

Inorganic Chemistry Concepts 2

Richard L. Carlin

A. J. van Duyneveldt

Magnetic Properties of Transition Metal Compounds



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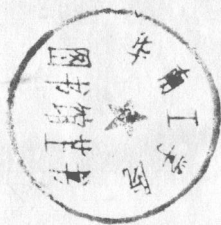
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PREFACE

This is a textbook of what is often called magnetochemistry. We take the point of view that magnetic phenomena are interesting because of what they tell us about chemical systems. Yet, we believe it is no longer tenable to write only about such subjects as distinguishing stereochemistry from the measurement of a magnetic susceptibility over a restricted temperature region; that is, paramagnetism is so well-understood that little remains to explore which is of fundamental interest.

The major purpose of this book is to direct chemists to some of the recent work of physicists, and in particular to a lengthy exposition of magnetic ordering phenomena. Chemists have long been interested in magnetic interactions in clusters, but many have shied away from long-range ordering phenomena. Now however more people are investigating magnetic behavior at temperatures in the liquid helium region, where ordering phenomena can scarcely be avoided.

The emphasis is on complexes of the iron-series ions, for this is where most of the recent work, both experimental and theoretical, has been done. The discussion therefore is limited to insulating crystals; the nature of magnetism in metals and such materials as semiconductors is sufficiently different that a discussion of these substances is beyond our purposes. The book is directed more at the practical experimentalist than at the theoretician.

Thus, this book tries to point the way that we believe the science of magnetochemistry should be going. In that regard, this book is very much an advertisement for the review article by L.J. de Jongh and A.R. Miedema which is referred to extensively throughout the book. RLC in particular has learned a great deal from this article and from conversa-

tions with Jos de Jongh, and would like to thank him for permission to depend so heavily on his thesis for our text.

We sincerely appreciate the secretarial assistance of Paula Hutton and Fran Petkus in the preparation of the manuscript. We would like to extend particular thanks to Yvonne Bosje, Astrid Durieux, Rita de Jong and Doky Lengkeek, who took care of typing the camera-ready copy, while at the same time carrying on their regular secretarial duties. We would also like to thank all the authors and copyright owners for permission to reproduce the published figures we have used. It was Wim Tegelaar who did all the work for the enormous number of figures throughout this book.

Chicago, Leiden

August 1977

R.L.C.

A.J.v.D.

INTRODUCTION

The authors of this book asked me whether I was willing to make some historical remarks as an introduction. I gladly accepted this invitation as it is certainly useful and interesting to look back when realising how fast the development of physics in general and certainly also in the field of magnetic research was, and is. It is not my intention to give here a well-documented complete history but I shall restrict myself to some remarks from the period in which I worked in the Kamerlingh Onnes Laboratory of Leiden University. I entered this laboratory in 1929 after my "candidaats examen", more or less comparable with a B.Sc.

At the end of the 'twenties an important subject of research was still the measurement of susceptibilities of compounds down to about 14 K and the determination of the magnetic moments of the ions in the iron- and rare-earth groups. I remember De Haas telling me about the enthusiasm of Sommerfeld when De Haas told him at the Solvay Conference in 1930 about Gorter's measurements of the susceptibility of chromic alum which showed a constant "spin-only" moment till low temperatures. From these data the untenability of the theory of Laporte and himself about the moments of ions in the iron group became clear.

Some years before (in 1923) Woltjer had been able to give, by means of his measurements on Gd sulphate down to 1.3 K, a nice confirmation of Boltzmann's theory; these measurements were therefore, as Ehrenfest pointed out, of a basic importance. Because of the large value of the magnetic moment and the moderate accuracy of the measurements at that time the difference between a Brillouin function and a Langevin function was not evident. By means of the more accurate measurements of the paramagnetic rotation by Becquerel and this author, some 17 years later,

it was shown that a satisfactory representation with a Langevin curve was not possible.

