Crystalline Electric Field and Structural Effects in *f*-Electron Systems

Crystalline Electric Field and Structural Effects in *f*-Electron Systems

Edited by

Jack E. Crow
Temple University
Philadelphia, Pennsylvania

Robert P. Guertin
Tufts University
Medford, Massachusetts

and

Ted W. Mihalisin
Temple University
Philadelphia, Pennsylvania

Plenum Press · New York and London

Library of Congress Cataloging in Publication Data

International Conference on Crystalline Electric Field and Structural Effects in *f*-Electron Systems, Philadelphia, 1979.
Crystalline electric field and structural effects in *f*-electron systems.

"Proceedings of the International Conference on Crystalline Electric Field and Structural Effects in *f*-Electron Systems, held in Philadelphia, Pennsylvania, November 12–15, 1979."
Includes index.
1. Crystalline electric field – Congresses. 2. Lattice dynamics – Congresses. 3. Electrons – Congresses. I. Crow, Jack E. II. Guertin, Robert P. III. Mihalisin, Ted W. IV. Title. V. Title: f-electron systems.
QC176.8.E35I57 1979 530.4'1 80-12454
ISBN-13: 978-1-4613-3110-0 e-ISBN-13: 978-1-4613-3108-7
DOI: 10.1007/978-1-4613-3108-7

Proceedings of the International Conference on Crystalline Electric Field and Structural Effects in *f*-Electron Systems, sponsored in part by and held at Temple University Philadelphia, Pennsylvania, November 12–15, 1979.

A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

PREFACE

Perhaps the title of this conference "Crystalline Electric Field and Structural Effects in f-Electron Systems" reflects best the growth and direction of the field. The title and the conference itself go beyond "CEF" in two broad and important respects. First, the inter-relations between CEF and mode softenings, distortions due to quadruplar ordering or the Jahn-Teller effect, have gained greater focus, hence the inclusion of... "Structral Effects." Second, much greater emphasis on the actinides and, in particular, comparisons between actinides and the lighter rare earths is seen in this conference, hence the more general terminology... "f-Electron Systems." It seems clear that this comparison will lead to an extension to the actinides of mixed valence and Kondo considerations, as well as CEF effects. The emergence of a broader discipline which includes all f-electron systems and which is concerned with unstable, as well as stable, valence reflects the maturation of the field and a coming to grips with the complexity, as well as the unity, of f-electron systems. This maturation is also seen in the growing realization of the effects of CEF on transport, thermodynamic properties, and superconductivity and its co-existence with magnetic order.

This volume contains 63 articles, all but two of which were presented at the Conference held in Philadelphia, U.S.A., on 12-15 November, 1979. About 100 conferees from 13 countries attended the meeting which consisted of four full days of lecture presentations. The conference included sessions on Crystalline field and Structure Effects, Lattice Effects, Actinides, Kondo and Intermediate Valence Properties, Transport and Thermodynamic Properties, Singlet Ground State Properties, Superconductivity and Lifetime Effects. Of the articles in this volume, 25 were invited talks and are generally of a more comprehensive review-like nature. An edited transcript of the question and answer sessions are found following each article. These discussions were unusually wide ranging, candid and intensive, and the editors feel their inclusion in the proceedings will help to convey accurately the interest and enthusiasm for

the topics presented. The comments may also prove useful to those seeking future research trends. An attempt was made to strike a balance between theory and experiment for the presentations, and the comments sections show the large extent to which there was discussion between theorist and experimentalists.

Many individuals helped make the conference a success, and made valuable contributions to the publication of these proceedings. The International Advisory Committee - W.J.L. Buyers, B.R. Cooper, P. Fulde, A. Furrer, C.Y. Huang, B. Luthi, J. Pierre and W. Suski, we thank for valuable suggestions for invited speakers. In particular, A. Furrer and W. Suski provided considerable assistance with the distribution of information and publicity all over Europe. A. Furrer also provided sagacious advice, based on his successful direction of the Zurich Conference in 1976. We also wish to thank G.H. Lander for many valuable suggestions. To the Temple University graduate students we owe much thanks for their handling of day to day operations during the conference, particularly in the recording of the discussion sessions. To Joan Crow our thanks for her expert assistance in all aspects of the preparation of this volume. Our thanks to Rhea Mihalisin for her extensive assistance in the administrative aspects of running the conference. Finally we thank Diane Keenan, indefatigable, accurate, dedicated and charming, without whose assistance this volume may not have been published at all.

