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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 Duyneveldt 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 Duyneveldt 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

Reference

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

Contents

List of symbols

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