectively). The overlap between similar orbitals on neighbour atoms is large, resulting in broad sp and spd conduction bands, respectively. On the other hand, the 3d and, in particular, the 4f wave functions are more localized inside the Wigner-Seitz cell. This results in narrow 3d and 4f bands: for bcc Fe $W(3d)= 6.0$ eV, and for hcp Gd $W(4f)=0.3$ eV. The variation of the calculated 3d band width of the elemental 3d metals is shown in fig. 2.9. Towards the end of the series, the spatial localization of 3d orbitals increases, resulting in a decrease of the band width. Calculations of 4f band widths in rare earth metals [2.14] have shown that $W$ decreases from 1.0 eV for La, to 0.2 eV for Lu. See fig. 2.10.
Calculations of $U$ for the 3d transition metal atoms in the elemental metals have been performed taking into account that in metals electrons and holes which are present after the hopping process are screened by the conduction electrons, such that charge neutrality on an atomic scale is maintained (the screening length is of the order of the Fermi wavevector) [2.15]. So an excess (or deficit) of one d electron on a certain atom, corresponding with a configuration with $q+1$ (or $q-1$) electrons in eq. (2.6), is compensated in part by a decrease (increase) by one of the number of $s/p$ conduction electrons on the same atom. The screening reduces $U$ to an effective value $U^{\text{eff}}$. Fig. 2.9 shows that $U^{\text{eff}}$ increases towards the end of the series. $U^{\text{eff}}$ is smaller than $W$, which implies that band structure theory is the best starting point in the discussion of the electronic properties and magnetic structure of the 3d transition metals. This is also true for metallic compounds based on 3d transition metals.

![Fig. 2.9. Coulomb correlation energy $U^{\text{eff}}$ and the band width $W$ for 3d states in transition metals.](image)

![Fig. 2.10. Coulomb correlation energy $U^{\text{eff}}$ and the band width $W$ for 4f states in rare earth metals.](image)
Results of calculations of $U_{\text{eff}}$ for the rare earth metals are included in fig. 2.10 [2.16]. In addition to the (screened) Coulomb repulsion between electrons on the same atom also the exchange interaction between electrons on the same atom with parallel spins was taken into account. This interaction was neglected in the results displayed in fig. 2.9 for the 3d metals. For all 4f metals $U_{\text{eff}}$ is much larger than $W$. Therefore, electrons in 4f shells are completely localized. **Band structure theory is inappropriate for 4f states.** One must use atomic theory, within which the magnetic properties follow from the Hund’s rules. One consequence is that, even in cases in which calculated band structures reveal a 4f-derived density of states at the Fermi level, 4f states do not contribute to the conduction. (It is noted that the situation is sometimes slightly more complicated, viz. when a rare earth atom shows fluctuations between two configurations.). A discussion of the variation of $U_{\text{eff}}$ across the series of rare earth atoms is beyond the scope of this lecture series. See [2.2] and references therein.

### 2.1.6. Calculated band structures and densities of states

Calculated spin-polarized densities of states (DOS) for the magnetic metals Fe (bcc), Co (hcp) and Ni(fcc), and of the nonmagnetic metal Cu (fcc) are shown in fig. 2.11. It is obtained from a selfconsistent calculation of the energy eigenvalues in a dense mesh of points within the Brillouin zone. The energy is with respect to the Fermi level. The numbers of majority and minority spin electrons per atom, $n_{\text{maj}}$ and $n_{\text{min}}$, follow by integrating the density of states per atom from the bottom of the valence band (at around $-10$ eV) to the Fermi level. The magnetic moment $m$ (in Bohr magneton, $\mu_{\text{B}}$) is equal $m = n_{\text{maj}} - n_{\text{min}}$.

![Fig. 2.11. Calculated densities of states for Fe, Co, Ni and Cu [2.2].](image)
Fig. 2.12. Calculated band structure of Fe, for majority spin (a) and minority spin (b) electrons, along lines in the Brillouin zone of high symmetry (see fig. 2.13) [2.17]. Dashed line: the Fermi level. For states at the \( \Gamma \) point the degeneracy is indicated. Red broken curve: position of the s/p derived free electron in the absence of hybridization (schematic).
Fig. 2.11 shows that the narrow 3d-derived band, with a width that decreases with increasing atomic number as shown already in fig. 2.9, is superimposed on a wide (more free-electron like) band that is derived from 4s and 4p states. For Cu the d-band is full. It is below the Fermi level for both spin-directions. The calculated 3d-band edge is at slightly less than 2 eV below the Fermi level. Its position determines the reddish color of Cu: photons with energies above the edge energy are much more strongly absorbed (giving rise to excitations from the 3d-shell to unoccupied states) than lower energy (‘red’) photons, which are more strongly reflected. Fe, Co and Ni do not, for both spin directions, have such a clear band edge in the visible range (1.5-3 eV), and have therefore a more grayish color.

The band structure of Fe, as calculated using the ASW-method [2.17], is shown in fig. 2.13. A band structure plot usually gives the calculated energy bands along lines in the Brillouin zone (fig. 2.12) which connect so-called high-symmetry points. For Fe the total number of valence electrons is equal to 8, so on average there are 8 bands (majority spin plus minority spin) below the Fermi level. The figures may suggest that there are less bands. However, along some of the lines some bands are symmetry-degenerate. The degeneracy in the central (Γ) point is indicated in the figure. The non-degenerate lowest energy state is a 4s-derived state. Closer to the Fermi-level, with an exchange splitting of approximately 2.2 eV, the five 3d-states (per spin) are situated. Where the s/p type free-electron like bands cross the energy region in which the d-band is situated hybridization takes place: the wavefunctions have a mixed s/p/d character. Without hybridization the s/p band would have a parabolic shape. This shape still can be recognized (the red broken curve in the case of the majority spin band structure along ΓH, e.g.).

![First Brillouin Zone of the bcc lattice](image)

*Fig. 2.13. First Brillouin Zone of the bcc lattice, showing the irreducible part of the zone (defined by the dashed lines), and indicating the standard notation for the points of high symmetry. The Γ point is the center of the Brillouin zone.*
Calculated band structures of transition metals such as Fe, Co, Ni and Cu and their metallic compounds are in fair to good agreement \[1.18\] with experimental results obtained from a variety of techniques such as

- **photoelectron spectroscopy** (incoming photons create in the solid by an excitation process an outcoming electron, of which the energy, momentum and spin is measured, leading to information on the energy bands below the Fermi level),
- **inverse photoelectron spectroscopy** (incoming electrons, with a well-known energy, momentum and spin create by a deexcitation process a photon spectrum, which is analysed, leading to information on the energy bands above the Fermi level),
- **de Haas van Alphen effect measurements** (measurements of the oscillatory magnetic moment of the metal as a function of the applied magnetic field, leading to the shape of the Fermi surface).

### 2.2. Magnetic moments in itinerant electron systems: formation, magnetic interactions and thermal stability

#### 2.2.1. The Stoner model

In this section the formation of magnetic moments in itinerant electron systems is discussed in terms of the so-called **Stoner model** \[2.19\]. It contains approximations which are not made in actual selfconsistent band structure calculations, but it gives a very useful insight into the way densities of states may be used to predict the size of magnetic moments and their stability against e.g. compression of the lattice or in a magnetic field.

![Spin flip process of d_Q electrons in a ferromagnet, resulting in electron transfer between the exchange split bands.](image)

*Fig. 2.14. Spin flip process of \(d_Q\) electrons in a ferromagnet, resulting in electron transfer between the exchange split bands.*

Let us consider a spin flip process of \(d_Q\) electrons, originally in spin down states at the Fermi level of a spin polarized material. The process is indicated schematically in fig. 2.14, which shows the density of states (DOS) for majority and minority spin electrons. The DOS, \(D^\uparrow(E)\), is defined as the number of states per unit energy, per atom and per spin. Within the subsequent discussion a monoatomic solid is assumed. The magnetic moment (in \(\mu_B\)) is, at \(T=0\), equal to
\[ m = n^\uparrow - n^\downarrow = \int (D^\uparrow(E) - D^\downarrow(E)) \, dE \]  

(2.7)

In the Stoner model, the shape of the DOS is assumed to be independent of the exchange splitting \( \Delta \) (rigid band model). The splitting increases with increasing \( m \), the magnetic moment per atom, in units \( \mu_B \) (Bohr magneton). The presence of an s/p band is neglected. On the one hand, the spin flip process costs kinetic energy, because the electrons go to less strongly bonding states:

\[ dE_{\text{kin}} = +\Delta(m) \, dQ = +\frac{1}{2} \Delta(m) \, dm . \]  

(2.8)

On the other hand, energy is gained due to the increase in the number of equal spin pairs. If the intra-atomic exchange energy per electron pair is given by the Stoner parameter \( I \), then the energy gain is:

\[ dE_{\text{xc}} = (-n^\uparrow dQ + n^\downarrow dQ) \, I = -\frac{1}{2} m \, I \, dm . \]  

(2.9)

This leads to an equation of state which is given by:

\[ E(m,V) = -\frac{1}{4} m^2 + \frac{1}{2} \int_0^m \Delta(m',V) \, dm' - \mu_0 \mu_B m H , \]  

(2.10)

if one also includes the Zeeman energy in an external field \( H \). \( V \) is the volume per atom. A purely elastic term is neglected. A number of important results can be obtained from this equation.

### 2.2.2. Size of magnetic moments

For very small values of \( m \), the exchange splitting \( \Delta(m) \) is determined by \( D(E_F) \), the DOS at the Fermi level in the non-spinpolarized state:

\[ \Delta(m) = \frac{2m}{D(E_F)} . \]  

(2.11)

If \( V \) is constant and \( H=0 \) then minimization of the total energy with respect to \( m \) yields that the nonmagnetic state is unstable with respect to magnetic moment formation if the total density of states at the Fermi level satisfies the Stoner criterion:

\[ I \, D(E_F) > 2 . \]  

(2.12)

This is a sufficient, but not a necessary criterion (why?). If \( m>0 \), minimization of the total energy yields the splitting \( \Delta \) at the equilibrium magnetic moment \( m_0 \):

\[ \Delta(m_0) = I \, m_0 . \]  

(2.13)
Studies of moment formation using the LSDA have resulted in a more refined version of the Stoner theory [2.20], within which the so-called exchange-correlation integral $I_{xc}$ takes the role of the Stoner parameter. It is defined implicitly by means of eq. (2.10), for values of $m$ close to zero [2.21]. Calculated values for $I_{xc}$ for this parameter for a large series of elemental metals have been given in [2.8]. Table 2.1 gives an overview for the 3d and 4d metals. The increasing degree of localization of d-derived wavefunctions at the Fermi level at the end of the 3d series leads to an increase of $I_{xc}$ towards the end of the 3d series. The degree of localization of the wavefunctions is less within the 4d series, resulting in lower values of $I_{xc}$.

The trend $I_{xc}$ in explains in part the stronger tendency towards ferromagnetism for alloys and compounds based on the late 3d elements Fe, Co and Ni, as compared to systems based on the 4d elements Ru, Rh and Pd. Whether ferromagnetism occurs is also dependent on the detailed band structure. As an example bcc-Fe and fcc-Fe are compared. Using eq. (2.13) one can predict magnetic moments, if the DOS is given. The partial DOS of non-magnetic bcc Fe is shown in fig. 2.15(a), calculated at the experimental volume of iron at $T=0$. The calculated value $I_{xc}=0.92$ eV implies that the Stoner criterium is fulfilled if $D(E_F)>2.17$ states/eV. This is clearly the case. Upon magnetic moment formation the majority and minority spin d-bands shift downwards and upwards, with respect to the Fermi level. The equilibrium moment can now be found using the graphical construction in fig. 2.15(b), which is based on eq. (2.13). The figure shows the exchange energy gain and the kinetic energy loss per unit increase of the magnetic moment. At the equilibrium magnetic moment both curves cross. In this way one obtains $m=2.20 \mu_B$, close to the experimental value $m_{\text{spin}}=2.13 \mu_B$ and close to the values obtained from selfconsistent band structure calculations (see section 2.1). From eq. (2.11) it can be seen that the area enclosed by the $I_{xc}m$ curve and the $\Delta$ curve is equal to two times the energy gain upon moment formation (at a fixed volume, and for $H=0$).

In fig. 2.15(c) the calculated non-magnetic DOS of hypothetical fcc Fe is given, for the lattice parameter for which the volume per atom is equal to that for bcc Fe ($a=0.361$ nm). The Stoner criterion is not satisfied in this case. Fig. 2.15(d) suggests that fcc Fe is close to ferromagnetism, with a magnetic moment of approximately $2.4 \mu_B$. It is indeed predicted by selfconsistent band structure calculations [2.22] that this situation could be realized by an expansion of the volume.

Experimentally, fcc-Fe is found at low temperatures as coherent precipitates in Cu (which is fcc, and also with $a=0.361$ nm), where it orders antiferromagnetically with a moment of about $0.7 \mu_B$ [2.23]. It has been possible to create high-volume ferromagnetic fcc Fe by depositing thin Fe layers on top of Cu-Au alloy layers, for which the lattice parameter is larger than that of pure Cu [2.24]. Deposition on Cu-Ni alloy layers, with a lower lattice parameter than for pure Cu, revealed a strong decrease of the magnetic moment with decreasing lattice parameter. See fig. 2.16.

### Table 2.1. Calculated effective exchange-correlation integrals, $I_{xc}$, for 3d and 4d transition metal elements, in eV. From [2.8].

<table>
<thead>
<tr>
<th>Element</th>
<th>$I_{xc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.68</td>
</tr>
<tr>
<td>V</td>
<td>0.69</td>
</tr>
<tr>
<td>Cr</td>
<td>0.75</td>
</tr>
<tr>
<td>Mn</td>
<td>0.81</td>
</tr>
<tr>
<td>Fe</td>
<td>0.92</td>
</tr>
<tr>
<td>Co</td>
<td>0.97</td>
</tr>
<tr>
<td>Ni</td>
<td>1.00</td>
</tr>
<tr>
<td>Zr</td>
<td>0.62</td>
</tr>
<tr>
<td>Nb</td>
<td>0.60</td>
</tr>
<tr>
<td>Mo</td>
<td>0.58</td>
</tr>
<tr>
<td>Tc</td>
<td>0.59</td>
</tr>
<tr>
<td>Ru</td>
<td>0.61</td>
</tr>
<tr>
<td>Rh</td>
<td>0.65</td>
</tr>
<tr>
<td>Pd</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Fig. 2.15.
(a) Density of states of hypothetical nonmagnetic bcc-Fe. Upon magnetic moment formation the majority and minority spin d-bands shift downwards and upwards, respectively. The new positions of the Fermi-level, assuming a rigid shift of the bands, have been indicated. Eq. (2.13), from which the moment can be derived, is equivalent to the statement that the shaded areas I and (II+II’) are equal.
(b) Rate of change of the kinetic and exchange energy with increasing \( m \), from which, with eq. (2.13), \( m \) can be obtained, using \( \Delta m \) as derived from the DOS given in (a).
(c)-(d) Similar as (a) and (b), for fcc-Fe.

