LECTURE NOTES
IN PHYSICS

M. Donath
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(Eds.)

Local-Moment Ferromagnets

Unique Properties for Modern Applications

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Markus Donath and Wolfgang Nolting, *Local-Moment Ferromagnets*,
Lect. Notes Phys. 678 (Springer, Berlin Heidelberg 2005), DOI 10.1007/b135699

Library of Congress Control Number: 2005930333

ISSN 0075-8450
ISBN-10 3-540-27286-0 Springer Berlin Heidelberg New York
ISBN-13 978-3-540-27286-1 Springer Berlin Heidelberg New York

Springer is a part of Springer Science+Business Media
springeronline.com

Printed in The Netherlands

Typesetting: by the authors using a Springer LaTeX macro package

Printed on acid-free paper SPIN: 11417255 57/Techbooks 5 4 3 2 1 0

Preface

For an understanding of the fascinating phenomenon of ferromagnetism, one needs a description of the mechanism that underlies the coupling of the magnetic moments. In some materials, the magnetic moments are caused by itinerant electrons of partially filled conduction bands: the band ferromagnets. In others, they are due to localized electrons of a partially filled atomic shell: the local-moment ferromagnets. The latter class comprises the classical local-moment systems like some rare-earth elements and compounds but also more complex materials like diluted magnetic semiconductors and half-metallic ferromagnets. These materials are a hot topic of current scientific research for two reasons. On the one hand, the exchange interaction between the localized magnetic moments and the quasi-free charge carriers in these materials is far from being fully understood. On the other hand, some of these materials are promising candidates for modern applications in magnetoelectronic as well as spintronic devices because of their unique magnetic properties. The present book provides a status report on our current knowledge about these interesting materials gained from experimental investigations as well as theoretical descriptions.

The various chapters in this book "*Local-Moment Ferromagnets: Unique Properties for Modern Applications*" are written in tutorial style by experts in the field. They were invited to an international specialists' conference held under the same title in Wandlitz near Berlin (Germany) from 15 to 18 March 2004. It was the third seminar of this type in Wandlitz. The first seminar in 1998 dealt with magnetism and electronic correlations in classical local-moment systems: *Magnetism and Electronic Correlations in Local-Moment Systems: Rare-Earth Elements and Compounds*, ed. by M. Donath, P.A. Dowben, W. Nolting (World Scientific Publishing, Singapore, 1998). The second seminar in 2000 was dedicated to the microscopic understanding of band-ferromagnetism as an electron correlation effect: *Band-Ferromagnetism: Ground-State and Finite-Temperature Phenomena*, ed. by K. Baberschke, M. Donath, W. Nolting, Lecture Notes in Physics 580 (Springer, Berlin, 2001). The *III. Wandlitz Days on Magnetism* in 2004 came back to the phenomenon of local-moment ferromagnetism but with a special focus on particular materials with unique properties as described above. The presentations of twenty-seven invited speakers from thirteen different countries initiated intense and

fruitful discussions between the sixty participants of the conference. More results were presented in form of posters during the three days of the seminar. The organizers hope that the lively discussions in Wandlitz support actual and future collaborations between the various specialists in the field of local-moment ferromagnets. Of course, this book cannot give a complete account of these fascinating subjects, given the tremendous worldwide activity, but rather focuses on the authoritative work of the contributors to the conference.

Generous financial support by the Deutsche Forschungsgemeinschaft for this conference made it possible to bring together experimentalists and theoreticians, senior researchers and graduate students, to discuss the present state of affairs, to learn from each other, and to define joint projects for the future. Sincere thanks are due to the staff and associates of the *Lehrstuhl Festkörperphysik* of the Institute of Physics at the *Humboldt-Universität zu Berlin* for doing an excellent job with the organization of the seminar. We wish to thank Prof. Dr. Jürgen Braun for his time-consuming work in collecting and composing the contributions to this book. We enjoyed the always effective collaboration with the Springer Verlag.