Other measurements by Woltjer, first with Kamerlingh Onnes, later with Wiersma, showed remarkable deviations from Curie's law for several anhydrous chlorides. They had some resemblance with ferromagnetism. This impression was strengthened by specific heat measurements of Schubnikow in Charkow, which also showed an anomaly. Just before the war these results were extended by measurements on a number of other compounds by Schultz and by Becquerel and the author, who spoke of metamagnetism. Also in other countries similar anomalous results were reported. Only later it became evident that these results were of an antiferromagnetic character. Though Néel had already put forward in 1932 a first indication of this new form of ordered magnetism, a suggestion which he developed further in 1936, only Van Vleck's article in 1941 made, after my impression, these ideas and their consequences more accessible, opening the doors to an immense field of research.

In 1939, a short time before the outbreak of the war, the first special magnetism conference took place in Strassbourg. I was already mobilized but obtained permission to replace J. Becquerel who was unable to come. The president of the congress was P. Weiss, professor in Strassbourg, which was a very important center of magnetic research. There were only some 30 official participants from 7 countries; about 9 others from these same countries took part in the discussions. Comparing this with the number of participants of the last magnetism conference, in 1976 in Amsterdam, that amounted to almost a thousand (980 from 34 countries), we see again the enormous increase of physical research. This Strassbourg conference can be considered as a closing of the first phase, and at the same time of the prewar period, a period in which the theoretical bases were drawn up and developed, and in which for instance the experimental application such as the obtaining of low temperatures by means of the adiabatic demagnetisation, as suggested by Debye and by Giauque and realised almost simultaneously in Berkeley and in Leiden, had also been further developed.

The postwar period was characterised by a rapid growth of the number of researchers and by the development of methods that had been discovered and worked out during the war for quite different purposes. I think here in particular of the application of cm waves used in EPR and also of other high-frequency techniques as necessary for NMR and magnetic relaxation. Also the rapid growth of the instrument industry, especially the electronics

industry, may not be forgotten.

With respect to the Leiden research in particular one may, amongst many other subjects, think in the first place of the paramagnetic relaxation studies in which, under the supervision of C.J.Gorter, who started this research, very much work has been done. He had already done some work in this field before the war and during the war he wrote a fundamental monograph on it. Also the subject of antiferromagnetism can be mentioned. On $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, researches were carried out with a variety of methods, again under the leadership of C.J.Gorter. In a theoretical article, written in collaboration with the mathematician J.Haantjes, he presented a nicely rounded-off picture of a simple form of this phenomenon, based on the ideas of Néel.

The wealth of forms in which the magnetic phenomena present themselves to us nowadays always increases and therefore the study of them becomes more and more intricate. In order to prevent those who start doing research in the field of magnetism from soon getting off the track, good guides are necessary and I hope that the present book will be able to play a role as such.

J. van den Handel

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CHAPTER I

PARAMAGNETISM: THE CURIE LAW

A. INTRODUCTION

This is a book concerning the magnetic properties of transition metal complexes. The subject has been of interest for a long time, for it was realized as long ago as the 1930's (1) that there was a diagnostic criterion between magnetic properties and the nature of the metal ion in a complex. Indeed, over the years, magnetic properties have continued to be used in this fashion. With time, the emphasis has changed, so that now chemists are becoming more interested in the magnetic phenomena themselves, and the subject is no longer a subsidiary one. One result of this new emphasis, which is hopefully rationalized and explained by this book, is that chemists must continue to decrease the working temperature of their experiments, with measurements at liquid helium temperatures now becoming common. In other words, the careful study of magnetic properties of transition metal complexes at low temperatures is essentially a redundant statement. Thus, little mention will be made of the many experimental results that pertain to high temperatures, that is, the temperatures of liquid nitrogen and above. The reason for this is simple, that the quantities which are being sought, such as the ground state energy levels, make a far more significant contribution to the measured phenomena at low temperatures. The emphasis is on measurements carried out on single crystals.