Compounds for which the DOS at the Fermi-level is sufficiently large can develop long range ferromagnetic order, even when the constituent metals are not (ferro)magnetic in their elemental form. Such cases have indeed been found. The classic example is ZrZn\(_2\), with a magnetic moment of 0.12 \( \mu_B \) per formula unit, and \( T_C = 21 \) K. Its calculated DOS is shown in fig. 2.17. The peak in the density of states around the Fermi level (from 0.4 to 0.5 Ry) is (slightly) higher than the Stoner limit, so (weak) ferromagnetism is expected. The Stoner limit
Fig. 2.16. Structure of an fcc Fe/Cu artificial superlattice with a 4% enhanced lattice parameter (left). Magnetic moment per Fe atom as a function of the lattice parameter ($\Delta a/a$ (in %) is with respect to pure Cu) [2.24].

Fig. 2.17. Calculated density of states of the intermetallic compound ZrZn$_2$. Non-magnetic calculation. The actual DOS will be spin-split, leading to a small magnetic moment (experimental value: 0.12 $\mu_B$ per formula unit). 1 Ry = 13.605 eV. One unit cell contains 4 formula units ZrZn$_2$. From [2.25].
is estimated as follows. The peak at the Fermi level is found, from the calculations, to be due to wavefunctions which are derived from Zr-4d states. In this energy range, hybridization with states that are derived from Zn-4s and Zn-4p states is weak. Neglecting the effect of hybridization, the Stoner criterion predicts that the non-magnetic state is unstable with respect to the formation of magnetic moments when the density of states per Zr atom is larger than 3.22 states/eV (eq. (2.12) and table 2.1), i.e. 176 states/Ry unit cell (red dashed line). Although the figure (and explicit calculations) show that the non-magnetic state is unstable with respect to the formation of a ferromagnetic state, the ferromagnetic state is not necessarily the most stable state. Antiferromagnetism (with, in principle, an infinitely large number of possible antiferromagnetic structures), could also occur. Indeed, the isoelectronic isostructural compound TiBe$_2$, which has a similar electronic structure as ZrZn$_2$ [2.25] is antiferromagnetic, with T$_N = 10$ K.

Another example of a weak ferromagnet is VAu$_4$, with a moment of 1.0 $\mu_B$ per formula unit and $T_C = 61$ K.

2.2.3. Magnetic susceptibility

From eq. (2.10) the spin-contribution to the magnetic susceptibility (per atom) at constant volume can be derived (Wohlfarth-Gersdorf formula):

$$\chi_{atom} = \frac{\partial (m \mu_B)}{\partial H} = \frac{4\mu_0 \mu_B}{\left( \frac{1}{D^\uparrow(E_F)} + \frac{1}{D^\downarrow(E_F)} - 2I_{xc} \right)}.$$  \hspace{1cm} (2.14)

The macroscopic susceptibility (dimensionless) is then

$$\chi = \frac{\partial M}{\partial H} = \frac{\partial (Nm \mu_B)}{\partial H} = \frac{4N\mu_0 \mu_B}{\left( \frac{1}{D^\uparrow(E_F)} + \frac{1}{D^\downarrow(E_F)} - 2I_{xc} \right)}.$$  \hspace{1cm} (2.15)

with $N$ the number of atoms per m$^3$. Unfortunately, the spin contribution to the susceptibility cannot be measured separately from the orbital contribution (see [2.26], [2.27]). These expressions can also be applied to non-ferromagnetic materials (paramagnetic materials), for which the density of states is not spin-polarized. It follows that the susceptibility is ‘exchange enhanced’. When then density of states approaches the Stoner limit (see eq. (2.12)) the susceptibility diverges. An example is Pd.

2.2.4. Volume dependence of the magnetization

The width of d-bands, and consequently also the exchange splitting for a given magnetic moment, $\Delta(m)$, is to a good approximation proportional to $V^{-3/5}$. From eq. (2.12) it then follows that

$$V \frac{\partial M}{\partial V} = \frac{\partial (Nm \mu_B)}{\partial V} = \frac{5}{3} \times \frac{2I_{xc}Nm \mu_B}{\left( \frac{1}{D^\uparrow(E_F)} + \frac{1}{D^\downarrow(E_F)} - 2I_{xc} \right)}.$$  \hspace{1cm} (2.16)
A general conclusion which follows from eqs (2.15) and (2.16) is that moments in systems for which either the majority and/or the minority spin DOS at the Fermi level are small are stable against a (small) variation of the external field or the volume. Moments in bcc Fe derive their stability mainly from the low value of $D^\downarrow(E_F)$, see fig. 2.11. Moments in Co and Ni, for which the majority spin d band is fully occupied, derive their stability from the low value of $D^\uparrow(E_F)$, see fig. 2.11. Co and Ni are called strong (saturated) ferromagnets, whereas Fe, with an unfilled majority spin d band, is called a weak (unsaturated) ferromagnet.

2.2.5. Finite temperatures – Stoner Curie temperature

The Stoner theory can be extended to finite temperatures [2.19]. Thermally induced spin-conserving excitations of electrons (single particle excitations), described by the Fermi-Dirac distribution $f(E)$, can be taken into account by replacing eq. (2.7) by the more general Stoner equations:

$$m = n^\uparrow - n^\downarrow = \int_{-\infty}^{\infty} \left[ f(E - \frac{\Delta}{2}) - f(E + \frac{\Delta}{2}) \right] \frac{1}{2} D(E) dE$$ \hspace{1cm} (2.17a)

$$n = n^\uparrow + n^\downarrow = \int_{-\infty}^{\infty} \left[ f(E - \frac{\Delta}{2}) + f(E + \frac{\Delta}{2}) \right] \frac{1}{2} D(E) dE$$ \hspace{1cm} (2.17b)

with $D(E)$ the total DOS per atom (in the absence of a spin splitting), $\Delta = I_{xc} m$ (eq. 2.13) and

$$f(\epsilon) = \frac{1}{\exp \left( \frac{\epsilon - \mu}{k_B T} \right) + 1}.$$ \hspace{1cm} (2.18)

Here $\mu$ is the chemical potential. From these expressions the unknown temperature dependent $m$ and $\mu$ can be derived. The ‘smearing of the Fermi level’ leads to a spatially uniform lowering of the magnetic moment with increasing temperature. At the Stoner Curie temperature, $T_{CS}$, the magnetization becomes zero. The values of $T_{CS}$ which are found for Fe, Co and Ni are, however, much higher than the experimental value [2.20], viz. 4400-6200, 3300-4800 and 2900 K, respectively, whereas the experimental values are 1040, 1390 and 630 K, respectively. There are other weakness of the Stoner theory (see e.g. [2.28]). An example is the incorrect prediction of the variation of the magnetization at low temperatures: $M(0)-M(T) \propto T^2$ is predicted, but experimentally $M(0)-M(T) \propto T^{3/2}$, (Bloch $T^{3/2}$ law) as expected on the basis of spin wave excitations. The Stoner Curie temperature provides only an upper limit. In Fe, Co and Ni, and in many other materials of practical interest, fluctuations of the magnetization direction, and not in the first place of the size of the magnetic moment, determine the Curie temperature.

2.2.6. Magnetic moments and $T_C$ in itinerant electron systems, case I: Heusler alloys

Within the Stoner model the thermal fluctuations that are considered are due to spin-conserving excitations between pairs of quantum-mechanical Bloch states with wavevectors $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$, respectively. As both states extend over the entire crystal, the effect of such excitations is a spatially uniform change of the magnetization.

Let us now consider spin-non-conserving excitations (‘magnetic excitations’) between pairs of Bloch states. Linear combinations of such excitations can be described as quantized spin waves (magnons). A classical treatment of the magnon energy as a function of the
wavevector, its quantum-mechanical form (dispersion relation of the form $\omega(q) = Dq^2$, with $D$ the spin wave stiffness), and the resulting effect of thermal excitation of magnons on the magnetization near $T=0$ (the Bloch $T^{3/2}$ law, already mentioned in sec. 2.2.5) is a subject of introductory textbooks on solid state physics (such as Kittel, [2.1]). The starting point of such treatments is often the Heisenberg exchange model, within which the assumption is made that the size of the magnetic moment of a certain atom is independent of its orientation with respect to the orientation of the other moments, and that the total interaction energy $E_{\text{ex}}$ of a system that consists of such localized magnetic moments is given by:

$$
E_{\text{ex}} = -\sum_{i \neq j} J_{ij} \frac{\vec{m}_i \cdot \vec{m}_j}{|\vec{m}_i| |\vec{m}_j|},
$$

(2.19)

where $J_{ij}$ is the (interatomic) exchange integral that represents the interaction between magnetic moments at sites $i$ and $j$ (not to be confused with the intra-atomic exchange-correlation integral $I_{\text{xc}}$). The summation is over all atoms $i$ (pair interactions are doublecounted). This is, if valid, a very powerful approach towards the problem of the temperature dependence of the magnetization, and the Curie temperature. It allows the application of mean field theory or of statistical mechanical approaches beyond mean field theory. Within mean field theory $T_C$ (or in fact the paramagnetic Curie temperature, see below) is given by:

$$
T_C = \frac{2}{3n} \frac{\sum_{i=1}^{n} \sum_{j \neq i} J_{ij}}{k_B} \eta, 
$$

(2.21)

where $\eta$ is the so-called quantum factor, which equals $(S+1)/S$, with $S$ the spin value: $S=\frac{1}{2}m$, with $m$ the magnetic moment in $\mu_B$. There is no general agreement whether the quantum factor should be taken into account. Often the classical formula with $\eta=1$ is used. The summation is over all $n$ (magnetic) atoms in the unit cell, and for each atom $i$ a summation is made over all other atoms $j$ within or outside the unit cell.

To what extent are magnetic moments localized in itinerant electron systems? Note that ‘localized’ refers here to the magnetic moments, not to the electronic states that give rise to the magnetic moments (the criterion for localization of electron states has been discussed in sec. 2.1.5). Following the definition of the word given above, localized magnetic moments can be reversed without an effect on their size.

Perhaps the best example of a class of metallic localized magnetic moment systems, within which the electrons are itinerant, is formed by the so-called Heusler alloys. In contrast to what is suggested by the word ‘alloy’, these are (highly) ordered intermetallic compounds. In sec. 2.3 we will discuss two very important members of this class of compounds, NiMnSb and PtMnSb, which are both halfmetallic ferromagnets, making them of potential interest for use in magnetoelectronic devices. Here we look at the prototype compound Cu$_2$MnAl, which has a cubic crystal structure that can be regarded as the sum of four interpenetrating fcc lattices. Mn, Cu, Al and Cu ions reside at sublattices of which the origin is at positions $(0,0,0)$, $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. See fig. 2.18. The cubic lattice parameter is 0.595 nm. The Mn atoms interact only indirectly, via the Cu and Al atoms. Although this interaction can be quite strong ($T_C = 603$ K), the size of the magnetic moments is only weakly affected by a change of the magnetic structure. This has been demonstrated in a classical study for Cu$_2$MnAl and for a large number of other Heusler alloys by Kübler et al. [2.29]. They
calculated the Curie temperature or the Néel temperature by deriving the Heisenberg exchange constants from the difference between the total energy for the ferromagnetic structure and for two antiferromagnetic (AF) structures. The two AF structures considered are shown in fig. 2.19. The structures AF-I and AF-II correspond to alternating magnetization directions on (001) and (111) planes.

Table 2.2. Calculated Mn magnetic moments and relative total energy (per four Mn atoms) for the Heusler compound Cu₂MnAl [2.29].

<table>
<thead>
<tr>
<th></th>
<th>m(Mn), in μB</th>
<th>E – E(F), in meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>3.36</td>
<td>0</td>
</tr>
<tr>
<td>AF-I</td>
<td>3.26</td>
<td>+123</td>
</tr>
<tr>
<td>AF-II</td>
<td>3.19</td>
<td>+184</td>
</tr>
</tbody>
</table>

Figure 2.18. Crystal structure of a X₂MnY Heusler alloy (so-called L2₁ type).

Figure 2.19. Antiferromagnetic configurations of types AF-I and AF-II for the fcc lattice. In the case of the Heusler compound Cu₂MnAl, the sites indicated accommodate the Mn atoms. (The role of the p-orbitals indicated on the Y sites is discussed in [2.29]).
The results of the calculations in Table 2.2 show that the Mn moments are, indeed, only weakly dependent on the magnetic configuration, and that the ferromagnetic configuration is, correctly, predicted to be more stable than the two AF configurations considered. The exchange constants $J_1$ and $J_2$ are defined as the sums of the exchange constants $J_{ij}$ between a site $i=\emptyset$ and all sites $j$ which are first and second nearest neighbours, respectively. They can be obtained from the two calculated energy differences if $J_3$ and higher exchange constants may be neglected. (Otherwise, $J_i$ ($i>2$) could be obtained by considering more, independent, configurations). Quantum fluctuations were taken into account ($\eta>1$). See table 2.3.

Application of eq. (2.21) then gives, within mean field theory, a first estimate of the Curie temperature. Mean field theory neglects correlations between the fluctuating magnetic moments. This is know to lead to an overestimation of the Curie temperature, in particular when first nearest-neighbour interactions are dominating, and for crystal structures for which the number of first nearest neighbours of each atom is small. Table 2.4 gives the exact Curie temperature (obtained numerically using advanced statistical mechanical methods for three-dimensional lattices with first nearest neighbour interactions only, assuming a Heisenberg spin lattice (i.e.: spins which can assume any direction, in contrast to so-called Ising spins, which can only point `up' or `down').

Table 2.3. Overview of results from [2.29], for a series of Heusler alloys, all ferromagnets except Pd$_2$MnIn. $J_i$ in meV per 4 Mn atoms.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$J_1$ (meV)</th>
<th>$J_2$ (meV)</th>
<th>$J_{\text{calc}}$ (K)</th>
<th>$J_{\text{exp}}$ (K)</th>
<th>$T_{\text{C,N,exp}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$MnAl</td>
<td>0.333</td>
<td>0.329</td>
<td>691</td>
<td>685</td>
<td>630</td>
</tr>
<tr>
<td>Co$_2$MnAl</td>
<td>0.840</td>
<td>0.062</td>
<td>808</td>
<td>697</td>
<td></td>
</tr>
<tr>
<td>Co$_2$MnSn</td>
<td>0.874</td>
<td>0.188</td>
<td>1142</td>
<td>829</td>
<td></td>
</tr>
<tr>
<td>Ni$_2$MnSn</td>
<td>0.221</td>
<td>-0.015</td>
<td>296</td>
<td>337</td>
<td>344</td>
</tr>
<tr>
<td>Cu$_2$MnSn</td>
<td>0.097</td>
<td>0.107</td>
<td>220</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>Pd$_2$MnIn AF</td>
<td>0.028</td>
<td>-0.047</td>
<td>42</td>
<td>52</td>
<td>142</td>
</tr>
<tr>
<td>Pd$_2$MnSn</td>
<td>0.178</td>
<td>-0.019</td>
<td>285</td>
<td>201</td>
<td>189</td>
</tr>
<tr>
<td>Pd$_2$MnSb</td>
<td>0.003</td>
<td>0.056</td>
<td>53</td>
<td>259</td>
<td>247</td>
</tr>
</tbody>
</table>

Table 2.4. Curie temperatures within the classical ($\eta=1$) Heisenberg model. From numerical calculations using the Monte-Carlo (MC) method, see [2.30], assuming only first-nearest neighbour interactions.

