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Magnetochemistry

With 244 Figures and 21 Tables

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Preface

This is a book about things in magnetism that interest me. I think that these are important things which will interest a number of other chemists. The restriction is important, because it is difficult to write well about those things which are less familiar to an author. In general, the chemistry and physics of coordination compounds are what this book is about.

Magnetochemistry is the study of the ground states of metal ions. When the ions are not interacting, then the study of single-ion phenomena is called paramagnetism. When the metal ions interact, then we are concerned with collective phenomena such as occur in long-range ordering. Several years ago, Hans van Dyneveldt and I published a book that explored these subjects in detail. Since that time, the field has grown tremendously, and there has been a need to bring the book up to date. Furthermore, I have felt that it would be useful to include more subsidiary material to make the work more useful as a textbook. This book is the result of those feelings of mine.

The subject of magnetism is one of the oldest in science, and the magnetic properties of atoms and molecules have concerned physicists and chemists since at least the turn of the century. The Nobel Laureate J. H. Van Vleck has written a brief but comprehensive review of magnetism [1], and he has argued that quantum mechanics is the key to understanding magnetism. I would go further and argue that magnetism is the key to understanding quantum mechanics, at least in the pedagogical sense, for so many physical phenomena can be understood quantitatively in this discipline. I hope the book expresses this sense.

Units are a troublesome issue here, for people working in the field of magnetochemistry have not yet adopted the SI system. I have converted literature values of applied magnetic fields from Oe to tesla (T) where feasible, and tried to use units of joules for energy throughout. In order to avoid total confusion, I have generally quoted parameters from the literature as given, and then my conversion to the SI units in parentheses.

I would once again like to dedicate this book to my wife, Dorothy, because she never answered my continual question, Why in heaven's name am I writing this book? I would like to thank Hans van Dyneveldt for reading the manuscript and offering perceptive criticism. He has also always been helpful in patiently explaining things to me. Jos de Jongh has also taught me a lot about magnetism. I would also like to thank my colleagues around the world who were kind enough to send me preprints and reprints, for allowing me to quote from their work, and for giving me permission to reproduce figures and tables from their publications. My research on the magnetic properties of transition metal complexes has been supported by a succession of grants from the Solid State Chemistry Program of the Division of Materials Research of the

National Science Foundation. Most of the typing was done by my good friends, Wally Berkowicz, Pat Campbell, and Regina Gierlowski.

Chicago, October 1985

Richard L. Carlin

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1. Van Vleck J.H., *Rev. Mod. Phys.* **50**, 181 (1978)

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List of symbols

M	= magnetization	H	= Hamiltonian
H	= magnetic field strength	S	= spin operator
κ	= magnetic susceptibility	$10Dq$	= cubic crystal field splitting
v	= molar volume	ν	= frequency
n	= principal quantum number	Q	= heat
l	= orbital quantum number	U	= internal energy
m	= magnetic quantum number	S	= entropy
m_s	= magnetic quantum number	E	= enthalpy
\mathcal{S}	= total spin	F	= free energy (Helmholtz)
\mathcal{L}	= total angular momentum	G	= free energy (Gibbs)
M_L	= total angular momentum quantum number	c	= specific heat
M_S	= total spin quantum number	$B_J(\eta)$	= Brillouin function
C	= Curie constant	τ	= relaxation time
T	= absolute temperature	ω	= frequency
μ	= magnetic moment	E	= energy
k	= Boltzmann constant	g_J	= splitting factor
g	= Landé constant	S	= total spin magnetic moment
N	= Avogadro's number	L	= total orbital magnetic moment
μ_B	= Bohr magneton	H	= magnetic field
h	= Planck's constant	λ	= spin-orbit coupling constant
c	= speed at light	J	= exchange constant
m	= mass of an electron	d	= distortion vector
e	= charge of an electron	T_c	= critical temperature
P	= pressure	λ	= Weiss-field constant
V	= volume	z	= magnetic coordination number
R	= molar gas constant	N	= demagnetization factor
J	= inner quantum number	p_c	= critical concentration
Z	= partition function	ε	= voltage
D, δ	= zero-field splitting parameter	n	= number of mols
		I	= current