Rare Earth Magnetism

Structures and Excitations

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PREFACE

The study of the magnetic properties of the rare earth metals may be said to have its origins in the 1930s, when the ferromagnetism of Gd was discovered, and the paramagnetism of the other heavy elements was investigated. The detailed exploration of these properties, and the concurrent development in our understanding of rare earth magnetism, occurred however as a result of two decisive advances in experimental technique during the 1950s. F.H. Spedding and his colleagues at Iowa State University began to produce large quantities of pure rare earth elements and to fashion them into single crystals, and during the same period, intense beams of thermal neutrons became available from research reactors. The neutron is a uniquely useful tool for studying the microscopic magnetic behaviour of materials, and neutron scattering has played the leading role in the progressive elucidation of the magnetic structures and excitations in the rare earths, and hence in understanding the magnetic interactions and their consequences.

This progress has of course been fully documented in the scientific literature and a number of compendia have served to consolidate the achievements of the many scientists involved. In particular, the review of the *Magnetic Properties of Rare Earth Metals*, edited by R.J. Elliott (Plenum Press 1972), which was written at a time when the field had recently become mature, set an exemplary standard of completeness, authoritativeness and, despite the large number of authors, coherence. More recently, a number of excellent surveys of different aspects of rare earth magnetism have appeared in the multi-volume series *Handbook on the Physics and Chemistry of Rare Earths*, edited by K.A. Gschneidner, Jr. and L. Eyring (North-Holland 1978 –), while Sam Legvold presented a largely experimental, but admirably balanced and complete review of the whole field in his chapter in Vol. 1 of *Ferromagnetic Materials*, edited by E.P. Wohlfarth (North-Holland 1980).

Our aim with this monograph has not been to produce a similarly comprehensive review, but rather to present a unified and coherent account of a limited but important area of rare earth magnetism, the magnetic structures and excitations, which both reflect the nature of the fundamental magnetic interactions, and determine many of the characteristic properties of the metals. We have tried to concentrate on the essential principles and their application to typical examples, generally restricting our discussion to the pure elements, and considering alloys and compounds only when they are necessary to illuminate particular topics. We have been involved for some time in the effort which has been made in Denmark to study, both theoretically and experimentally, the magnetic structures and especially the excitations in the rare earths. This account of the subject represents the results of our experience, and we have written it in the hope that it will be useful not only to those who have a special interest in rare earth magnetism, but also to a wider audience who wish to learn something about the methods and achievements of modern research in magnetism. We have therefore attempted to make the theoretical treatment reasonably complete and self-contained, starting from first principles and developing the argument in some detail. On the other hand, no pretence is made to completeness in our survey of the experimental results. Rather, they are used for illustrative purposes, and the specific properties of the individual elements may therefore have to be found in one of the reviews to which we frequently refer. However, we have tried to include the most important developments from recent years, with the aim of incorporating in this book most of the available information about rare earth magnetism, or directions as to where it can be found.

With very few exceptions, the magnetic properties of the rare earth metals can be understood in terms of what we will call the standard model, according to which the magnetic $4f$ electrons in the metal have the same angular-momentum quantum numbers as in the free ion. They interact, however, with the surrounding electric field of the crystal, and with each other through an indirect exchange mediated by the conduction electrons. Since the emergence of the standard model in the late 1950s, a primary aim of the rare earth-research community has been to determine these interactions, by a combination of experiment and first-principles calculations, and thereby to explain qualitatively and, where possible, quantitatively all features of the magnetic behaviour. In this way the limitations of the model can be explored, and appropriate modifications and extensions formulated where necessary. In fact, the standard model is remarkably successful; only in the relatively rare instances where the number of $4f$ electrons per atom is non-integral does it fail seriously. We discuss one such example, the electronic structure of α–Ce, in some detail, but otherwise say rather little about the interesting phenomena associated with itinerant f electrons that are called, depending on the circumstances, intermediate valence, valence fluctuations, or heavy-fermion behaviour, and are manifested in both the lanthanides and the actinides.