<table>
<thead>
<tr>
<th>Lattice Type</th>
<th>$T_{\text{C,MC}}/T_{\text{C,mean field}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic (sc)</td>
<td>0.722</td>
</tr>
<tr>
<td>Body centered cubic (bcc)</td>
<td>0.771</td>
</tr>
<tr>
<td>Face centered cubic (fcc)</td>
<td>0.794</td>
</tr>
</tbody>
</table>

For 3-dimensional (3D) lattices the mean field model provides a correct prediction of the paramagnetic susceptibility $\chi$ (far) above the ordering temperature, where it is described by the Curie-Weiss law, $\chi=C/(T-\Theta)$, with $C$ the Curie constant and $\Theta$ the paramagnetic Curie temperature which can be obtained from a plot of $1/\chi$ versus $T$. Close to $T_C$ such a plot is often not quite linear, so the high temperature part of the $1/\chi(T)$ curve should be used. This provides $\Theta$, as given by eq. (2.21), not $T_C$. The difference between $\Theta$ and $T_C$ is not always as
high as may be suggested by table 2.4, due to the importance of interactions beyond the first nearest neighbour shell. For Ni (fcc), e.g., Θ=648 K whereas $T_C=629$ K = 0.97×$T_C$. See e.g. Kittel [2.1, p. 445].

Kübler et al. obtained for Cu$_2$MnAl $\Theta_{\text{calc}} = 691$ K, whereas $\Theta_{\text{expt}} = 685$ K. The very good agreement is a little bit fortuitous, in view of the neglect of higher order exchange constants. However, for most compounds the prediction is a good first order result. In cases in which the paramagnetic Curie temperature is not known $\Theta_{\text{calc}}$ tends to be higher than $T_C^{\text{expt}}$, as expected from table 2.4. The prediction for AF Pd$_2$MnIn is fair: it is correctly predicted to be an antiferromagnet, with about the correct value of $\Theta$. However, for Pd$_2$MnSb the prediction is not very good. Inclusion of higher exchange coupling constants could be important for all compounds: comparison of $J_1$ and $J_2$ shows that the exchange coupling does certainly not (always) decrease monotonically with increasing distance. In fact, one does not expect a monotonic decrease with distance: the coupling is indirect, via s/p type states, whose induced polarization can oscillate with distance. A well-known dramatic consequence of this is the oscillatory interlayer exchange coupling between ferromagnetic layers across non-magnetic spacer layers [1.1, Chapter 2 in vol. 2], with observed wavelengths of 2 monolayers (a few tenths of nm) up to 2 nm.

### 2.2.7. Magnetic moments and $T_C$ in itinerant electron systems, case II: 3d transition metals

*Can 3d transition metals also be regarded as local moment systems, like the Heusler alloys? To what extent does the Heisenberg model provide a proper description of the energy of the system as a function of the magnetic structure? Can the Curie temperature of Fe, Co and Ni be predicted on the basis of a local moment theory, using results of first principles band structure calculations?*

Pioneering work on this theme has been done over a period of about 15 years, starting at the end of the 1970s, by the group of Heine in Cambridge [2.31-2.42]. Important contributions are due to the Russian group of Gubanov, Lichtenstein and others [2.1 (Gubanov et al.), 2.43-2.48] and Kübler and coworkers (Darmstadt) [2.49-2.50].

A first approach that has been used to answer these questions is to study, theoretically, the magnetic moments and total energy of spiral magnetic structures: helical antiferromagnetic structures within which the magnetization direction of atoms in subsequent lattice planes is rotated over an angle θ (fig. 2.19). Within the Heisenberg exchange model the total energy is expected to be proportional with (1 – cos θ). Fig. 2.20 shows that for Fe the moments are almost unchanged up to $\theta=90^\circ$, but that they are for Ni considerably reduced at $\theta>30^\circ$. For both metals the energy is well described by the Heisenberg model for angles up to 90°, but for larger angles the model does not provide a good description. For Fe the decrease of the short range order with increasing temperature will be slower than expected on the basis of the Heisenberg model, whereas for Ni short range order will already disappear at lower temperatures (as compared to the prediction from the Heisenberg model).

In the 1990s a breakthrough has taken place in this field on the basis of a novel method for calculating pair interactions using band structure theory (Lichtenstein et al. [2.43]). This method made it possible to calculate the exchange parameters $J_{ij}$ between arbitrary pairs of magnetic moments, in the limit of small angles between $\mathbf{m}_i$ and $\mathbf{m}_j$ [2.1(Gubanov et al.), 2.43-2.48]. If the Heisenberg model is well obeyed (pair energy proportional to (1-cos θ)), or if at the Curie temperature the angle between the magnetic moments on pairs of interacting atoms is small, $T_C$ can then be derived via eq. (2.21).
Section 2.5 gives calculated Curie temperatures as obtained by Sabiryanov et al. [2.44]. As discussed in section 2.2.6 mean field overestimates the Curie temperature, as it neglects correlation between moments. The error can be a 20-30 %, depending on the crystal structure, in the case of nearest neighbour interactions only, and less if interactions beyond the first nearest neighbour shell are important. Taking this into account, the agreement between theory and experiment for the cases given in table 2.5 seems quite good.

![Spin spiral](image)

**Fig. 2.19.** Spin spiral structures. From [2.33].

![Energy vs. angle](image)

**Fig. 2.20.** Calculated total energy (relative units) and magnetic moments for spin spiral structures of bcc Fe and fcc Ni (from Gubanov et al., [2.1]).

**Table 2.5.** Curie temperatures of crystalline elemental metals. Theoretical values are obtained within mean field theory from calculated exchange constants [2.29].

<table>
<thead>
<tr>
<th></th>
<th>$T_C$,theory (K)</th>
<th>$T_C$,experiment (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bcc Fe</td>
<td>1270</td>
<td>1040</td>
</tr>
<tr>
<td>Hcp Co</td>
<td>1520</td>
<td>1360</td>
</tr>
<tr>
<td>Fcc Co</td>
<td>1530</td>
<td>1388</td>
</tr>
</tbody>
</table>
Calculations of the Curie temperature for Y-Fe intermetallic compounds with complex crystal structures have recently been carried out successfully by Sabiryanov et al. [2.46]. See fig. 2.21. The Curie temperatures show a remarkable minimum as a function of Y concentration at the composition Y$_2$Fe$_{17}$. The calculated values were obtained from the exchange constants using Monte Carlo calculations, and were found to be about 0.76 of that of the mean field value. Interactions up to the third nearest neighbour shell were taken into account.

![Curie temperature vs Y-concentration](image)

**Fig. 2.21.** Calculated (red, •) and experimental (black, •) Curie temperatures [2.46] of Y-Fe compounds.

![Pair exchange parameters and spin wave stiffness](image)

**Fig. 2.22.** Calculated pair exchange parameters for bcc Fe (a) and spin wave stiffness as calculated from a real space sum when taking into account interactions up to the range indicated [2.48]. Circles (triangles): with (without) using the GGA (sec. 2.1.3) in the LSDA. $a_{\text{lat}}=0.287$ nm. Good agreement between experimental and calculated magnon energies, up to $q=0.25 \times 2\pi/a$ has also been reported in [2.47].
It is of interest to look in more detail at the range of interactions. The interaction energies $J_{ij}$ with atoms at a distance $R_{ij}$ and the calculated spin wave stiffness $D$ as obtained from taking into account interactions up to a distance $R_{ij}$ are shown in figures 2.22 and 2.23 for Fe and Ni, respectively [2.48]. Interactions up to at least 1.0 nm have to be taken into account, in order to obtain the spin wave stiffness. A difficulty is that, although interactions with far neighbours are weak, their number (per unit of distance to the central atom) grows quadratically with the distance.

![Fig. 2.23. Calculated pair exchange parameters for fcc Ni (a) and spin wave stiffness as calculated from a real space sum when taking into account interactions up to the range indicated [2.31]. Circles (triangles): with (without) using the GGA (sec. 2.1.3) in the LSDA. $a_{lat}=0.354$ nm.](image)

Figures 2.22 and 2.23 show rather ‘wild’ variations of the exchange interaction with distance. For $R_{ij}/a_{lat}>1$ these interactions must be indirect. How does the exchange interaction vary with distance for smaller distances? Nearest neighbour d-shells interact by direct d-d exchange, which may be (naively) be expected to decrease with increasing distance, due to the decreasing overlap between d-orbitals. Sabiryanov and Jaswal have obtained the distance dependence of the exchange parameters for bcc Fe, hcp Co, and fcc Fe with small and large lattice parameters ($a=0.3615$ nm, the lattice parameter of Cu, i.e. at the edge of the ferromagnetic stability region, see fig. 2.24, and $a=0.370$ nm, i.e. when it is a fairly stable ferromagnet) [2.47]. They used results of a series of calculations for distorted lattices (‘frozen magnons’).

Fig. 2.24 shows that the naively expected decrease of the interaction parameter is obtained indeed for Co and, less pronounced, for bcc-Fe, but that for fcc-Fe the direct exchange can even increase with increasing distance. This can be explained, qualitatively, as
follows. Co is a strong ferromagnet, so when considering a pair of atoms the moment on each of the atoms does not change when increasing the mutual distance (leaving all other distances on the average the same). The decreasing d-d overlap is then the only important distance dependent contribution to the exchange interaction. As expected, this contribution decreases rapidly with increasing interatomic distance. In contrast, bcc-Fe is a weak ferromagnet: its magnetic moment increases with increasing interatomic spacing. The increase of the spin-polarization with increasing distance then partially cancels the decreasing overlap. So for bcc-Fe the decrease of the exchange interaction with increasing distance is less then for Co. High volume fcc-Fe is close to strong ferromagnetism, with a large dependence of the magnetic moment on the interatomic distance. Apparently the decrease of the interaction with distance due to the decreased d-d overlap is now more or less balanced by the effect of the increasing magnetic moment with increasing distance. Low volume fcc-Fe is an extremely complicated case, with prevailing antiferromagnetic interactions at small interatomic distances.

![Graph showing the dependence of the exchange parameters on the interatomic distance for bcc Fe, hcp Co, and fcc Fe.](image)

**Fig. 2.24.**
Calculated dependence on the interatomic distance of the pair exchange parameters for bcc Fe, hcp Co, and fcc Fe [2.47].

### 2.2.8. Magnetic moments and $T_C$ in itinerant electron systems: overview

In sections 2.2.6 and 2.2.7 some issues were discussed which arise when calculating the Curie temperature for systems for which the local moment approximation is not bad. A summary:

A. Is the Heisenberg model correct (eq. (2.19), local moments)?
B. Quantum or classical Heisenberg model?
C. Interactions beyond the 1st nearest neighbour shell important?
D. Mean field or beyond mean field (Monte Carlo)?
Improved theories of the Curie temperature should deal with the following issues:

E. How can the situation within which the moment is not independent of the alignment with respect to its neighbours be treated? What are the relevant modes of excitation?

F. Inclusion of Stoner excitations.

G. Are dynamic effects important? No, if spin wave frequencies are much smaller than interatomic hopping frequencies (i.e. if the highest spin wave energies are far below the 3d band width). This is a reasonable approximation in practice.

H. Are electron correlation effects important? Can standard band structure theory be used for obtaining the strength of interactions at elevated temperatures?

Issues E and F require the formulation of a unified theory, which combines the Stoner model (the magnetization decreases with increasing temperature due to longitudinal fluctuations, i.e. due to a decrease of the average size of the moments) and the Heisenberg local moment model (decrease of the magnetization due to transverse fluctuations, i.e. due to fluctuations of the direction of the moments). See fig. 2.25.

Older work in this direction has been reviewed by Moriya [2.28,2.51] and by Shimizu [2.52]. The starting point of a unified theory could be a calculated set of curves $E(m,q)$ of the total energy as a function of the size of the magnetic moment, for wavevectors $q$ which range from $q=0$ (ferromagnetic alignment) to wavevectors at the edge of the first Brillouin zone. The excitations considered could be spiral structures (fig. 2.19). These sets of curves can have various shapes, as shown schematically in fig. 2.26. The temperature dependent magnetic moment, the variance of the magnetic moment, and the Curie temperature can then be obtained from a calculational method within which all excitations are given their appropriate thermodynamic weight (“Boltzmann factor”). The first quantitative first principles implementation of this approach has been performed recently by Uhl and Kübler for Fe, Co and Ni [2.49]. A discussion of their method and of their results is beyond the scope of this lecture series.

$$\begin{array}{c}
T=0 & \uparrow\uparrow\uparrow\uparrow\uparrow\uparrow & \uparrow\uparrow\uparrow\uparrow\uparrow & \uparrow\uparrow\uparrow\uparrow\uparrow \\
T<T_c & \uparrow\uparrow\uparrow\uparrow\uparrow & \downarrow\downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow\downarrow \\
T>T_c & \cdot\cdot\cdot\cdot\cdot\cdot & \leftarrow\rightarrow\rightarrow\rightarrow & \leftarrow\rightarrow\rightarrow\rightarrow \\
\text{Stoner} & \text{Unified} & \text{Heisenberg}
\end{array}$$

Fig. 2.25. Comparison of the Stoner, Heisenberg and unified models.

Experimentally, the nature of magnetic fluctuations can be studied in various ways:
1. Inelastic neutron scattering around and above $T_C$. Are there spin waves above the Curie temperature?
2. Temperature dependence of the specific heat. How large is the peak around $T_C$?
3. Thermal expansion
4. A decrease of the size of the magnetic moment leads to a decrease of the volume, which can counteract the non-magnetic positive thermal expansion due to anharmonic lattice vibrations [2.35]. A well known case is formed by INVAR alloys (around Fe$_{65}$Ni$_{35}$).
5. Spin polarized photoemission. Is there a spin splitting above the Curie temperature? See [2.36, 2.53].

6. Curie temperature of thin films, and magnetic fluctuations at interfaces. Measurements of the layer thickness dependence of the Curie temperature can reveal the range of the exchange interaction. See later this chapter. **Thermal fluctuations are generally stronger at interfaces than in the bulk of materials.** For applications of magnetoelectronic devices this is of great importance.