Münster, Berlin
March 2005

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Introduction

M. Donath, W. Nolting

The phenomenon of spontaneous collective order of the magnetic moments in some solid materials (ferro-, ferri-, antiferromagnetism), still attracts the interest of researchers working in experiment and theory alike. Experimentalists carefully characterize the magnetic properties of these interesting materials as a function of the structure, morphology, composition, magnetic field, pressure, and temperature. The ultimate goal is to tailor the magnetic properties and optimize them for certain applications. The theoretical description is not a trivial task because collective magnetism is a many-body phenomenon of quantum-mechanical nature. So far, no complete theory is available which could describe all kinds of ferromagnetic materials. Two major classes of ferromagnets are distinguished according to the kind of electrons carrying the magnetic moments: itinerant or band ferromagnets on the one side and local-moment ferromagnets on the other side. In the latter case, the exhange interaction is not a direct interaction due to the localization of the electrons with no significant overlap of their wave functions from one atomic site to the next. An interaction between the localized magnetic moments and the itinerant charge carriers or interspaced anions is needed for a so-called indirect exchange interaction. The contributions of this book concentrate on three different subjects within the topic of local-moment ferromagnetism. The first part deals with concentrated local-moment systems comprising classical local-moment ferromagnets as well as manganites, which show the colossal magnetoresistance (CMR) effect. The second part covers a relatively new class of materials, the diluted magnetic semiconductors. The origin of ferromagnetic order in these materials is subject of an intense debate today. The third part focuses on half-metallic ferromagnets, an interesting class of materials, well-known for decades, but with new perspectives for applications in magnetoelectronic and spintronic devices.

Concentrated Local-Moment Systems

The complex critical behaviour of Gd remains a highly controversial issue both from experimental and theoretical points of view, and that has been the case for nearly four decades. An elaborate analysis of high-resolution ac susceptibility and bulk magnetization data taken along the c-axis (easy axis

of magnetization) of a high-purity Gd single crystal made it possible to reveal several crossovers close to the Curie temperature T_C: Gaussian regime, isotropic short-range Heisenberg, isotropic dipolar, uniaxial dipolar - as predicted by renormalization group calculations. The experimental investigations evidenced the decisive role played by dipolar interactions, despite their weak strength, in establishing uniaxial magnetic order in Gd for temperatures near T_C.

The ferromagnetic Kondo-lattice model is considered a candidate for describing CMR-manganites. Monte-Carlo simulations, assuming classical spins, reveal that the double-exchange mechanism does not lead to phase separation in the one-dimensional model but rather stabilizes inidvidual ferromagnetic polarons. The ferromagnetic polaron picture can explain the pseudogap in the one-particle spectral function.

The physics of classical local-moment systems such as the "concentrated" ferromagnetic semiconductor EuS and the ferromagnetic 4f metal Gd is mainly due to the same interband-exchange interaction that also provides the carrier-induced ferromagnetism of the diluted magnetic semiconductors and, at least partly, the various magnetic phases of the manganites. The ferromagnetic Kondo-lattice model, better s-f (s-d) model, certainly covers the main aspects of the magnetic and quasiparticle features, however only if the model treatment goes beyond mean field. It can be shown that spin exchange processes, neglected by mean-field theories from the very beginning, are responsible for just the characteristic properties of such local-moment systems. It is demonstrated that a combination of a many-body evaluation of the Kondo-lattice model with a first-priniciples band structure calculation can reproduce almost quanitatively the temperature-dependent electronic and magnetic properties of Gd.