The conference was supported by the National Science Foundation, U.S.A.F. Office of Scientific Research, the Office of Naval Research, Temple University, the Radio Corporation of America, Magnetic Metals Corporation and the Advanced Products Division of Air Products and Chemicals, Inc.

Jack E. Crow

Robert P. Guertin

Ted W. Mihalisin

CONTENTS

Crystalline Electric Field and Structural Effects in f-Electron Systems

SYMMETRY AND EXPERIMENT IN MAGNETISM

K.W.H. Stevens

Department of Physics, University of Nottingham
University Park
Nottingham NG7 2RD, England

INTRODUCTION

In the invitation to give this talk it was suggested that I might give a historical perspective on the subject of crystal field effects in rare earths, while at the same time feeling free to range more widely. This was an attractive invitation for altogether I have been associated with rare earths, on and off, for some thirty years. They have provided me with interesting problems, the opportunities to do some theory, and I anticipate they will continue to do so for some time to come.

I first became interested in magnetism in about 1947 just as it was beginning to recover from the almost complete halt of the war years. It was like beginning on a fresh subject except that the pre-war literature was available, and quite remarkable this was.

I shall begin by reviewing some of the pre-war literature, then go on to speak about the developments in the 1950's and finally say something about developments in more recent years. Apart from the period 1940 to 1950, each decade has been characterized by enormous growth in the literature, and the nearer I come to today, the more I should cover. For this part, I shall take advantage of the invitation and simply pick topics which particularly interest me.

THE PRE-WAR YEARS

My impression of the pre-war years is that most of the experimental work was being done in Europe, particularly in Leiden, and

most of the theoretical work was being done in the United States. In exploring it I have found two articles extremely helpful.[1,2] The story begins in 1908 when Becquerel discovered the paramagnetic rotation of the plane of polarization of light passing through natural crystals of xenotime and tysonite. Xenotime is YPO_4, but the crystals seem to have contained erbium. Tysonite (fluocerite) is a cerium lanthanum fluoride. There followed a period when quite a lot of magnetic measurements were made of room temperature susceptibilities, particularly on rare earth sulphates (see Van Vleck[3]). In 1925, before the advent of quantum mechanics, Hund explained the room temperature susceptibilities, except those of europium and samarium salts, with the Landé g-factor. The exceptions were resolved in 1929, when Miss Franks and Van Vleck realized that the multiplet structures of Eu^{3+} and Sm^{3+} are comparable with kT. By 1932 something more was needed and the first application of crystal field theory to the rare earths was made by Penney and Schlapp[4] who were working in the United States with Van Vleck. They attributed the properties of powders of praesodymium and neodymium sulphates to ions in a fourth-order octahedral crystal field. The fit was reasonably satisfactory, but it was fortuitous because a number of assumptions were made which we now know were inappropriate. What is not clear, from the literature, is whether there was confidence that crystal field theory would account for the properties of rare earth ions in crystals. I have some reason to suppose that the question was still open.

What ought to have been an important event in rare earth research occurred in 1940, when van den Handel's thesis appeared on the Faraday rotations in ethyl sulphates. But by that time most workers were otherwise engaged. For the first time, comprehensive results were available on single crystals, of known structures, with one magnetic ion per unit cell, and over a wide range of temperatures. (The Faraday rotation varies in the same way as the susceptibility, and for some crystals it was an easier property to measure. The results were mostly for light propagating along the crystal axis.)

Also in the pre-war period there were important developments which were relevant but not specifically related to rare earths. Heisenberg's theory of ferromagnetism[5] removed the mystery of the origin of the Weiss molecular field and appeared to open the door to the understanding of co-operative magnetism. Slater[6] was applying band theory to ferromagnetism. Collective electron ferromagnetism[7] came in 1938. Perhaps even more remarkable is that the first papers on antiferromagnetism were appearing as early as 1932 (e.g. see remarks in Van Vleck[1]). In Van Vleck's book[3], he was considering the question of nuclear magnetism. By 1939 he was looking into the scattering of neutrons by magnetic moments.[8] To link with later remarks, Casimir used equivalent operators in 1936, and Van Vleck[9] used a spin-Hamiltonian.

It is really remarkable how many ideas had been produced by that time. Spin deviation waves are implicit in Bloch's original paper[10] and Holstein and Primakoff's[11] famous use of them, dates from 1940.