7. Temperature dependence of the (magneto)resistance. And measurements of other electrical transport effects, in bulk systems and thin films. See later this chapter.

Fig. 2.26. Schematic examples of the free energy variation due to spin polarization, for a ferromagnetic alignment (\(q=0\)), an alignment corresponding to a wavevector at the edge of the first Brillouin zone (\(q=k\)), and for a random spin structure. Curves (a) are appropriate for local moment systems, curves (b) represent the case of Stoner ferromagnets, curve (c) describes the case of Fe, and curve (d) describes Ni, for which the magnetic moment disappears in the AF state. There will be materials that are described by other sets of curves, such as (e) (Stoner magnet, but with fairly large \(T=0\) magnetic moments), and (f) (a material which can show a metamagnetic transition to a higher magnetic moment in an applied magnetic field). After [2.28].
2.3. Halfmetallic ferromagnets

2.3.1. Overview

Conceptually, a perfect magnetoelectronic switch could be formed by a junction consisting of two ferromagnetic layers, within which the electrical conduction is 100 % spin-polarized, separated by a non-magnetic layer which magnetically decouples the two ferromagnetic layers so that it becomes possible to change their relative magnetization directions in a magnetic field. The spacer layer could be metallic or insulating (but then sufficiently thin, so that tunneling across this layer is possible), and the device geometry used could be as discussed in section 1 (e.g. CPP-GMR structure, magnetic tunnel junction, Johnson spin switch (layer stack or lateral structure), Monsma spin transistor, etc.). In the absence of spin flip in the separation layer or in the electrode layers near the interfaces the devices could be switched from conductive to insulating by switching the relative direction of the magnetization of the electrode layers from parallel to antiparallel.

![Fig. 2.27. Possible spin-polarized density of states of a halfmetallic ferromagnet.](image)

This outlook makes it of great interest to study so-called halfmetallic ferromagnets (HMF). These are materials which are metallic for one type of spin, and an insulator (or semiconductor) for the other type of spin (fig. 2.27). The electrical conduction is then 100 % spin-polarized. The term ‘halfmetallic ferromagnet’ was introduced in 1983 by de Groot et al. [2.54], who discovered this property theoretically (by performing band structure calculations) for the Heusler alloys NiMnSb and PtMnSb. There is strong experimental evidence that these theoretical predictions are correct. These are still the prototype examples of itinerant electron HMF systems, and will be discussed in some detail in section 2.3.2. Whereas the discovery of halfmetallic ferromagnetism in these itinerant electron systems, with wide bands, was a big surprise, this property was already known for the narrow band oxide compound magnetite, Fe₃O₄ and was soon shown to be possessed also by CrO₂ (sections 2.3.4 and 2.3.3, respectively).

A more recent development is the discovery of halfmetallic ferromagnetism in oxides which show the colossal magnetoresistance (CMR) effect, an insulator-metal transition in a large applied magnetic field, leading to a huge change of the electrical conduction.
is observed e.g. in manganite compounds such as La$_{1-x}$Sr$_x$MnO$_3$ or La$_{1-x}$Ca$_x$MnO$_3$. The conduction in the metallic (high field) state conduction is 100% spin-polarized. A discussion of the CMR effect is not within the scope of this lecture series. However, a brief discussion of the HMF character of these oxidic compounds is included in section 2.3.5 for the sake of completeness. It is emphasized that in fact for all oxidic ferromagnets electron correlation beyond the LSDA is very important ($U=W$ or $U>W$, see section 2.1.5), and their electrical transport properties are not properly described in terms of band structure theory.

### 2.3.2. NiMnSb, PtMnSb and related Heusler alloys

The halfmetallic ferromagnetism of NiMnSb and PtMnSb is intimately connected to their special so-called $C1_b$ crystal structure. This is strongly related to the so-called $L2_1$ crystal structure shown in fig. 2.18 of ordinary Heusler alloys with the composition $X_2YZ$. In both cases the overall crystal structure is cubic, and the atoms reside on interpenetrating fcc lattices. For the $L2_1$ crystal structure the atoms reside on the four fcc lattices characterized by the positions $X_1(\frac{1}{4} \frac{1}{4} \frac{1}{4}), Y(0 0 0), X_2(\frac{3}{4} \frac{3}{4} \frac{3}{4})$ and $Z(\frac{1}{2} \frac{1}{2} \frac{1}{2})$, and for the $C1_b$ crystal structure the same situation holds, except that the $X_1$ position are empty. This lowers the point symmetry of the Mn atoms at the Y sites from cubic, for the the $L2_1$ structure, to tetrahedral for the $C1_b$ crystal structure.

Fig. 2.28 shows the band structure of NiMnSb, as obtained by de Groot et al. using an ASW band structure calculation [2.54]. The minority spin band structure shows an (indirect) gap around the Fermi level, whereas the system is metallic for majority spin electrons. The calculated magnetic moment is (exactly) 4 $\mu_B$ per Mn atom. For all halfmetallic ferromagnets the magnetic moment per unit cell, $m = n_{maj} - n_{min}$ (with $n_{maj}$ and $n_{min}$ the numbers of majority spin electrons per unit cell), is an integer, because $n_{maj}$ and $n_{min}$ must both be an integer. This already provides a first test of the calculations. Magnetization measurements and neutron diffraction yield experimental moments of 3.85 $\mu_B$ and about 4.0 $\mu_B$ per Mn atom, respectively [2.55,2.56].

Generally, within a series of isostructural compounds based on isoelectronic constituents the band structures are very similar. Indeed, when replacing Ni by Pt halfmetallic ferromagnetism is also found. The calculated minority spin band structure around the $\Gamma$ point is shown in fig. 2.29 (upper left). The experimental magnetic moment of PtMnSb 3.95 $\mu_B$ [2.58], within the experimental error in agreement with the moment of 4 $\mu_B$ expected when it would be a HMF. In contrast, the replacement of Sb by Sn (which contributes one electron less to the valence band), leads to a Fermi level that crosses the top of the minority spin valence band (fig. 2.29, lower left): PtMnSn is not a HMF. The calculated (experimental) magnetic moment for PtMnSn is 3.60 (3.42) $\mu_B$, clearly not an integer. Ir and Rh contribute one valence electron less then Ni, and Os contributes two valence electrons less then Ni. None of these non-isoelectric $C1_b$ compounds is a HMF. The number of electrons contributed to the valence band by the nonmagnetic atoms is clearly very important.

Although not all compounds for which a part of the band structure is given in fig. 2.29 are HMF, all show a distinct gap in the minority spin density of states. Such a gap is not commonly found for transition metal based intermetallic compounds, even not for ordinary Heusler alloys of the type $X_2YZ$. What makes the $C1_b$ structure so special? Let us first look at
Fig. 2.28 Calculated band structure of the half-metallic ferromagnet NiMnSb [2.54]. The horizontal dashed line indicates the Fermi level.
the overall density of states. Fig. 2.30 shows calculated results for PtMnSb [2.57]. The calculated DOS can be decomposed in contributions from states with a different wavefunction character. Based on such a decomposition (not shown) a rough assignment of the peaks in the DOS is given. The Ni 3d majority and minority spin 3d-bands are completely filled. Hence the Ni contribution to the magnetic moment is essentially zero. In addition, the Mn-3d majority spin bands is also completely filled, whereas the Mn-3d-minority spin 3d-band seems, on first sight, to be essentially unoccupied. However, we know already that this rough picture cannot be quite correct, because the Mn magnetic moment is not $5 \mu_B$, but $4 \mu_B$. We have to look in more detail at the wavefunction character of the states close to the Fermi level, and at the symmetry of the wavefunctions in a solid.

The symmetry of isolated atoms is, of course, spherical. All directions are equivalent. The wavefunctions or single electron states are classified by the well-known $n, l, m$ quantum numbers. Each eigenstate is characterized by a unique combination of these quantum numbers: the spherical potential does not mix these states. When placed in a solid, the spherical symmetry is lost, and hybridization between states with a different wavefunction symmetry will generally occur. E.g. d-states can mix with s or p states. Generally, the wavefunction of an electron in a solid can be written as a linear combination of states derived from different atomic orbitals. Whereas hybridization between two identical atomic states, centered on chemically identical neighbouring atoms, leads to the formation of a split pair of bonding and antibonding states (see fig. 2.1), the hybridization between two different atomic states (at different energies), leads to a repulsion. When is, in a solid, hybridization between

Fig. 2.29. Calculated minority spin band structures of several C1$_b$-Heusler compounds [2.56].
Fig. 2.30. Calculated majority and minority spin density of states of PtMnSb [2.57].
atomic orbitals important? The translational symmetry of a crystal lattice gives rise to a new quantum number, the wavevector. The eigenfunction of the Schrödinger equation are Bloch states $\phi(\mathbf{k}, \mathbf{r}) = u(\mathbf{k}, \mathbf{r}) \exp(i \mathbf{k} \cdot \mathbf{r})$, where the function $u(\mathbf{k}, \mathbf{r})$ has the periodicity of the crystal lattice. When $\mathbf{k}$ is at a general point in the Brillouin zone $u(\mathbf{k}, \mathbf{r})$ may be written as a linear combination of all atomic orbitals which together form the valence band. However, at some special points (sometimes also lines and planes) in the Brillouin zone, the Bloch states are not only characterized by the wavevector $\mathbf{k}$, but also by a symmetry label which tells how the wavefunction transforms under the set of space group operations which keep $\exp(i \mathbf{k} \cdot \mathbf{r})$ unchanged for all $\mathbf{r}$. Obviously, the $\Gamma$ point, at the center of the Brillouin zone ($\mathbf{k} = (0,0,0)$), is always such a special point. Only atomic states (or combinations of atomic states) with the same symmetry with respect to the set of space group operations mentioned can, at the $\mathbf{k}$-point considered, hybridize. E.g., in crystals with inversion symmetry atomic states which are symmetric with respect to inversion (s and d states) cannot hybridize at the $\Gamma$ point with states which are antisymmetric with respect to inversion (p and f states); s-p and p-d hybridization are then forbidden. Bands with different symmetry can therefore be degenerate at special points. This is apparent from the band structure of bcc Fe, shown in fig. 2.12 (along the high symmetry line $\Gamma$-N some bands, with different wavefunction symmetries, cross, whereas other bands, with the same wavefunction symmetry, hybridize; at a general point in the Brillouin zone, not shown in fig. 2.12, there is no crossing of bands). The wavefunction symmetry of states is conventionally indicated with a number, defined in handbooks. It should be remarked that in the case of a complex crystal structure a consideration of the formal space group symmetry is less useful when considering the hybridization between states centered on an atom with states centered on its neighbours. Instead, hybridization is then governed by the point symmetry of that site.

De Groot et al. have given the following analysis of the electronic structure of NiMnSb and related compounds [2.54]. The discussion focusses on the electronic structure at the $\Gamma$-point of the Brillouin zone. All Mn atoms are surrounded by six Sb nearest neighbours (for the Mn atom at the (0 0 0) these neighbours are at ($\frac{1}{2}$ 0 0), (0 $\frac{1}{2}$ 0), (0 0 $\frac{1}{2}$), (-$\frac{1}{2}$ 0 0), (0 -$\frac{1}{2}$ 0) and (0 0 $\frac{1}{2}$)). As a result the Mn-3d derived states split in so-called $t_2g$ states ($d_{xy}$, $d_{xz}$ and $d_{yz}$) and in $e_g$ states ($d_{x^2-y^2}$, $d_{3z^2-r^2}$), which have an angular part of the wavefunction that is a linear combination of the spherical harmonic $Y_{l}^{m}$ functions:

\[
\begin{align*}
|d_{xy}\rangle & = \frac{-i}{\sqrt{2}} (Y_{2}^{2} - Y_{-2}^{-2}) = \sqrt{\frac{15}{4\pi}} (\cos \phi \sin \theta)(\sin \phi \sin \theta) \\
|d_{xz}\rangle & = \frac{-1}{\sqrt{2}} (Y_{2}^{1} - Y_{-1}^{-1}) = \sqrt{\frac{15}{4\pi}} (\cos \phi \sin \theta) \cos \theta \\
|d_{yz}\rangle & = \frac{i}{\sqrt{2}} (Y_{2}^{1} + Y_{-1}^{-1}) = \sqrt{\frac{15}{4\pi}} (\sin \phi \sin \theta) \cos \theta \\
|d_{x^2-y^2}\rangle & = \frac{1}{\sqrt{2}} (Y_{2}^{2} + Y_{-2}^{-2}) = \sqrt{\frac{15}{16\pi}} (\cos^2 \phi \sin^2 \theta - \sin^2 \phi \sin^2 \theta) \\
|d_{3z^2-r^2}\rangle & = Y_{2}^{0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)
\end{align*}
\]

\[\text{(2.22)}\]
The angular parts of these wavefunctions are shown schematically in fig. 2.31. In the present case (octahedral coordination of the transition metal atom) the interaction between with the Sb-4p states splits the Mn-3d states into a low-lying triplet of \( t_{2g} \) states and a higher lying doublet of \( e_g \) states. The splitting is partly due to the different electrostatic repulsion, which is strongest for the \( e_g \) states which directly point at the Sb atoms ('crystal field splitting'). The largest part of the splitting is, however, due to the different hybridization ('ligand field splitting').

In fig. 2.28 the \( t_{2g} \) and \( e_g \) wavefunctions at the \( \Gamma \) point are indicated with the labels ‘4’ and ‘3’, respectively. For majority spin electrons there are below the Fermi level two threefold degenerate \( \Gamma_4 \) levels, with mainly Mn-3d-\( t_{2g} \) and Ni-3d-\( t_{2g} \) wavefunction character, and two twofold degenerate \( \Gamma_3 \) levels, with mainly Mn-3d-\( e_g \) and Ni-3d-\( e_g \) wavefunction character. A threefold degenerate \( \Gamma_4 \) level formed by states with predominantly Sb-4p character is situated well above the Fermi energy, at about 0.8 Ryd (≈ 1.9 eV above \( E_F \)). The interaction between the \( \Gamma_4 \) level below the Fermi level and the \( \Gamma_4 \) level below the Fermi level leads to a strong mutual repulsion. The Sb-4p derived \( \Gamma_4 \) level is pushed up, and contains a large amount of mixed-in Mn-3d character. So there is Mn-3d majority spin wavefunction character above the Fermi-level. The reverse situation occurs for the minority spin bands. Now the \( \Gamma_4 \) level formed by the Mn-3d-\( t_{2g} \) states is, due to the exchange splitting, situated above the Fermi level. The interaction with the Sb-4p states that form the second \( \Gamma_4 \) level level is again strong, but now the repulsion leads to a lowering of the energy of these states, and to mixing in of minority spin Mn-3d wavefunction character. So the majority spin Mn-3d band is not fully occupied and the minority spin Mn-3d band is not entirely empty, leading to the calculated non-saturated magnetic moment. More importantly, this mechanism leads to the opening of a band gap, producing semiconducting behaviour for the minority spin electrons.