The rich physics of the manganites $La_{1-x}D_xMnO_3$ (D=Ca^{2+}, Sr^{2+}), which exhibit the CMR effect, appears to a large extent to be due to an exchange coupling between localized t_{2g} electrons and itinerant e_g electrons. The t_{2g} particles form a localized $S = 3/2$ magnetic moment while the correlated e_g band allows for a maximum filling $n = 1$ (Mott insulator for $x = 0$). Besides the complicated magnetic phase diagram, the convincing explanation of the metal-insulator transition, coinciding with the magnetic phase transition in the Ca-doped manganites, poses a sophisticated problem. It is commonly accepted that the exchange coupling of localized and itinerant particles is much bigger than the bandwidth, so that the double-exchange model, which is the strong coupling version of the ferromagnetic Kondo-lattice model, may represent a good frame for a description. However, there is evidence that the coupling of electrons to local phonon modes should be taken into consideration. The insulator-metal transition and the origin of the CMR has been investigated alternatively by using Monte-Carlo methods on finite-size clusters. Counter-intuitive observations are made with respect to the influence of randomness. The latter comes into play as charge randomness

(valence mixing Mn^{3+}/Mn^{4+}) or by lattice distortion (Jahn-Teller effect). Direct consequences are stabilization of short-range correlations of charge ordering, while long-range order is suppressed. A charge gap opens due to these correlations, and double-exchange ferromagnetism turns out to be robust against randomness. The ferromagnetic phase, therefore, delves into the charge order region what explains some pecularities in the temperature dependence of the resistivity. Most striking and really counter-intuitive is the finding that the insulator-to-metal transition may be due to randomness.

Towards Diluted Magnetic Semiconductors

Currently, experimentalists worldwide are highly active in preparing and characterizing diluted magnetic semiconductors and related systems, e.g., MnAs as bulk samples, MnAs thin films deposited on GaAs, $Ga_{1-x}Mn_xAs$ thin films, MnAs clusters embedded in paramagnetic GaMnAs. From an applications point of view, high Curie temperatures are highly desirable. Therefore, the conditions for high transition temperatures have to be explored. For MnAs, a non-typical first-order transition from a hexagonal low-temperature ferromagnetic phase to an orthorhombic high-temperature paramagnetic phase has stimulated intense research activity. Spin-polarized neutron scattering provides insight into magnetic correlations in MnAs, where magnetism is related to a structural instability. Neutron scattering sees magnetic correlations to be ferromagnetic with essentially no temperature dependence. This is in contrast to magnetization measurements which indicate an unusual temperature dependence in the orthorhombic phase. Epitaxial MnAs films on GaAs were characterized by ferromagnetic and spin wave resonance aiming at anisotropy and intrinsic exchange interaction. The first order phase transition described above manifests itself in the resonance spectra as a jump of both the resonance field and the resonance line width and turns out to be dominated by a coexistence of phases (stripe pattern).

A granular hybrid structure formed by ferromagnetic MnAs clusters embedded in paramagnetic GaMnAs exhibits ferromagnetism above room temperature ($T_C = 330$ K) due to the MnAs clusters. By co-doping with Te, the majority carrier type of the matrix can be changed from holes to electrons. The magnetoresistance of p-type and n-type samples differs considerably because of different s-d and p-d exchange integrals. The experimental data can qualitatively be understood as a result of the interplay between Zeeman splitting (field-induced tuning of band states), band filling and disorder.

In $Ga_{1-x}Mn_xAs$, Mn atoms substituting Ga promote ferromagnetism by exchange interaction with GaAs holes. The highest Curie temperature reported so far is 172 K. Interstitial Mn ions are thought to counteract this tendency via antiferromagnetic superexchange interaction with neighbouring substitutional Mn ions. An increase of the Curie temperature was observed for epitaxial GaMnAs layers after low-temperature post-growth annealing.

The interstitial Mn segregates from the bulk to the surface during annealing, giving rise to a further enhancement of the bulk magnetic transition temperature. Experimental evidence of Mn interstitial enrichment at the surface comes from x-ray absorption spectroscopy and x-ray resonant magnetic scattering. It is widely accepted that Mn interstitials are mainly affected by annealing. In addition, measurements have shown that co-doping with Be ions increases the number of Mn interstitials at the expense of substitutional Mn resulting in a strong decrease of T_C without an appreciable change of the free hole concentration. Theoretical studies have been performed to understand the magnetic properties of Mn ions in interstitial positions. One finds that the p-d exchange interaction matrix element is strongly reduced for interstitial Mn ions. The transfer of Mn ions from substitutional to interstitial positions (tetrahedral sites) diminishes the number of magnetic ions contributing to the carrier-induced ferromagnetism. That explains the experiments on GaMnBeAs. Furthermore, interstitial Mn acts as double donor, thus reducing the hole concentration with a respective influence on the ferromagnetism of the diluted magnetic semiconductor. The interaction between neighbouring interstitial and substitutional Mn ions could theoretically be identified as antiferromagnetic superexchange. - Since some difficult technological issues connected with the growth and lithography of magnetic semiconductors are now solved, it has become possible to explore the physics of nanostructures for promising spintronic applications.