THE DECADE 1950 to 1960

By about 1950 ESR results were being produced on diluted rare earth ethyl sulphates, and there was the question of interpreting them. Knowing the crystal structure it was, in principle, simple enough to write down a possible crystal field and proceed by the established pre-war technique. It was, however, quite tedious. I had been interested in nuclear quadrupole effects in atomic spectra, and I remember being puzzled as to where the standard form for this came from. It contained

$$3(\underline{I}\cdot\underline{J})^2 + \frac{3}{2}(\underline{I}\cdot\underline{J}) - I(I+1)J(J+1).$$

I knew how the magnetic interactions led to expressions in $\underline{I}$ and $\underline{J}$, for magnetic moments and angular momenta are closely connected. But how did something which was entirely electrostatic come to be expressed in angular momentum operators? It was surprisingly difficult to find where the expression originated, but I eventually tracked it down to a Prize Essay, written by H.B.G. Casimir in 1936 (since reprinted: ref. (12)). He used the Wigner-Eckart theory to replace a coulombic expression of the form $\Sigma\rho(3z^2 - r^2)$ by an expression of the form $Q[3I_z^2 - I(I+1)]$. The extension to more complicated solutions of Laplace's equation was just what was needed for the rare earth work. So, as far as I am aware, the first use of operator equivalents was in 1936, by Casimir[12]. It illustrates the climate for rare earth research at that time if I add that my paper on operator equivalents was rejected by the first journal to which I sent it, on the grounds that there was insufficient interest in rare earths! With the operators we soon knew that we could explain the ethyl sulphate results using crystal field theory. To illustrate how rapidly things were moving I received a letter from Professor Van Vleck saying that Dr. Finkelstein and he had used van den Handel's results and crystal field theory, but had not been able to find a satisfactory explanation. While he wished us success, he was not optimistic, and he would send me a photocopy of Finkelstein's thesis. By the time it arrived, we knew we had succeeded. I remember being absolutely amazed how far they had got with just the parallel susceptibility results, and indeed they would have succeeded had they had one further piece of evidence, which we had; that the Gd^{3+} ESR spectrum was not isotropic in the perpendicular plane. This can only come from O_6^6 type terms, which they had omitted.

In 1952 came the Conference on Magnetism, in Washington. Rare earths were hardly mentioned: it seems to have been accepted that

crystal field theory could be used for insulators and, had we realized it, the era of the great expansion in rare earth work, largely due to Professor Spedding, was just beginning. I shall single out three non-rare earth papers for comment. The first, by Professor Slater[13] contained a strong attack on crystal field theory. Slater[13] had become convinced that the only way to understand ferromagnetism was through band theory, and that it was necessary to compare the energies of determinantal wavefunctions based on Bloch functions. If the lowest state had a large spin then this would explain ferromagnetism. By implication he turned his back on the concept of localized moments, a basic concept of crystal field theory. I suspect this paper had a great deal of influence. Certainly for many years there has been a distinct division into those who begin with localized moments in crystal fields. It is interesting that for rare earth conductors it seems necessary to have a foot in both camps, localized for magnetic properties, and Bloch-type for the conduction properties, with the exchange couplings between the localized moments and the conduction electron spins being added almost as an afterthought. Presumably, what Slater disliked is that since one is usually treating a periodic lattice, and electrons are indistinguishable, it is unacceptable to pay a good deal of attention to the local symmetry and treat these other symmetries in a rather cavalier fashion. I remember being impressed and concerned by Slater's argument, for in the second of my choice of three papers I had been trying to understand exchange interactions between a pair of copper ions[14] and had behaved in just this way. I had been led to believe that exchange arises because electrons are indistinguishable, while the whole ethos of crystal field theory is to distinguish them. Even today many rare earth researchers do not seem to appreciate that there is this difficulty. The typical effective ionic Hamiltonian consists of operators describing localized moments, with various interaction terms. Many of the latter are described as due to exchange, and yet the concept of a localized moment, in so far as it comes from crystal field theory, definitely distinguishes electrons (see later). My problem with Slater's argument was that I knew that crystal field theory worked for magnetically dilute crystals, and there were many indications that it would succeed in concentrated crystals, provided that suitable interactions to crystal field theory restores the lost symmetries, which Slater wanted to retain from the beginning.