This makes immediately clear that the halfmetallic character of these compounds is highly sensitive to the crystal structure and symmetry. E.g., the cubic point symmetry at Mn sites in ordinary \( X_2 \)MnZ Heusler alloys gives, at the \( \Gamma \) point, rise to a symmetry of Mn-3d-\( t_{2g} \) states that is different from the symmetry of the Sb-4p states. Hence, these states do not hybridize, so that a no gap is opened in the minority spin band [2.54]. The type of ordering of the C1\(_b\) Heusler alloy is also important. This follows from the calculated results given in table 2.6. The energy difference between the stable and non-stable configurations are, in this case, Table 2.6. Calculated total energy (eV/formula unit) and magnetic moment (\( \mu_B \)/ Mn atom) for NiMnSb for all possible ordered site occupancies. Structure 1 is the experimentally stable one. From [2.56].
Table 2.7. Calculated spin polarization $P$ and s-electron spin polarization $P_s$ for electrons at the Fermi level in disordered NiMnSb. From [2.63].

<table>
<thead>
<tr>
<th>No.</th>
<th>(0 0 0)</th>
<th>($\frac{1}{4}\frac{3}{4}\frac{1}{4}$)</th>
<th>($\frac{1}{2}\frac{1}{2}\frac{1}{2}$)</th>
<th>($\frac{3}{4}\frac{3}{4}\frac{3}{4}$)</th>
<th>$\Delta E$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn</td>
<td>-</td>
<td>Sb</td>
<td>Ni</td>
<td>0</td>
<td>4.00</td>
</tr>
<tr>
<td>2</td>
<td>Ni</td>
<td>-</td>
<td>Sb</td>
<td>Mn</td>
<td>18.3</td>
<td>3.32</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>Mn</td>
<td>Sb</td>
<td>Ni</td>
<td>21.9</td>
<td>3.11</td>
</tr>
</tbody>
</table>

huge (a few times the binding energy per atom, and much larger than $k_BT$). Experimentally, bulk NiMnSb prepared by arc melting shows very little site disorder [2.56]. However, IrMnGa, e.g., which also crystallizes in the C1b structure, was observed to show very strong site disorder [2.56].

Although disorder is very weak in well annealed bulk NiMnSb compounds (below 10 % [2.58]) it is expected and in fact experimentally observed to be present in thin films deposited or post-annealed at low temperatures (to be discussed later). The effect on the polarization of the density of states at the Fermi level has recently been calculated by Orgassa et al. [2.63], defined as

$$P = \frac{N_{maj} - N_{min}}{N_{maj} + N_{min}},$$

(2.23)

where $N_{maj}$ and $N_{min}$ are the majority spin and minority spin densities of states at $E_F$. The starting point is the thermodynamically stable configuration (type 1 in table 2.6). Three types of disorder (1’, 1'' and 1''') have been considered by the authors. As shown in table 2.7 5 to 10 % disorder can already lead to a drop of the polarization from 100 % to in one case less then 10 %. If only s-type states are considered (the states which are often assumed to dominate in spin-polarized conduction in a magnetic tunnel junctions) the drop is less, but still quite significant. Note that these values are 0 K predictions. Magnetic disorder due to thermally excited fluctuations will further decrease the polarization. Of course, when making a comparison with experimental data also other complicating effects, such as the modified electronic structure at or interfaces surfaces (to be discussed later), has to be taken into account.
So far (full) substitutions of the non-magnetic atoms Ni and Sb by other non-magnetic atoms have, theoretically and experimentally, not led to the discovery of other HMFs. However, substitutions of Ni by other magnetic atoms, have led to interesting results. In fact, band structure calculations for all compounds of the type XMnSb, with X= Ni, Co, Fe, Mn and Cr and with the crystal structure and site order of NiMnSb yield a halfmetallic ground state. The predicted magnetic moments are 4, 3, 2, 1 and 0 µB per formula unit. When going from Ni to Cr the filling of the majority spin bands decreases, whereas the filling of the minority spin band remains the same. Apparently, the presence of the gap stabilizes the halfmetallic structures. FeMnSb would be a halfmetallic ferrimagnet, with a sizeable Fe moment antiparallel to the Mn moment, and CrMnSb would even be a halfmetallic antiferromagnet. It is a special antiferromagnet in the sense that the majority spin and minority spin densities of states are not identical, as for common antiferromagnets. See the density of states in fig. 2.32 and 2.33. The material is better described as a fully compensated ferrimagnet, having a magnetic moment that is, due to the halfmetallic character, precisely equal to zero. Such a halfmetallic antiferromagnet would be, if existing and if single domain, an very interesting magnetoelectronic material. It would be a perfectly stable spin-polarized electrode in a junction device, or as a tip in a spin-polarized STM which does not give rise to stray flux, and hence does not distort the domain structure of soft-magnetic systems to be studied. Unfortunately, CrMnSb does not crystallize in the ordered C1b crystal structure. However, these results show that such an important magnetoelectronic material could exist. An overview is given in table 2.8.

### Table 2.8. Calculated and experimental properties of XMnSb compounds in the C1b structure.

Magnetic moments per formula unit (total moment) and per atom [2.64].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Calculated magnetic moments (µB): Total, X, Mn, Sb,</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMnSb</td>
<td>[2.54]</td>
<td>4, 0.31, 3.74, -0.05</td>
<td>Stable ordered C1b structure; m = 3.85 µB.</td>
</tr>
<tr>
<td>CoMnSb</td>
<td>[2.60]</td>
<td>3, -0.09, 3.20, -0.11</td>
<td>Disordered structure (Co atoms partly at empty sites); m = 3.93 µB.</td>
</tr>
<tr>
<td>FeMnSb</td>
<td>[2.61]</td>
<td>2, -0.90, 2.94, -0.04</td>
<td>Compound does not exist. For partially disordered Ni1-xFexMnSb m extrapolates to 2.7 µB.</td>
</tr>
<tr>
<td>MnMnSb</td>
<td>[2.59]</td>
<td>1 -1.93, 2.94, -0.01</td>
<td>Compound crystallizes in another structure.</td>
</tr>
<tr>
<td>CrMnSb</td>
<td>[2.59, 2.62]</td>
<td>0 -2.35, 2.44, -0.09</td>
<td>Compound crystallizes in another structure.</td>
</tr>
</tbody>
</table>

Van Leuken and de Groot have recently suggested a possible route towards a halfmetallic antiferromagnet, viz. by making substitutions in the existing C1b type compound VFeSb [2.59]. This compound is a non-magnetic semiconductor. It is isoelectronic with the non-existing halfmetallic antiferromagnet CrMnSb. A 12.5% substitution of Mn for V, and (in order to keep the system isoelectronic, In for Sb) was predicted to already yield...
halfmetallic ferromagnetism, with local Mn moments of about 2.3 $\mu_B$ and a band gap of about 0.35 eV.

Fig. 2.32. Calculated spin-polarized density of states of the (hypothetical) halfmetallic antiferromagnet CrMnSb in the C1$_b$ crystal structure [2.64]. Red line: Fermi energy.
Strictly speaking, perfect halfmetallic ferromagnetism is not possible, because spin-orbit coupling mixes majority and minority spin states \((eq. (2.5))\). When spin-orbit coupling is taken into account there are no separate majority and minority spin band structures: each wave function is a linear combination of majority and minority spin wavefunctions, \(\psi = \alpha \phi_\uparrow |s_\uparrow\rangle + \beta \phi_\downarrow |s_\downarrow\rangle\), where \(\phi_\uparrow\) and \(\phi_\downarrow\) are normalized Bloch functions and where \(|s_\uparrow\rangle\) and \(|s_\downarrow\rangle\) are the spin wavefunctions (spinors) for spin parallel and antiparallel to the quantization axis.

Fig. 2.33. Atom and spin resolved density of states of the hypothetical halfmetallic antiferromagnet CrMnSb in the Heusler C1\textsubscript{b} structure [2.64]. 1 Ryd = 13.605 eV. Red line: Fermi energy.
However, it is still possible to derive from the calculated band structure the \textit{spin-projected densities of states}. The majority and minority spin contributions from each wave function to this DOS are equal to $|\alpha|^2$ and $|\beta|^2$, respectively. This means that the ‘polarization of the density of states at the Fermi level’, defined in eq. (2.23) is still a well defined concept.

It is easily shown that in \textit{atoms} the level splitting (between $m_l=-l$ and $m_l=l$ states) due to the spin orbit interaction is $(2l + 1) \lambda_l$ for states with orbital quantum number $l = 1, 2, 3, \ldots$ (p, d, f, .. states). There is no spin orbit interaction for s-states, which have no orbital moment. In \textit{solids} the atom and $l$ dependent effective spin-orbit parameters $\lambda$ are very close to those in isolated atoms, because $\lambda$ is determined by the expectation value of the potential gradient around the atom, which is mainly determined by the steep gradient in the region close to the nucleus where it is hardly affected by the presence of the neighbour atoms. For Mn-3d, Ni-3d and Pt-5d orbitals $\lambda$ is about 0.02, 0.05 eV and 0.5 eV, respectively, and for Sb-5p states $\lambda$ is about 0.5 eV. For a given type of orbital the spin-orbit parameter increases with increasing atomic number $Z$. In solids the degeneracy of states with the same $l$ quantum number is lifted by the non-spherical potential. Bands are formed, with in the cases in which we are interested at present (NiMnSb e.g.) widths of several eV, much larger than the atomic spin orbit splitting. For compounds for which the magnetism is derived from 3d transition metal atoms (Mn, e.g.) spin-orbit interaction leads only to a small modification of the spin magnetic moment, and only to a small orbital contribution to the magnetic moment (which is absent without spin orbit coupling). Nevertheless it can have a large effect on the electronic structure in individual points in $k$ space where the crystal field splitting is small. The effect of spin orbit coupling on the electronic structure of NiMnSb and PtMnSb has been studied in [2.57, 2.65, 2.66]. The main conclusions from these studies are as follows:

\textbf{NiMnSb}

The effect of spin orbit on the electronic structure of NiMnSb is almost negligible. \textit{The polarization $P$ is still very close to 100 %}. The relevant spin orbit parameters are small as compared to the distance of the Fermi level to the edges of the minority spin band gap (it is situated close to the middle of the $\approx 0.6$ eV gap). The width of the gap changes hardly. Calculated orbital magnetic moments on the Ni, Mn and Sb sites are 0.01 (0.017) $\mu_B$, 0.04 (0.033) $\mu_B$ and -0.01 (-0.0044) $\mu_B$ respectively [2.66 (2.67)], the total calculated magnetic moment is 4.065 $\mu_B$ [2.67].

\textbf{PtMnSb}

The effect of spin orbit interaction is larger than for NiMnSb, because (1) the Fermi level is situated more closely to the top of the minority spin valence band, and because (2) the spin orbit splitting of Pt-5d states, which are mixed in the $\Gamma_4$ states at the top of the valence band, is larger than for Ni-3d states. De Groot et al. find [2.57] that PtMnSb is halfmetallic in the absence of spin orbit coupling, and that its inclusion gives rise to a 0.5 eV splitting of the threefold degenerate $\Gamma_4$ states at the top of the minority spin valence band, which are described as predominantly Sb-5p derived states, into $m_l=-1, 0$ and $+1$ states. The $m_l=+1$ type state is, at $\Gamma$, situated slightly above the Fermi level, so that there are now minority spin holes. See fig. 2.29.

In contrast, Youn and Min [2.65] find that PtMnSb is not a HMF in the absence of spin orbit coupling (the top of the valence band just touches the Fermi level), but spin orbit coupling not only produces a level splitting ($\approx 0.3$ eV in their case) but also an overall downward shift of these states with respect to the Fermi level. See fig. 2.34 and 2.35. \textit{“PtMnSb becomes a HMF when spin-orbit interaction is taken into account”}. Of course, also when spin orbit interaction is included the polarization must be smaller than 100 %, but this is
not (explicitly) recognized in [2.65]. Obviously the energy differences are small, and numerical and methodological errors can be of influence (see [2.66] and references therein). In practice, these details will be of minor importance when considering the effects of some atomic site disorder. Calculated orbital magnetic moments on the Pt, Mn and Sb sites are $-0.05$ $(+0.31) \mu_B$, $0.04$ $(0.051) \mu_B$ and $-0.01$ $(-0.027) \mu_B$, respectively [2.66, (2.67)]. The total calculated magnetic moment is $4.080 \mu_B$ [2.67]. Much experimental work supports the HMF character of NiMnSb and PtMnSb. An overview is given in Appendix 2A.

![Fig. 2.34. Total and minority spin-projected densities of states for PtMnSb, from a fully relativistic band structure calculation (including spin-orbit coupling) [2.66].](image1)

![Fig. 2.35. (a) Semirelativistic and (b) fully relativistic band structures of PtMnSb. In (a) solid (dotted) lines represent majority (minority) spin bands [2.65].](image2)
For a large number of other C1\textsubscript{b} type Heusler alloys a gap in the minority spin density of states has been found from band structure calculations. However, halfmetallic ferromagnetism has not been predicted for experimentally existing (stoichiometric) compounds other than NiMnSb and PtMnSb. Some other systems have already been mentioned in table 2.8. See also [2.68-2.70]. A few remarks:

**Other C1\textsubscript{b} type Heusler alloys: RuMnSi and RuMnGe.**
In the case of ferromagnetic ordering these systems would be HMFs, with band gaps at $E_F$ of about 0.15 eV for minority spin electrons [2.68]. However, these compounds are antiferromagnets [2.69].

**Other C1\textsubscript{b} type Heusler alloys: NiUSn.**
From a scalar-relativistic calculation this is nearly a HMF. There is a gap for minority spin electrons, but the bottom of the minority spin conduction band just crosses the Fermi level. The calculated moment is 1.99 $\mu_B$, whereas the experimental moment at high temperatures is 3.08 $\mu_B$. The discrepancy, which might become even larger when taking the low temperature magnetic moment, might be due to the neglect of the very large spin-orbit coupling for U [2.70].

**L2\textsubscript{1} type Heusler compounds: Co\textsubscript{2}MnSi and Co\textsubscript{2}MnGe**
Recently Ishida et al. have predicted halfmetallic ferromagnetism for the L2\textsubscript{1} type Heusler compounds Co\textsubscript{2}MnSi and Co\textsubscript{2}MnGe (structure: fig. 2.18) [2.71]. For Co\textsubscript{2}MnSi presently available experimental data do not disagree with this. Table 2.9 shows good agreement between the total calculated and experimental moments. The calculated moments on the Co, Mn and Si sites are 1.05, 2.98 and -0.08 $\mu_B$, respectively. The calculated band gap is very small, and the Fermi level is only 0.11 eV from the bottom of the conduction band. See fig. 2.36. Although a HMF, this small gap and this small distance of the Fermi level to the conduction band edge would make the realization of a perfect switch very difficult. Calculations on thin films and films coated with surface layers show large sensitivity of the electronic structure to the film orientation and surface coverage [2.72]. When explaining the occurrence of halfmetallic ferromagnetism for NiMnSb and PtMnSb the special low symmetry environment of the Mn atoms was emphasized. Covalent (repulsive) interactions between states which would otherwise form a broad band crossing the Fermi level where shown to lead to the formation of a gap. This mechanism does not work for some L2\textsubscript{1} type Heusler compounds (Ni\textsubscript{2}MnSb does not show a gap in the DOS). No simple explanation has been given for the (small) gap formed for Co\textsubscript{2}MnSi. An analysis of the wavefunction symmetry and of the interactions between states at the $\Gamma$ point has been given in [2.74].