A model study in the framework of the ferromagnetic Kondo-lattice model was used to explore the influence of magnetic moment disorder in diluted magnetic semiconductors. The carrier-induced ferromagnetism exhibits a strong band occupation dependence. In "concentrated" local-moment systems rather low electron (hole) concentrations favour ferromagnetic ordering. By a CPA-type evaluation of the static susceptibility it was shown that this effect transfers to the diluted systems, i.e. for ferromagnetism the number of free carriers must be substantially smaller than the number of magnetic ions. Compensation effects (antisites) appear to be a necessary precondition for ferromagnetism.

With a combination of first-principles calculations of interatomic exchange integrals for a classical Heisenberg model and Monte Carlo simulations, the observed Curie temperatures of a series of diluted magnetic semiconductors (Mn-doped GaAs and GaN, Cr-doped ZnTe) could be reproduced with good accuracy. However, a random moment distribution appears to be necessary to explain the measured T_C values. An ordered structure of the magnetic moments leads to transition temperatures that are by far too high. The actual exchange interaction seems to be exponentially damped by disorder. Magnetic percolation plays an important role for the magnetic properties of diluted magnetic semiconductors. Furthermore, the role of the holes for the carrier-mediated exchange interaction has been reexamined in a parameter-free theoretical scheme. Holes must be delocalized from the magnetic ion, but

simultaneously must experience a strong (local) exchange interaction with the magnetic impurity, which seems somewhat conflicting. By inspecting the resulting correlation energy, the different magnetic behaviour of $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xN$ can be understood.

Collective spin excitations in diluted magnetic semiconductors have been studied in the frame of the p-d (s-f, Kondo-lattice) model. It turns out that a proper modeling of the band structure by a six-band Kohn-Luttinger ansatz is important. The multiplet of spin wave dispersions (one optical and several acoustic modes) exhibits a strong band-occupation dependence reflecting to a certain degree the carrier-concentration dependence of the Curie temperature.

Highly promising new magnetic materials might be a group of diluted ferromagnetic oxides such as (Co,Fe,Mn)-doped ZnO, TiO_2, and SnO_2. These wide-gap semiconductors exhibit, surprisingly, Curie temperatures well in excess of room temperature. They could fulfill the fundamental criteria for spin electronics: Long diffusion lengths realized in a semiconductor or semimetal and a Curie temperature above 500 K. There are doubts, however, that this can be fulfilled by $Ga_{1-x}Mn_xAs$. All these oxides are n-type, often partially compensated. The average moment per transition-metal ion is higher than the spin-only moment of the magnetic ion, maybe because of the spin-split 4s band. Ferromagnetism is already present for very low magnetic impurity concentrations, far below the percolation threshold for nearest-neighbour coupling. The materials can be metallic or semiconducting. Unfortunately, so far, the properties depend critically on the preparation method. Model calculations show that the minority-spin 3d level must be pinned at the Fermi energy in order to get high Curie temperatures.