As part of the initial attack on crystal field theory Kleiner[15] calculated the crystal field at a chromium ion in an octahedron of O^{2-} ions, with the oxygen ion having an extended charge. He found that the crystal field was opposite in sign from that given by the original point charge model, and which had been so successful. Such a conclusion was so much at variance with what was known to occur experimentally that it seemed certain that something was seriously wrong with the calculation. Not long after, Tanabe and Sugano[16] performed a more refined calculation and restored the

status quo. This, in turn, was upset by Freeman and Watson[17] who produced a crystal field of the right sign, but much too small in magnitude. I shall not go into the whole history of this topic, as it is really concerned with iron group ions, and the early part is surveyed by Anderson[18]. The argument about how to calculate crystal fields for iron group ions is still going backwards and forwards, and the position is one of some confusion (see ref.(19), p. 715 for later references).

POST-1960

It generally seems to be assumed, with rare earth insulators, that because the 4f electrons are relatively further away from the neighbouring ions than are the 3d electrons in the iron transition group, it should be easier to calculate the crystals fields, though there is the possible complication of shielding effects from the outer electrons of the magnetic ion. Knowing of the difficulties with the iron group and the Slater-type objections to crystal field theory one should, perhaps, have reservations about how reliable these calculations are. The conductors raise further problems.

So how do we stand? From experiment there is plenty of evidence that phenomenological spin-Hamiltonians account, with a relatively small number of parameters, for wide ranges of observations. So spin-Hamiltonians must have some significance. On the other hand there are problems over the parameters, and the whole concept has been criticized. It therefore seems sensible to take account of the objections, and seek another route to our usual spin-Hamiltonian.

THE PROBLEM OF CRYSTAL FIELD THEORY

As already indicated there are objections to crystal field theory. I shall elaborate on this point. In treating a single magnetic ion in a crystal, say Nd^{3+} for example, the electrons are distinguished by ascribing electrons 1, 2 and 3 to the 4f shell and regarding all the others as simply constituting part of the electrostatic field. A typical crystal field term is

$$\sum_i A_4^o(35z^4 - 30r^2z^2 + 3r^4)_i$$

where the summation is only over electrons 1, 2 and 3. So electrons have been distinguished. If there are several magnetic ions, the 4f electrons on the respective sites are distinguished in crystal field terms for each site. Further, to obtain these terms an expansion in a small parameter is made. The criticisms are that the method distinguishes electrons and that such an expansion must be invalid, since a particular electron is not always near a par-

ticular site.

RECENT DEVELOPMENTS

It seems that the best thing to do is to go back to a more basic Hamiltonian where electrons are not distinguished, and are mutually repelling through coulomb interactions. Such a Hamiltonian has much more symmetry, indistinguishability and translational invariance. This is consistent with the Slater requirements, but it does not imply that his proposals for coping with the problem have to be followed. A number of other avenues are being explored. In the case of the insulators, it is already possible to map out a route from such a basic Hamiltonian to a spin-Hamiltonian in angular momentum operators, which is indistinguishable from that usually written down, from crystal field theory with exchange-like interactions.[19,20,21] The route is not a short one, and it does not have the simplicity of crystal field theory. Nevertheless, the basic features can be readily given: (1) at no point should any of the basic symmetries be lost; (2) the intention is to obtain an effective Hamiltonian which is to describe only the low-lying energy levels, not the eigenstates and not all the energy levels; (3) a good first approximation to the low-lying eigenstates is obtained by specifying that each magnetic and each non-magnetic ion has a definite number of electrons in each of its atomic shells. By this means a sub-space of the full Hilbert space is determined, which has the right number of eigenstates. The effective Hamiltonian is to be an operator in this sub-space. Extensions to cover conductors are being made, with some success.[22,23] Where it is not possible to specify definite numbers of electrons in each shell, as in the materials which show intermediate valence, it seems doubtful whether one can have descriptions in terms of conventional spin-Hamiltonians. I can now draw attention to my third choice of paper at the 1952 conference: a consideration of I.V., albeit in the context of iron group ferromagnets.[24]

CONCLUSION

The combination of extensive experimental work with the idea of spin-Hamiltonians, which comes directly from crystal field theory, supplemented by phenomenological exchange interactions, has been enormously successful. The symmetry criticisms which crystal field theory has received cannot be dismissed, and the problem has been to know how best to deal with them. Promising ways have recently been found, and although the end results can be expected to conform with the forms already used, they may lead to a better understanding of how the spin-Hamiltonian parameters arise. These can be expected to be functionally related to the basic Hamiltonian and therefore, possibly, obtainable by methods which have not yet been invented.