Co\textsubscript{2}MnGe is predicted to be a HMF, too, with an even smaller band gap (0.21 eV) [2.71]. However, the experimental magnetic moment is significantly lower than the calculated value (table 2.9), casting doubt on the HMF character of this compound. A very recent polarized neutron diffraction study of Co\textsubscript{2}MnSi, Co\textsubscript{2}MnGe and some related structures has led to the conclusion that neither Co\textsubscript{2}MnSi nor Co\textsubscript{2}MnGe is a HMF [2.76]. However, I am not quite sure whether such a conclusion can be drawn from the results presented.

Other L2\textsubscript{1} type Heusler compounds which are predicted to be a HMF are Fe\textsubscript{2}MnSi [2.73, 2.74], Ru\textsubscript{2}MnSi and Ru\textsubscript{2}MnSb [2.75]. However, Fe\textsubscript{2}MnSi is only a ferromagnet at high temperatures (Curie temperature 219 K), having a complex magnetic structure in an intermediate temperature interval, and being AF below 67 K. And Ru\textsubscript{2}MnSi and Ru\textsubscript{2}MnSb are actually (fully metallic) antiferromagnets.
Table 2.9. Calculated [2.71] and experimental [2.76] properties for the proposed halfmetallic ferromagnets \( \text{Co}_2\text{MnSi} \) and \( \text{Co}_2\text{MnGe} \).

<table>
<thead>
<tr>
<th></th>
<th>( m ) (calc.)</th>
<th>( m ) (expt.)</th>
<th>( T_c ) (K)</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co}_2\text{MnSi} )</td>
<td>5 ( (\mu_B)/ \text{formula unit} )</td>
<td>4.96 ( (\mu_B)/ \text{formula unit} )</td>
<td>985</td>
<td>0.42</td>
</tr>
<tr>
<td>( \text{Co}_2\text{MnGe} )</td>
<td>5 ( (\mu_B)/ \text{formula unit} )</td>
<td>4.84 ( (\mu_B)/ \text{formula unit} )</td>
<td>905</td>
<td>0.21</td>
</tr>
</tbody>
</table>

2.3.3. \( \text{CrO}_2 \) – the simplest of all halfmetallic ferromagnets?

\( \text{CrO}_2 \) is a ferromagnetic metal with a Curie temperature of 392 K, and has found a technologically important application as medium material in magnetic tape recording. The compound crystallizes in the tetragonal rutile structure, shown in fig. 2.37, with \( a=0.442 \text{ nm} \) and \( c/a=0.6596 \). The unit cell contains two (crystallographically equivalent) Cr atoms and four (crystallographically equivalent) O atoms. The six O nearest neighbours of the Cr atoms form a slightly distorted octahedron.

In 1986 Schwarz predicted from selfconsistent band structure calculations that \( \text{CrO}_2 \) is a halfmetallic ferromagnet (HMF) [2.77]. The calculated (spin) magnetic moment is 2 \( \mu_B \) per unit cell, in good agreement with the experimental value of 2.01 ±0.03\( \mu_B \). The calculated spin-
polarized density of states (DOS) is shown in fig. 2.38. From the calculation, the HMF
character of CrO\(_2\) can be understood relatively straightforwardly within an ionic model
(Cr\(^{4+}\)(O\(^{2-}\))\(_2\)). The Cr\(^{4+}\)-ion is in a so-called high spin configuration \((3d\uparrow)^2(3d\downarrow)^0\), with spin
\(S=1\) and a spin magnetic moment of 2 \(\mu_B\) and with the two majority spin electrons in \(t_{2g}\)
orbitals. The figure shows, indeed, that the Fermi level is within the \(t_{2g}\) part of the crystal field
split majority spin 3d band, and that the minority spin 3d shell is empty. The presence of a
gap between an essentially filled O-2p derived band (broken curves in fig. 2.38) and an
essentially empty conduction band is quite generally observed for 3d-transition metal oxides.

![Fig. 2.38. Calculated spin, site and orbital resolved DOS of CrO\(_2\). Cr-3d (full curves), O-2s (dotted curves), and O-2p (broken curves). The energy is with respect to the Fermi level [2.77].](image)

The electronic structure of CrO\(_2\) and the nature of its halfmetallic ferromagnetism are thus,
seemingly, very simple. However, a more explicit inclusion of the effect of electron
correlation between d-electrons, as expressed by an effective Coulomb correlation energy \(U\)
(see section 2.1.5), has been argued by Korotin et al. [2.78] to change the picture. They have
investigated the effect of correlation using a so-called LSDA+\(U\) band structure calculation.
This method, which is still under development, aims at providing an improved prediction of
the ground state properties (total energy, charge and spin densities) and of the low energy and
high energy excitations [2.79]. The LSDA+\(U\) calculation with a calculated value \(U = 3\) eV
leads to a modified electronic structure, shown in fig. 2.39. The resulting change of the
electronic structure is, on first sight, not very strong, as expected from the fact that \(U_{\text{eff}}\)
is smaller than the Cr-3d band width of about 5 eV. CrO\(_2\) is still predicted to be a halfmetallic
ferromagnet. However, there are a few differences:
• The minority spin band gap is even larger (about 2.5 eV) than obtained using the standard LSDA calculation. Compare this wide gap with the much smaller gaps for the Heusler compounds discussed above!

• The dip in the majority spin DOS at the Fermi level is much deeper. The calculations showed that for $U>6$ eV a gap would develop for majority spin electrons, leading to the formation of a Mott-Hubbard insulator [2.80].

• The majority spin d-band overlaps with the O-2p band. Korotin et al. argue that the effect of the majority spin d-p overlap is crucial for understanding the ferromagnetism of CrO$_2$. In the ground state the valence of Cr is now mixed 4+ and 3+, and the so-called double exchange mechanism [2.81-2.82] is argued to give rise to the ferromagnetic ground state. Otherwise, the compound would be an (insulating) antiferromagnet. A discussion of the double exchange mechanism is beyond the scope of these lectures. Whereas CrO$_2$ seems to be the simplest of all half–metallic ferromagnets, the non-negligible effects of electron-correlation make the electronic structure and magnetic properties less trivial. Some experimental results (Appendix B) support this point of view.

An LSDA calculation of the electronic structure at the CrO$_2$ (001) surface [2.83] has shown that the halfmetallic character is maintained at the surface. The minority spin gap in the density of states of the surface atomic layer is only slightly smaller than the bulk gap (1.8 eV and 2.3 eV, respectively, in this paper).

Many experimental results support the HMF character of bulk CrO$_2$. An overview of the properties of this metastable compound is given in Appendix B. The spin polarization of $90 \pm 3.6\%$ for states at the Fermi level from Andreev reflection experiments (at 4.2 K and below) using a Nb/CrO$_2$ point contact is higher than observed for the HMFs NiMnSb and La$_{0.7}$Sr$_{0.3}$MnO$_3$. This result, and the recent successful selective deposition of thin single phase epitaxial CrO$_2$ films on insulating substrates (Appendix B), may be expected to lead soon to devices. At low temperatures these may be close to the perfect magnetoelectronic switch. However, an issue of concern, from the viewpoint of applicability, is whether their properties will be suitable for applications at room temperature, in view of the relatively low Curie temperature. It would be most important and timely to study the thermal stability of the magnetic moments at interfaces of CrO$_2$ with other materials.

---

**Fig. 2.39. Partial Cr-3d and O-2p density of states of CrO$_2$ [2.78].**

-8 -6 -4 -2 0 2 4 6 8

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Density of states (states/eV atom spin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-8 -6 -4 -2 0 2 4 6 8</td>
<td>Cr-3d</td>
</tr>
</tbody>
</table>

Novel Magnetoelectronic Materials and Devices – Reinder Coehoorn
Appendix 2-A. Experimental studies of the halfmetallic ferromagnets NiMnSb and PtMnSb: bulk properties, thin films, and devices

The theoretical discovery by de Groot et al. of halfmetallic ferromagnetism of NiMnSb and PtMnSb in 1983 [2.54], and the discovery by van Engen et al. in the same year that PtMnSb has a record high magneto-optical Kerr rotation effect for transition-metal based compounds at room temperature [2.55] has initiated much further work. A statistical, non-scientific, overview is given in fig. 2-A.1. After a dip in the beginning of the nineties, these compounds have again received much attention in the second half of the nineties, with the focus on thin film and magnetoelectronic device studies, improved theory (on e.g. the MO Kerr effect), and the application of novel techniques such as the Magnetic X-ray Circular Dichroism (MXCD) effect. There is not yet a comprehensive review paper on this subject. An overview of recent literature has been given in [2-A.1]. This appendix gives a brief overview of the properties studied and the methods used. For us the main question of interest is: are these compounds of interest as parts of future magnetoelectronic devices?

Ground state properties
NiMnSb:
• Spontaneous magnetization at 4 K varies from 3.98-4.2 $\mu_B$, depending on the sample preparation (see [2-A.2] and references therein), with value of 4.01±0.02 $\mu_B$ for one well characterized sample [2-A.2].
• Spin-polarized momentum density, as derived from positron annihilation experiments in good agreement with halfmetallic band structure (number of minority spin electrons is within ±0.01 and –0.02 electrons equal to the number expected for a HMF) [2A-4].

PtMnSb:
• Spontaneous magnetization at 4 K is 4.0 $\mu_B$ [2-A.3].

Properties related to low-energy excitations
First principles calculations of the paramagnetic Curie temperature $\Theta$, using the Heisenberg local moment model as outlined in section 2.2.6, have been carried out successfully by Kübler [2.60]. Similar as for the Heusler compounds discussed in sec. 2.2.6 the paramagnetic Curie temperature is for these systems 10-20 % larger than $T_C$. Table 2-A.1 gives an overview.

![Fig. 2-A.1. Statistical overview of numbers of publications in two-year periods on NiMnSb or PtMnSb, as obtained using the INSPEC electronic database.](image-url)
Table 2-A.1. Calculated \([2.60]\) and experimental \([2-A.3]\) Curie temperatures for NiMnSb and PtMnSb, in K.

<table>
<thead>
<tr>
<th></th>
<th>(T_C) (expt)</th>
<th>(\Theta) (expt)</th>
<th>(\Theta) (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMnSb</td>
<td>728</td>
<td>780-910</td>
<td>770</td>
</tr>
<tr>
<td>PtMnSb</td>
<td>572</td>
<td>610-670</td>
<td>650</td>
</tr>
</tbody>
</table>

In a HMF the only magnetic excitations possible at low energies are magnons. Single electron excitations with spin flip can only occur above a threshold energy, \(\Delta E_{th}\). This minimum energy is equal to the smallest of two energies: the distance of the top of the minority spin valence band to the Fermi level, or the distance between the Fermi level and the bottom of the minority spin conduction band. From the calculated band structure in fig. 2.28 this would be about 200 meV (Fermi level to bottom conduction band); taking also other calculated band structures, an uncertainty interval of maybe 75-225 meV follows (see \([2-A.2]\) and references therein). This would mean that magnon dispersion curves \(E(q)\) should be measurable (by inelastic spin-polarized neutron scattering) up to energies of at least this threshold value, without severe broadening due to the degeneracy of magnon and Stoner type excitations. A more detailed discussion should take into account the \(q\)-dependence of the border of the Stoner-continuum. See fig. 2-A.2.

Fig. 2-A.2.
(a) Schematic picture of a single electron-excitation with spin flip in a free-electron type ferromagnet. Case \((\Delta E,\Delta k)=(\Delta,0)\).
(b) Case \((\Delta E,\Delta k)=(0,k_{F\uparrow}-k_{F\downarrow})\).
(c) Diagram showing the possible single-electron excitations with spin-flip for a free-electron type ferromagnet (shaded region, “Stoner continuum”). Magnons are well-defined, long-living excitations outside this continuum. When magnons are degenerate with single particle excitations, their lifetime is limited (broad peaks in inelastic neutron scattering spectra).
(d)-(f) As (a)-(c), for a halfmetallic ferromagnet, with in (e): \(\Delta E=\Delta E_{th}\). No magnon peaks visible.
The observed magnon dispersion curves (fig. 2-A.3) are sharp below $E=75-80$ meV, but broadened above this energy (no structure visible along XK, e.g.). For the polycrystalline sample studied the Fermi level is thus located quite closely to one of the minority spin band edges.

The observed spin wave stiffness constant as obtained from neutron scattering is in good agreement with the spin wave stiffness as obtained from the observed decrease of the magnetization, which shows the expected Bloch $3/2$ law: $M(T)=M(0)(1-AT^{3/2})$, up to a temperature of about 70 K [2-A.2]. The detailed analysis of the spin wave spectrum in terms
of exchange constants $J_1$ and $J_2$ leads a value of the paramagnetic Curie temperature which is very close to the (directly measured) experimental value and to the calculated value [2.60] (see table 2-A.1). Also the separate experimental values of $J_1$ and $J_2$ are in good agreement with the separately calculated values [2.60].

![Graph](image)

Fig. 2-A.5. Resistivity of bulk NiMnSb (lower curve) and of a thin film deposited at 573 K (upper curve). The continuous curve is a fit to the power law $R = R_0 + BT^{1.35}$ [2-A.2]. The is no a priori reason for expecting this power law, but the fit serves to make clear that something happens around 70-80 K.

However, around the rather low temperature of 70 K the $M(T)$ curve starts to deviate from the $(1-AT^{3/2})$ form. In addition, resistivity measurements for bulk and thin film samples reveal a discontinuity in the temperature derivative near 70-80 K. See figs. 2-A.4 and 2-A.5. This crossover at 70-80 K in the magnetization and resistivity curves is not yet understood. Hordequin [2-A.2] remarks: “It is observed for single crystals, polycrystalline samples, and more or less ordered thin films, thus extrinsic origin must be ruled out, except if some fixed (sample independent) proportion of Mn or Ni goes into the vacancy sites”. Note that the temperatures are much smaller than the temperature related to the threshold energy (80 meV, 900-1000 K).