We begin with a lengthy introductory chapter in which, after a brief historical survey, those elements of rare earth magnetism which constitute the standard model, and are necessary for the comprehension of the rest of the book, are concisely summarized. Our approach is deliberately reductionist. The starting point is the electronic structure of the atoms, and we show how the magnetic moments and their interactions arise, and how they are expressed in the magnetic properties. In order that this survey should be reasonably comprehensive, there is some overlap with topics treated in more detail later in the book, but we have judged that this degree of repetition does no harm; rather the contrary. We then present the mean-field theory of magnetic structures, and in order to illustrate its power and generality, apply it in a number of typical but sometimes relatively complex situations, with emphasis on the disparate structures of Ho. To prepare for our discussion of the magnetic excitations, we give an account of linear response theory and its application to the magnetic scattering of neutrons, thus covering the principal theoretical and experimental techniques which are used in this field. The excitations are treated in three chapters, in each of which the theory, which is based on the use of the random-phase approximation, is presented in parallel with a selection of the experimental results which it purports to explain. The very extensive results which have been obtained on the ferromagnetic heavy rare earths, especially Tb, are treated in considerable detail, followed by a chapter on the spin waves in periodic structures, which are still under active investigation. The crystal-field excitations in the light rare earths, which have a somewhat different character from the previously discussed spin waves, are considered separately, and illustrated by the example of Pr, which has been by far the most comprehensively studied, and displays many interesting features. We conclude with a summarizing discussion, in which the emphasis is placed on those aspects of the subject which are not yet satisfactorily understood.

In the writing of this monograph, and during the many years of work which preceded it, we have benefitted inestimably from the advice and collaboration of our colleagues and friends in the rare earth-research community. To all of them, we express our sincere appreciation, while absolving them from responsibility for the faults which, despite their best efforts, remain. Two deserve special mention; Dr. Hans Skriver provided us with many unpublished results of his calculations of electronic structures, which we have used liberally in Chapter 1, and Professor Keith McEwen read the manuscript and made many constructive comments. We produced the book ourselves, in a form ready for printing, using TEX, which we found admirably suited for the purpose, and enjoyed a harmonious and effective cooperation with Oxford University Press throughout this process. The illustrations were prepared by the drawing office of the H.C. Ørsted Institute, and we are grateful to them for the care which they took in translating our sketches into elegant and informative figures. At various stages during the writing of the book, A.R.M. was director of NORDITA, visiting scientist at the Institute of Theoretical Physics and St. John's College, University of Oxford, and Miller Visiting Professor in the Physics Department of the University of California, Berkeley. The hospitality of all of these institutions is gratefully acknowledged. Finally, we thank our families for their support and forbearance with our mental abstraction during this lengthy enterprise.

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A number of misprints has been removed in this digital version of the book compared to the printed one. Among these, the most disturbing one was the missing Kronecker delta, $\delta_{\alpha\beta}$, in the expressions (1.4.26) and (5.5.2b) for the magnetic dipole–dipole interaction. The factor $1/2S$ has been moved from (1.2.19) to (1.2.17). The right charge of the electron $-e$ has been introduced in (1.4.1) and (1.4.3). The signs in the argument of the last δ-function in equation (4.2.9a) have been changed. The lattice sum for the dipole–dipole interaction introduced by (5.5.6) is small but not zero in the case of an hcp lattice with an ideal c/a ratio. This circumstance has required some modifications in the text below (5.5.6). The big left-bracket in (5.6.4a) has been moved to its right position. The signs in front of $\frac{\hbar\omega}{2}$ have been changed in the Fermi function arguments in the last line on page 267. The expression for the denominator at the bottom of page 277 has been squared. The expression for $\chi_{xy}(\mathbf{q},\omega)$ has been added to equation (6.1.18). The AB indices in some of the functions in (7.2.1b), (7.2.2a) and (7.2.3) now all read BA. A Δ was missing in the equations just before (7.2.8a). The fraction $\frac{1}{5}$ in front of A^2 in (7.3.25b) has been changed to its right value $\frac{1}{15}$, and the quadrupolar contribution makes a 1.5% correction to the susceptibility at T_N as told now in the sixth line on page 351. The intrinsic value of the quadrupole interaction is $P_{\|} = -0.128$ mK (not meV) in the fourth line on page 351. The phrase "magnetization density", which appeared repeatedly in the text, has been replaced by "magnetization" or "moment density". In addition to these corrections, a few number of trivial typographic errors has been removed. – I want to thank M. Rotter, H. M. Rønnow and M. S. S. Brooks for their contributions to this list of corrections.

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