REFERENCES

1. J.H. Van Vleck, Am. J. of Phys., 18, 495 (1950).
2. J.H. Van Vleck, Chapter in "Physical Sciences, Some Recent Advances in France and the United States", New York University Press, (1962).
3. J.H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, (1932).
4. W.G. Penney and R. Schlapp, Phys. Rev., 41, 194, (1932).
5. W. Heisenberg, Z. Physik, 49, 619, (1928).
6. J.C. Slater, Phys. Rev., 49, 537, (1936).
7. E.C. Stoner, Proc. Roy. Soc., 165A, 372, (1938).
8. J.H. Van Vleck, Phys. Rev., 55, 924, (1939).
9. J.H. Van Vleck, Phys. Rev., 57, 426, (1940).
10. F. Bloch, Zeits f. Physik 61, 206, (1930.
11. T. Holstein and H. Primakoff, Phys. Rev. 54, 388, (1941).
12. H.B.G., Casimir, On the Interaction Between Atomic Nuclei and Electrons: Freeman and Co., San Francisco and London, (1963).
13. J.C. Slater, Rev. Mod. Phys., 25, 199, (1953).
14. K.W.H. Stevens, Rev.Mod. Phys., 25, 166, (1952).
15. W.H. Kleiner, J. Chem. Phys., 20, 1784, (1952).
16. Y. Tanabe and S. Sugano, J. Phys. Soc. Japan, 11, 864, (1956).
17. A.J. Freeman and R.E. Watson, Phys. Rev., 120, 1254, (1960).
18. P.W. Anderson, Magnetism, Vol. I, p.54, Edit. G.T. Rado and H. Suhl, Academic Press, New York and London, (1963).
19. B.H. Brandow, Advances in Physics, 26, 651, (1977).
20. K.W.H. Stevens, Phys. Rev. 24C, 1, (1976).
21. Fuchikami and Tanabe, J. Phys. Soc. Japan, 45, 1559, (1978).
22. K.W.H. Stevens, Crystal Field Effects in Metals and Alloys, p. 1, Edit. A. Furrer, Plenum Press, New York and London, (1977).
23. L.L. Hirst, Advances in Physics, 27, 231, (1978).
24. J.H. Van Vleck, Rev. Mod. Phys., 25. 220, (1952).

COMMENTS

COOPER: One of the points was, it will not give the eigenstates of these levels; can you say a little more about that?

STEVENS: I didn't really emphasize this, but if you think of a Hilbert space, the eigenstates are vectors in this Hilbert space. If you decide you are going to work in a subspace, then, in a sense, what the mathematics does is project the actual eigenstates into the subspace. The subspace is limited in dimensions, then the eigenstates of the effective Hamiltonian are these prejected things. Or alternatively, if you look at it in perturbation theory, you take an unperturbed state and mix bits into it, but we take those bits and we don't mix them into the states but into the energies. The effects of them go into the energies rather than the states.

STRUCTURAL PHASE TRANSITIONS AND MAGNETOSTRICTION IN METALLIC RARE-EARTH COMPOUNDS

H.R. Ott

Laboratorium für Festkörperphysik
ETH-Hönggerberg
8093 Zürich, Switzerland

INTRODUCTION

In solid state physics, materials containing rare earth ions have been and still are a playground for many experimental and theoretical studies, and a good part of all the efforts are investigations of various types of phase transitions observed in these substances. These materials, no doubt, owe their interesting properties to a usually localized, unfilled 4f shell of the rare earth ions and, depending on the material, the interaction of those ions with neighbouring ions, the lattice and/or conduction electrons.

A very important interaction is the influence of crystalline electric fields on the possible energy states of the localized 4f electrons. The Hund's rule ground state of the 4f electrons is split by these crystalline electric fields and depending on the number of 4f electrons per ion and the symmetry of the crystal lattice, various substates with different degeneracies are formed. In metallic rare earth compounds the crystalline electric field acting on a particular ion is not only given by the charges of the neighbouring ions, but is strongly influenced by the electric charge distribution on and close around that ion itself, as recent evidence indicates.

The crystal field splitting of the 4f electron states in metallic rare earth compounds ranges from about 10 K to a few hundred Kelvin and, therefore, its influence on physical properties is usually observed at low temperatures, say below room temperature. The same is true for most of the phase transitions, usually magnetic ordering or structural phase transitions or both, which are deter-