The resistivity measurements could be interpreted in terms of the opening of a new channel for scattering around 70-80 K, may be as a result of the closing of the minority spin gap, so that spin flip scattering would become possible. The fact that at higher temperatures the resistance curve does not show a $T^2$ form, a form which is often taken as an indication of spin-flip scattering, is not a counterargument against this, because the temperature dependence of the contribution of spin flip scattering to the resistivity would depend in a non-trivial way on the temperature dependence of the threshold energy. However, it must be mentioned that there is no experimental indication, from inelastic neutron scattering, that the threshold energy changes considerably in the temperature range up to 300 K [2-A.2].

In summary:
1. For NiMnSb and PtMnSb the local magnetic moment model provides a fair description of the low-energy magnetic excitations.
2. For NiMnSb the bottom of the minority spin conduction band is, at low temperatures, about 80 meV above the Fermi level.
3. The temperature dependences of the magnetization and the resistance show features at 70-80 K which have not yet been explained.

**Research options:**
- Temperature dependent measurement of the effective polarisation of tunnel junctions (with NiMnSb as the cathode).
- Band structure calculations of NiMnSb with low-energy magnetically excited structures (such as spin-spiral structures), to see what the effect is on the threshold energy.

**Properties related to high-energy excitations (infrared, visible, UV, X-ray)**

From infrared and visible light reflectance spectroscopy of NiMnSb films Mancoff et al. [A-2.6] have determined a rather sharp threshold energy, approximately 90 meV, above which the scattering rate increases sharply. They have associated this with the onset of an additional scattering channel which can be connected to spin-flip processes.

![Reflectance spectrum for a 500 nm NiMnSb film on sapphire, at 300 K and at 80 K (inset).](image1)

![Scattering rate spectrum, derived from the reflectance spectrum using a Kramers-Kronig analysis [2-A.6].](image2)
Consistent with the analysis given above for the magnon spectrum, the threshold energy is associated with the distance from the Fermi level to the bottom of the conduction band. The experimental reflection data, and the resulting frequency dependent inverse scattering rate curve are given in fig. 2-A.6. Interestingly, the threshold is at 80 K and at 300 K at the same energy. An assumed “realistic” density of states within which the minority spin band gap is has a width of about 0.75 eV, the Fermi level is at about 90 meV from the bottom of a sharp conduction band edge, and in which the polarization of the density of states at the Fermi level is assumed to be imperfect (50 %, assumed to be the result of ) provides a reasonable fit to the scattering rate curve [2-A.6].

Historically, the discovery of half-metallic ferromagnetism of these Heusler alloys was inspired by the discovery by Buschow and van Engen of a record high magneto-optical Kerr rotation of PtMnSb at room temperature [2.55]. The experimental data are shown in fig. 2-A.7. Annealing can increase the maximum Kerr rotation even to –2 ° [2-A.7]. This experimental work, carried out at Philips Research, was aimed at finding novel materials for magnetooptical storage media. Now, 20 years later, this interest in PtMnSb has disappeared, in view of the advent of optical recording at blue and violet wavelengths (around 400 nm). For bcc-Fe the maximum Kerr angle is almost –0.6 °, and for NiMnSb it is only –0.3 °.

Fig. 2A-7. Kerr rotation and ellipticity for PtMnSb [2.55] at room temperature. Color bar: not precisely on scale.
Similarly low values have been obtained for related Heusler compounds. The MO Kerr effect is the result of the combination of the exchange splitting and the spin-orbit interaction, which can give rise to a difference of the optical constants for left and right circularly polarized light (non-diagonal elements of the dielectric tensor). The large effect for PtMnSb led to the early belief that the special band structure of PtMnSb, with \( m_l = 1 \) holes in the top of the minority spin valence band at the \( \Gamma \) point, was responsible for the large Kerr rotation \[2.57\]. Recent theoretical work on the Kerr effect in this and related compounds has shown that the effect is not due to these holes, and that the HMF character of this compound is not or only very indirectly relevant [2-A.8-10]. These recent publications show that good progress in being made on the theory of the magneto-optical Kerr effect, which (as any optical effect in the visible range) can only be understood when taking intraband as well as interband excitations into account. However, the focus on the energy scale above typically 1 eV makes this work of less direct importance to the study of the detailed electronic structure near the Fermi level. The magneto-optical Kerr effect in alloys and compounds is reviewed in \[2-A.11\].

Unlike optical spectroscopy, which suffers from the fact that neither the initial state or the final state are obtained from the experiment (making some modelling necessary), photoelectron spectroscopy can, in principle, be used to obtain rather straightforwardly information on the electronic structure. Upon photoemission of electrons by UV or X-ray photons (of a fixed energy) electrons are emitted from the solid. The optical excitation process is energy-conserving, and this is also true for the transport of the photoelectron, provided that the excitation takes place within the escape depth (a few atomic layers, with for most substances a broad minimum of about 0.5 nm at electron energies around 100 eV). UV or X-ray photoelectron spectroscopy (UPS and XPS) are therefore surface-sensitive techniques. The kinetic energy (\( E_{\text{kin}} \)) spectrum of the emitted photoelectrons can be related to the spectrum of initial state energies (\( E_i \)) by using \( E_i = E_{\text{kin}} - h\nu + \Phi \). Here \( h\nu \) and \( \Phi \) are the photon energy and the surface work function, respectively. The optical excitation process is also spin-conserving, so when no spin flip takes place upon transport from the site of excitation to the vacuum, the spin of the initial state can also be measured. Finally, when a single crystal is used, the conservation of momentum parallel to the surface plane (due to the translational variance of the system in this direction) can be used for extracting the \( k \)(parallel) wavevector in the initial state. The energy resolution is determined by the quality of the light monochromator and of the electron analyser. Although various photoemission studies have been performed \[2-A.12\], none of them have given specific information about the spin polarization at the Fermi level, or the width of the minority spin band gap.

Bona et al. have applied a variant of this technique, photothreshold emission spectroscopy, to polycrystalline magnetically saturated NiMnSb: as a function of the photon-energy the spin-resolved energy integrated intensity of photoelectrons was measured, for photon energies just above the surface work function (energy range \( h\nu = 4.5-5.4 \text{ eV} \) \[2-A.13\]). Electrons with a kinetic energy smaller than the energy difference between the top of the valence band and the Fermi level are expected to be +100 % spin polarized. From fig. 2.28 this should be so for kinetic energies below about 0.4 eV. The emitted electrons are expected to have an escape depth (average perpendicular component of the inelastic mean free path) of the order 5 nm, so that the experiment is not extremely sensitive to surface disorder. However, even in this case zero polarisation for emission from the first unit cell (0.6 nm) would already reduce the polarization to 89 %, if the polarization from the bulk were 100 % \[2-A.12\]. In fact, the authors indirectly, by Auger analysis of Ni and Mn, some surface segregation of Sb.
The result obtained is shown in fig. 2-A.8. The largest observed polarization is about 50%. After careful analysis of a number of factors which play a role (escape depth, possible spin depolarization at the surface) the authors conclude that the energy gap in the density of states is certainly smaller than 0.5 eV. It is noted that they seem to mean, from their fig. 1, that in fact the distance between the top of the minority spin valence band and the Fermi level is less then 0.25 eV (instead of the calculated 0.4 eV).

NiMnSb and PtMnSb have also been studied using X-ray Magnetic Circular Dichroism [2-A.14], a technique within which the circular polarization dependence of the X-ray absorption due to spin-orbit split core levels is measured. From its analysis atom-resolved magnetic spin and orbital moments can be derived. So, although this may seem a bit paradoxical for a techniques which involves high-energy excitations, XMCD provides ground-state information. The results obtained are consistent with the theoretical and experimental results presented above and in the main text of this chapter. No detailed information about the minority spin gap has been obtained.

**Thin films and multilayers**

Thin film and multilayer studies have been motivated by the prospects of recording applications of the high MO Kerr effect of PtMnSb, and of magnetoelectronic device applications, for which NiMnSb is the more appropriate candidate. Conversely, the Kerr rotation has also been used for judging the quality of the films. Issues are composition, structural order and surface segregation.

Important results / highlights on the way to possible magnetoelectronic device applications:

- First successful deposition of NiMnSb films by evaporation onto heated glass or sapphire. Moodera group MIT, 1990 [2-A.15].
- Deposition of epitaxial PtMnSb and NiMnSb by dc magnetron cosputtering on sapphire(0001), White group Stanford, 1997 [2-A.16].
- Rf magnetron sputtering from a single composite target, 250-350 °C, no post anneal, layer thickness 10 nm, lowest resistivity $65 \times 10^{-8} \Omega m$. Childress group, Florida [2-A.17].
- Sputter deposited NiMnSb films with MO Kerr rotation and ellipticity very close to the bulk spectra [2-A.18]. “Magnetotransport and tunneling experiments being developed”. Florida, Orsay, IBM Almaden collaboration.
Devices
In the past three years several efforts towards magnetoelectronic devices based on NiMnSb have been reported. Table 2-A.2 gives an overview. There is a slow increase in GMR ratios obtained, but the potential perfect switch seems still far away. A difficult issue is of course the choice of the spacer layer, and its effect on the electronic structure of the interfaces. Recently, the first tunnel junction has been realized, within the group of Moodera at MIT. Although this is a big accomplishment, the effective spin polarization of tunneling electrons, as derived from the I-V curves of NiMnSb/I/Al junctions in a magnetic field and from the magnetoresistance of a NiMnSb/I/Py junction is even at 4.2 K only 28 %. This ‘polarization’ is not necessarily identical to the polarisation of the bulk DOS, as discussed in chapter 6. In that chapter also the novel Andreev reflection technique for determining the polarisation of the (or a ?) density of states at the Fermi level will be discussed. It may be concluded that it has not yet been possible to realize a large MR in NiMnSb based devices, but that there is strong progress during the past three years.

Table 2-A.2. Devices based on NiMnSb: measurement of the MR and of the effective spin polarization of NiMnSb.

<table>
<thead>
<tr>
<th>System</th>
<th>Device</th>
<th>MR ratio</th>
<th>Group</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMnSb / Mo / NiMnSb</td>
<td>CIP spin Valve</td>
<td>1 %</td>
<td>Pierre, Grenoble, 98</td>
<td>[2-A.19]</td>
</tr>
<tr>
<td>NiMnSb / V / NiMnSb</td>
<td>CIP spin Valve</td>
<td>-</td>
<td>German/French collaboration, 99</td>
<td>[2-A.20]</td>
</tr>
<tr>
<td>(NiMnSb / Cu / NiMnSb)_n</td>
<td>CIP-GMR CPP-GMR</td>
<td>2.5 % (4.2 K) 4 % (4.2 K)</td>
<td>Florida, Michigan, Orsay, 98</td>
<td>[2-A.21]</td>
</tr>
<tr>
<td>NiMnSb / Cu / Ni_80Fe_20</td>
<td>CPP-GMR</td>
<td>7 % (4.2 K)</td>
<td>Florida, Michigan, Orsay, 98</td>
<td>[2-A.21]</td>
</tr>
<tr>
<td>NiMnSb / Cu / NiMnSb/ Fe_50Mn_50</td>
<td>CPP-GMR</td>
<td>9 % (4.2 K)</td>
<td>Florida, Michigan, Orsay, 99</td>
<td>[2-A.22]</td>
</tr>
<tr>
<td>NiMnSb / Al_2O_3 / Al</td>
<td>F/I/S junction</td>
<td>Polarisation of NiMnSb at 4.2 K is 28 %</td>
<td>Moodera, MIT, 99.</td>
<td>[2-A.23]</td>
</tr>
<tr>
<td>NiMnSb / Al_2O_3 / Ni_80Fe_20</td>
<td>F/I/F junction (TMR)</td>
<td>19.5 % (4.2 K). Polarisation of NiMnSb at 4.2 K is 28 %.</td>
<td>Moodera, MIT, 99.</td>
<td>[2-A.23]</td>
</tr>
<tr>
<td>NiMnSb / Nb-Tip</td>
<td>F/S contact, Andreev reflection Technique</td>
<td>Polarisation of NiMnSb at 4.2 K is 58±2.3 %</td>
<td>NRL, Washington, MIT, Toulouse, Trinity College, 99</td>
<td>[2-A.24]</td>
</tr>
</tbody>
</table>

References Chapter 2, Appendix A

Appendix 2B. Experimental studies of the halfmetallic ferromagnet CrO$_2$

In the 1960s and 1970s studies of CrO$_2$ were often motivated by its use in magnetic tape recording media. A review from 1977 by Chamberland [2-B.1] covers the phase diagram, the preparation of the bulk compound, the bulk properties, the effect of substitutions, and the reactivity. The prediction of half metallic ferromagnetism and the possible application in magnetoelectronic devices has sparked renewed interest in the 1980s and 1990s. The introduction in a recent publication by Watts et al. [2-B.2] gives many references to recent work. This appendix focusses on work related to the halfmetallic ferromagnetism, and its applications in magnetoelectronic devices.

**Phase stability**

At room temperature CrO$_3$ is the stable oxide of chromium. CrO$_2$ can be obtained by thermal decomposition. The phase diagram (fig. 2-B.1) shows that heating at temperatures around 400 °C is required, at a high oxygen pressure. At 400 °C and 1 bar, Cr$_2$O$_3$ is the thermodynamically stable oxide. It is an antiferromagnet with a Néel temperature of $T_N=307$ K.

**Thin films**

Already in the 1960s a group at General Electric showed that CrO$_2$ films can be grown epitaxially on single crystals or polycrystals of other compounds with the rutile structure, preferably TiO$_2$ (rutile), but also on the (0001) planes of Al$_2$O$_3$ and Fe$_2$O$_3$. The method used was thermal decomposition of CrO$_3$ in a high pressure vessel at 425 °C and 320 bar [2-B.4] (guided by the phase diagram (fig. 2-B.1)). This Chemical Vapour (CVD) deposition technique has been adopted in recent studies of thin films, see e.g. [2-B.5]. The recent observation of 90 % spin polarization from an Andreev reflection experiment using a point contact has been obtained from a study of such films [2-B.6]. There are no large single crystals of CrO$_2$, so it cannot be excluded that the quality of some thin films is, from some points of view, better than that of bulk powders. However, one should be aware of the possibility that the CVD film deposition process leads to a high density of nucleation sites, resulting (after filling in of space in between the nucleation sites in a later stage) in irregular film surfaces. See fig. 2-B.2. See also ref. 2-B.11.

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Fig. 2-B.1.
*Phase diagram of Cr-O [2-B.1, 2-B.3]. Not undisputed (see [2-B.1] for details).*
A practical problem when making devices is that CrO$_2$ films are not readily etched in a reactive plasma or with wet chemicals (the conventional methods of patterning thin films using photolithography). Researchers at MIT (and later IBM and Brown University) showed that this problem can be solved by selective deposition of CrO$_2$ (using the CVD method discussed above). One possibility is to deposit a thin layer of Ti, e.g. on glass, oxidize it so that TiO$_2$ is formed, and pattern this layer. CrO$_2$ films grow readily on the rutile template, but does not nucleate well on bare glass (fig. 2-B.3(a), [2-B.7]). Selective growth on a TiO$_2$ single crystal substrate is an alternative method (fig. 2-B.3(b), [2-B.8]).