Half-Metallic Ferromagnets

Half-metallicity means in the ideal case that only electrons with one and the same spin direction will contribute to the electric current, i.e. the Fermi edge lies in a gap of one spin part of the density of states. Heusler alloys such as (Fe,Co,Ni,Cr,Pt)MnSb are promising candidates. Actually, NiMnSb with a T_C of 728 K is in the center of intensive investigation. The origin of the band gap is equally diverse as the origin of half-metallicity. Therefore, the origin of the bandgap is chosen as a criterion for the classification of half-metals: (1) weak ferromagnets with a covalent band gap, where structure and symmetry matters (NiMnSb), (2) strongly ferromagnetic ionic systems with a charge-transfer band gap (manganese perowskites $La_{1-x}(Ca,Pb,Sr)_xMnO_3$, CrO_2), (3) narrow-band ferromagnets with a d-d band gap like Fe_3O_4, which is nearly a Mott insulator. The preservation of the band gap, however, is intimately related to the surface/interface structure, imperfections and temperature.

Incoherent non-quasiparticle states in the band gap near the Fermi edge are theoretically predicted and may give considerable contributions to ther-

modynamic and transport properties. LDA+DMFT calculations for NiMnSb give evidence for the existence of these non-quasiparticle states which have not been observed experimentally yet. Core-level spectroscopy has been proposed as possible tool for this purpose. These states should also influence the temperature dependence of impurity scattering in a system like CrO_2 tunneling junction.

An important question is whether it is possible to get 100% spin polarization at the Fermi level, at least at $T = 0$, as first-principles bandstructure calculations predict. And if so, is this also true for surfaces and interfaces with their broken symmetry? Theoretically, insight into the stability of different NiMnSb surface terminations can be gained by density-functional calculations and by studying MnSb, NiSb, and NiMn surfaces. Furthermore, the influence of surface and interface electron states within the gap can be examined for uncovered surfaces and selected interfaces. What happens with the gap at finite temperatures? Magnon and phonon effects may lead to a depolarization, so that strict half-metallicity appears to be limited to $T = 0$. Proper doping and certain geometrical structures may lead to an optimization of spin polarization at the Fermi energy. It was shown that embedding NiMnSb in a NiScSb matrix, i.e. alloying $NiMn_{1-x}Sc_xSb$, the system changes for $x = 1$ to $x = 0$ from a nonmagnetic semiconductor via a diluted and even quasi-concentrated magnetic semiconductor to a genuine half metal.

Surface sensitive experiments on NiMnSb so far failed to detect 100% spin polarization at the Fermi level. Spin-resolved (inverse) photoemission as well as spin-resolved appearance potential spectroscopy give smaller spin polarization values by at least a factor of two. This is true not only at the Fermi level but also for the minority density of Mn states above the Fermi level. Besides the problem of surface/interface states destroying the complete surface spin polariztion at the Fermi level, the surface magnetization appears to be reduced. The reason for that is not clear at present. Spin-resolved photoemission on epitaxial $Fe_3O_4(111)$ films grown on W and Al_2O_3 exhibit a spin polarization of about -80% at room temperature. For epitaxial $CrO_2(100)$ films deposited on $TiO_2(100)$ substrates, a "record" value of 95% spin polarization at the Fermi level was found at room temperature, yet with a relatively small density of states.

Half-metallic ferromagnets are particularly attractive for spin injection. In this respect, NiMnSb turns out to be advantageous compared with oxides because no barriers are needed to protect the semiconductor from oxidation. Experiments suggest that it may be feasible to fabricate half-metallic NiMnSb/GaAs contacts. However, it is not straightforward to combine a low chemical disorder with a stoichiometrically and structurally controlled interface to suppress the formation of metallic interface states. Better results have been obtained by introducing a tunnel barrier, which results in about 6% spin injection at 80 K from polycrystalline NiMnSb films across an amorphous AlO_x barrier. Better results are achieved with the diluted magnetic

semiconductor $Ga_{1-x}Mn_xAs$, which, to a certain degree, can also be considered as a half-metal and can be combined with III-V semiconductors. In combination with a Zener tunnel junction to convert holes into polarized electrons, more than 80% spin injection was reported at 4.2 K. It is known that defects influence the electronic properties, electric transport, and magnetic coupling, which is also true for the insulating oxides used as tunnel junctions. Therefore, the importance of defects in magnetic tunnel junctions has to be considered in detail in the future.