THE THEORY OF TRANSITION-METAL IONS

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BY

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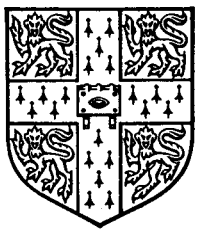

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PREFACE

I have tried to present a unified and deductive introduction to that part of theoretical physics which is becoming known as ligand-field theory. The field of application of this theory is rapidly spreading at the present time and, because of this, it appears more suitable and more helpful to concentrate upon the methods of the theory rather than the details of applications. Hence, although a considerable survey of experimental measurements appears in chs. 10–12, it is by no means exhaustive. The exclusion of almost all reference to rare-earth or actinide ions and to chemical applications—for which the reader is referred to L. E. Orgel's book, *Transition-metal Chemistry* (London: Methuen, 1960)—stems from similar considerations.

There are a number of essential prerequisites to a proper understanding of the theory of the physical properties of ions in compounds. Chs. 1–6, together with §§ 8.4, 8.6 and 8.7, include those things I deem necessary. Three seem to me especially important: a detailed understanding of the selection rules and other numerical restrictions upon matrix elements implied by the classification of the behaviour of the constituent operators and functions under the elements of symmetry groups; the use of Dirac's equation to derive the spin-orbit coupling and nuclear hyperfine energy; the complex of ideas which has as particular manifestations Kramers's theorem on degeneracy, Wigner's operation of time reversal, and Frobenius and Schur's discussion of the relation between an irreducible representation and its complex conjugate. These matters play a central role in my presentation of the theory.

When deciding the contents of the book it soon became apparent to me that there were many important propositions which workers in the field regarded as 'obvious' and used in order to streamline calculations, but which had never been formally proved. A particular example is the relation between 'holes' and 'particles'. Following the work of Shortley and Racah, it is to be expected that the matrix elements of quantities of interest between hole states are simply related to those between particle states in ligand-field configurations as they are in atomic configurations. But to use this relationship with confidence in calculations it is necessary to know and prove its precise form, including the specification of relative phases. In this case and otherwise I have tried to present and prove results in the forms which are actually needed in calculations.

With a book of this size in a fast-expanding field it is inevitable that the contents should represent in the main the author's position at a time past. Most of the book was written in 1958 and it was submitted in the spring of 1959 but I have referred to later work when it has cast a genuinely new light on some topic.

Finally, it is a pleasure to acknowledge my benefit from many discussions on theoretical physics and theoretical chemistry with Professor H. C. Longuet-Higgins and members of his department, especially with L. E. Orgel on the theory of transition-metal ions. I am also indebted to C. K. Jørgensen for his kindness in preparing Table 11.3 for me and to him and C. E. Schäffer for the data in Appendix A 40.

J. S. GRIFFITH

June 1960