An alternative method has been reported by researchers at Bell Labs [2-B.9]:
1. Dissolving CrO$_3$ powder in de-ionized water.
2. Uniformly applying the solution on a single metal SrTiO$_3$ substrate.
3. Curing the specimen in a dry air atmosphere (this leaves a thin polycrystalline CrO$_3$ layer on the substrate).
4. Treatment in a few hundred bars of oxygen with increasing pressure, in the temperature range given by the phase diagram (fig. 2-B.1).

**Ground state properties: low temperature magnetic moment**

The experimental low temperature magnetic moment per Cr atom is $2.01 \pm 0.03 \, \mu_B$. The good agreement between the calculated spin contribution to the magnetic moment ($2 \, \mu_B$) and this...
(total) experimental magnetic moment per Cr atom suggests that the orbital magnetic moment is almost fully quenched by the crystal field. X-ray Magnetic Circular Dichroism experiments have confirmed this: the orbital moment is at most 0.01 µB [2.B.10]. The experimentally confirmed integer value of the magnetic moment provides strong support to the view that CrO₂ is a half-metallic ferromagnet.

Properties related to low-energy excitations

Specific heat

Barry et al. [2-B.11] have measured the specific beat, C, of a commercial CrO₂ powder, and fitted the results below 15 K to the expression \( C = \gamma T + \beta T^3 + \alpha T^{3/2} \), where the three terms represent the electron, phonon and magnon contributions, respectively (see textbooks, e.g. Kittel [2.1]). Assuming \( C_{\text{el}} = \gamma T = (1/3)\pi^2 N(E_F) k_B T \), which is valid for a gas of independent (non-interacting) electrons the experimental value \( \gamma = 5.1(9) \text{ mJ/mol K}^2 \) leads to \( N(E_F) = 2.2 \text{ states/eV atom} \), much larger than the experimental results of about 0.5 states/eV atom, or even less, obtained by Schwarz or by Korotin et al. (figs. 2.38 and 2.39). (An experimental value \( \gamma = 7 \text{ mJ/mol K}^2 \) is quoted in [2-B.12]). The value of \( \gamma \) can be enhanced by a factor \((1 + \lambda)\) due to the electron-phonon interaction. For non-magnetic metals superconductivity can occur when the enhancement is large. An electron-phonon enhancement parameter \( \lambda > 1 \) is considered to be extremely unlikely for CrO₂; this discrepancy between theory and experiment is regarded as an indication that the specific heat enhancement is due to electron correlation, beyond the LSDA [2-B.12].

Magnetization at finite temperatures

Up to at least 100 K the magnetization is found to be described by the Bloch \( T^{3/2} \) law: \( M(T) = M(0)(1 - BT^{3/2}) \). The parameter \( B \) is inversely proportional to the spin wave stiffness constant \( D \), leading to \( D = 150 \text{ meV A}^2 \) [2-B.12]. No results of inelastic neutron scattering experiments, which could give an indication of the energy above which magnons become degenerate with single-electron excitations (see Appendix 2A, NiMnSb), have been reported. Such experiments would be extremely interesting. In addition, a theoretical effort to predict the spin wave stiffness constant from band structure calculations would be of great interest, in particular in view of the ideas put forward on the origin of the ferromagnetic ground state put forward by Korotin et al. (see the main text).

Resistivity

Much experimental work and some theoretical analysis has been done on the resistivity of bulk samples and thin films. Only a selection of the thin film results will be discussed. Fig. 2-B.4 gives the bulk resistivity, compared with that for Ni and Nb. CrO₂ is a fairly good metal at low temperatures, but has a very high resistivity at room temperature, as compared to a more ordinary ferromagnetic metal such as Ni. It is therefore often called a “bad metal”. For the magnetic metals CrO₂ and Ni an additional contribution to the resistivity is evident, which may be ascribed to spin flip scattering. From the experimental data, combined with calculated Fermi surfaces, Lewis et al. [2-B.12] have derived an effective average mean free path for electrons in CrO₂ of 1.4 nm at 300 K, and 70 nm at 5 K. It is not yet clear how the very high resistance at room temperature can be explained, and how this may be related to the halfmetallic character. Barry et al. [2-B.11] and Watts et al. [2-B.2] have found that, phenomenologically, the resistivity is well described by the expression \( \rho(T) = \rho_0 + \alpha T^2 \exp(-\Delta/kT) \), with \( \Delta/k = 80 \text{ K} (\Delta = 5-10 \text{ meV}) \). A \( T^2 \) term in the resistivity is often attributed to electron-magnon scattering, and the exponential factor in this term could be interpreted as the result of suppression of electron-magnon scattering due to the presence of a gap of energy \( \Delta \) in the electron-magnon spectrum [2-B.2]. Although there is clearly a large gap at T=0 in the

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spectrum of single electron excitations with spin flip (because this requires at least an energy that is equal to the distance between the bottom of the minority spin conduction band and the Fermi energy (which is, from fig. 2.38 approximately 350 meV), this does not automatically imply that there is also a large gap (i.e. minimum excitation energy) in the magnon spectrum. Experimentally, Barry et al. [2-B.11] have not found evidence for the presence of a gap from the measured magnetization (which nicely follows the Bloch $T^{3/2}$ law), specific heat or magnetostrictive anisotropy. They proposed an (oversimplified) model, in which at finite temperatures regions with a diameter of the order of the minimum magnon wavelength excited at that temperature have opposite magnetization directions. On an atomic scale the halfmetallic electronic structure is assumed to persist. If the new length scale becomes smaller than the T=0 mean free path enhanced scattering takes place. Other models include as an additional ingredient a temperature dependence of the degree of electron localization [2-B.2, 2-B.11 and references therein]. Although the issue is still unresolved, it seems clear that understanding of the T=0 ground state is not sufficient for understanding the finite temperature properties.

**Magnetoresistance**

The magnetoresistance of thin films has been studied by several authors. See e.g. [2-B.2], [2-B.9] and [2-B.13-15]. For thin CrO$_2$ films with (antiferromagnetic insulating) Cr$_2$O$_3$ grain boundaries [2-B.9], and for powder compacts of CrO$_2$ with most likely a thin layer of the more stable antiferromagnetic Cr$_2$O$_3$ phase at the outer surface [2-B.15] (fig. 2-B.5) a magnetoresistance of 22 % and 29 % at 5 K has been found. It decreases with increasing temperature like $\exp(-T/T_{mr})$, with $T_{mr} \approx 40-50$ K.

![Fig. B-2.4. Measured bulk resistivity of CrO$_2$ (left) (data for current parallel to the [010] direction shifted by 100 $\mu\Omega$cm for clarity), compared with the bulk resistivity of Ni and Nb (right). The solid curves are Bloch-Grüneisen functions fitted to the low-temperature data (describing the electron-phonon contribution to the resistivity well up to approximately the Debye temperature). Figures taken from 2-B.12.](image)

Fig. 2-B.4. Measured bulk resistivity of CrO$_2$ (left) (data for current parallel to the [010] direction shifted by 100 $\mu\Omega$cm for clarity), compared with the bulk resistivity of Ni and Nb (right). The solid curves are Bloch-Grüneisen functions fitted to the low-temperature data (describing the electron-phonon contribution to the resistivity well up to approximately the Debye temperature). Figures taken from 2-B.12.

![Fig. B-2.5. Powder compact, of grains separated by a (thin) grain boundary region (green area).](image)

Fig. B-2.5. Powder compact, of grains separated by a (thin) grain boundary region (green area).
The most obvious explanation of the MR is that the degree to which the magnetization directions of neighbor grains are parallel increases with the application of a magnetic field. In the absence of coupling between the grains, the magnetization would be directed along the easy axis (c-axis). The effect of coupling between the grains can be reduced by making the separation larger. Coey et al. have therefore studied mixed powder compacts, consisting of equally large CrO$_2$ and Cr$_2$O$_3$ grains (the latter obtained by thermal decomposition of the part of the CrO$_2$ powder used) \cite{2-B.15}. See fig. B-2.6. For less than 23 volume % CrO$_2$ grains, the percolation limit, the resistivity was observed to become infinite. For a slightly larger fraction of CrO$_2$ grains (a 25 % ratio was studied most intensively) the conductance is then expected to be dominated by tunneling across Cr$_2$O$_3$ grains which are just small enough to provide a percolating path through the sample. This experiment is interesting because:

- Conductance is now most likely via tunneling. Indeed, the conductance was only weakly temperature dependent. The MR was now 56 % at 5 K, whereas for a perfect HMF (with random magnetic moments at zero field) an MR of 60 % would be expected, as argued by the authors.

  \[ \rightarrow \text{the spin polarization of the tunneling electrons is nearly complete at } 5 \text{ K.} \]

- The conductance is influenced by the Coulomb gap, which arises as a result of the change of charge on the (125 nm) particles involved upon interparticle electron tunneling jumps.

Properties related to high-energy excitations (infrared, visible, UV, X-ray)

Optical spectroscopy

Optical spectra are consistent with the predicted half-metallic ferromagnetism of CrO$_2$. In 1993 Brändle et al. showed that the measured optical reflection in the 0.8-5 eV range shows
good agreement with the predicted spectrum, taking interband and intraband excitations into account. The dielectric function was obtained by combining the results of first principles (ASW) band structure calculations for calculating the interband optical absorption spectrum with a semi-empirical Drude term for describing the absorption at low energies due to intraband excitations [2-B.16]. In 1999 Singley et al. reported results of an experimental study that included the near infrared range, down to 3 meV, studied in between 10 and 300 K [2-B.17]. In fig. 2-B.7(a,b) part of their results are given, expressed in terms of the (real part of the) optical conductivity $\sigma(\omega)$. The results are analyzed by the authors in terms of the simplified spin resolved density of states given in the inset I nfig. 2-B.7(a). Compare this with the figures 2.38 and 2.39. The peak at energy $E_1\approx 2$ eV is attributed to interband transitions across the pseudogap at the Fermi level within the majority spin band. The peak at energy $E_2\approx 3.35$ eV is attributed to transitions of minority spin electrons across the gap at the Fermi level. This energy is in good agreement with the result of a prediction for the minority spin contribution to the optical conductivity, obtained from band structure theory (thin line in (a), reference given in [2-B.16]), from which the optical gap in the minority spin band is approximately 2 eV. For energies below approximately 300 meV the optical conductivity was found to be temperature dependent (fig. 2-B.7(b)). This low energy part of the spectrum can reasonably well be described within the Drude model, within which $\sigma(\omega,T) \propto \tau/(1+\omega^2\tau^2)$, in which $\tau$ depends on $T$. An increase of $\tau$ with decreasing temperature, as can be deduced from the resistivity measurements (see above), can then (at least qualitatively) explain the observed temperature dependence of $\sigma$. From the low energy part of $\sigma(\omega,T)$ the authors estimate that the distance $E_3$ from the Fermi level to the bottom of the minority spin conduction band is in between 60-250 meV. The sharp peaks in the low energy part of the spectrum are due to optical phonons.

![Optical conductivity](image)

Fig. 2-B.7. Experimental optical conductivity of CrO$_2$ films. Overview (a) and the low energy part of the spectrum (b). From [2-B.17].

**Photoelectron spectroscopy**

The large low temperature conductivity of CrO$_2$ shows that the majority spin density of states at the Fermi level is non-zero, and may be even quite high. The predicted minimum in the majority DOS at the Fermi level is thus just a dip, not a real gap. However, spin-polarized photoelectron spectroscopy of CVD deposited thin films carried out in 1987 by...
Kämper et al. revealed an extremely low intensity of initial states at the Fermi level. 100% spin-polarization was observed, however, not at the Fermi level, but for states 2 eV below the Fermi level [2-B.18]. An experimental difficulty of photoemission experiments of CrO$_2$ is that surface preparation by the usual combination of Ar sputter cleaning and annealing is dangerous, in view of the metastability of CrO$_2$. In recent work by Tsujioka et al. the combination of photoemission and inverse photoemission (not spin-polarized) was used to study the density of occupied and unoccupied states around $E_F$ [2-B.19]. The sample was in this case a single phase polycrystalline powder compact, cleaned in situ by diamond filing at the measurement temperature (25 K for UPS, 80 K for inverse XPS). This low-temperature procedure aimed at creating a well-defined CrO$_2$ surface, not transformed to a more stable Cr-O compound. In contrast to the earlier results by Kämper et al. they now observed a (small) density of states at the Fermi level. See fig. 2-B.8. As predicted, the DOS has a deep dip at $E_F$. Their quantitative analysis suggests that the LSDA+$U$ theory provides a better description than the LSDA theory (see the figure), with $U\approx 3.4$ eV. This is close to the value of $U=3$ eV used for obtaining the DOS given in fig. 2.39. The authors concluded that the LSDA+$U$ theory should be a good starting point to understand the electronic structure of CrO$_2$.

Fig. 2-B.8.

UPS ($h\nu=40.8$ eV) and BIS ($h\nu=1486.6$ eV) spectrum (solid curves) compared with theoretical densities of states from the LSDA and LSDA+$U$ calculations [2-B.19 and references therein].

UPS=Ultraviolet photoelectron spectroscopy (photons in, electrons out). BIS='Bremsstrahlung Isochromat Spektroskopie'=inverse X-ray Photoelectron Spectroscopy (electrons in, photons out).

Tunnel junctions

Recently Barry et al. (Trinity College group) have presented the first tunnel junctions based on CrO$_2$ bottom electrode [2-B.20]. The barrier was formed by exposing the CVD grown CrO$_2$ films for several weeks to air. The top electrode was Co. The authors expect that this leads to a barrier consisting of Cr$_2$O$_3$ (2 nm thick). The observed MR ratio is 1%, at 77 K. In view of the possibly strong temperature dependence of the spin flip probability in the antiferromagnetic barrier layer experiments at much lower temperatures would be of much interest. Unfortunately, the paper does not report on the MR ratio at lower temperatures. The authors did not give information on the surface roughness of the CrO$_2$ bottom electrode, an expected difficulty when attempting the preparation of well defined junctions (see fig. 2-B.3).

References Chapter 2, Appendix B

References Chapter 2

2.1. See also the introductions to this subject in text books on solid state physics


2.17. R. Coehoorn, unpublished.

2.18. The excited hole states of Ni metal cannot be described completely in terms of the calculated band structure below the Fermi energy. Photoelectron spectra show bands, but also excitations which can only be explained within a localized model within which the ground state is regarded as a superposition of only a limited number of atomic configurations, (mainly) 3d⁹ and 3d¹⁰.


2.21. The definition of the Stoner parameter used here leads to values of I xc that are a factor 2 larger than the values given in [2.8].


2.64. R. Coehoorn, unpublished (2000).
2.73. S. Fujii et al., J. Phys. Soc. Japan 63, 1881 (1994);
2.81. C. Zener, Phys. Rev. 82, 403 (1951).

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