Magnetic susceptibilities and specific heats are among the principal measurements that chemists and physicists carry out on magnetic systems, and they therefore comprise the major part of the discussion. We hope to show how intimately connected the two are, and will attempt to correlate these magnetic properties with chemical structure.

Of course, one cannot, and should not, ignore the EPR spectra of metal ions in a work of this sort, but they are not discussed here at length. An introduction is presented, and some of the results are used, but the subject has already been discussed in many other books and reviews. Some subjects, such as neutron diffraction and nuclear resonance, are of special importance in magnetism, particularly in the study of ordered states, and some of the results obtained from these techniques are described here. Yet, these subjects cannot be treated in detail in a book of this length.

B. DIAMAGNETISM AND PARAMAGNETISM

The magnetic properties of transition metal compounds arise from the ground state of the metal ion as well as those thermally populated states. Thus, any energy level whose behavior in a field contributes to a magnetic susceptibility at a temperature T must lie within the order of kT of the ground state of the system. Conversely, the contribution of a particular level to the magnetic properties may in turn be altered by varying the temperature. The excited states of metal ions, which are of primary importance in determining the colors and optical spectra of these ions, are only of second order importance to magnetism.

Paramagnetic substances are those in which a magnetic field tends to align the magnetic moment of electron spins with the field. This will be discussed in detail below, but clearly the prerequisite for a sample to be paramagnetic is that the particular substance have unpaired electron spins. One result of this situation is that paramagnets are attracted into a magnetic field, and the fact that they therefore weigh more forms the basis of the familiar Gouy and Faraday balance experiments. The phenomenon of paramagnetism is a single-ion effect, by which we mean that we can explain paramagnetic behavior without invoking any interactions between the magnetic ions. Given the properties of an individual ion, we can calculate the properties of a mole of ions by a straightforward procedure, using Boltzmann thermal averaging. It is therefore appropriate to begin with some of the properties of the individual ions.

Briefly, atomic magnetism is due to the orbital motion (quantum number L) of the electrons, as well as the spin angular momentum (quantum number S). The resultant total angular momentum, $J = L + S$, is the important quantity, but L is often effectively zero, at least for the ground state of compounds of the iron series ions.

The majority of chemical substances is made up of ions or atoms with

the noble gas configuration of filled electron shells, and it is found that $L = S = J = 0$, and only diamagnetism is exhibited. Diamagnetism is the property of being repelled by a magnetic field, and in the Gouy experiment, causes a sample to weigh less when a field is applied than in the absence of a field. There is a diamagnetic contribution even for paramagnetic substances, but it is usually small and can be accounted for by standard procedures.

Paramagnets are the subject of this book. The oxygen molecule, with two unpaired electrons, has $S = 1$, and is a well-known example. More relevant for our purposes are compounds containing such ions as Cr^{3+} and Mn^{2+} which have magnetic moments due to unpaired electron spins outside filled shells. The orbital motion is usually quenched by the ligand field, resulting in spin-only magnetism. Consider an isolated ion, acted on only by its diamagnetic ligands and an external magnetic field H (the Zeeman effect). The field will resolve the degeneracy of the various states according to the magnetic quantum number m , which varies from $-J$ to J in steps of unity. Thus, the ground state of a free manganese(II) ion, which has $L = 0$, has $S = 5/2 = J$, and yields six states with $m = \pm 1/2, \pm 3/2$, and $\pm 5/2$. These states are degenerate (of equal energy) in the absence of a field, but the magnetic field H resolves this degeneracy. The energy of each of the sublevels in a field becomes

$$E = mg\mu_B H, \quad (1.1)$$

where m is the magnetic quantum number and μ_B is the Bohr magneton,

$$\mu_B = \frac{|e|\hbar}{2mc} = 9.27 \times 10^{-21} \text{ erg/gauss}$$

and g is a (Landé) constant, characteristic of each system, which is equal to 2.0023 when $L = 0$, but frequently differs from this value. The convention used here in applying Eq (1.1) is that the 6S ground state of the manganese ion at zero-field is taken as the zero of energy (2).

The situation is illustrated in Figure 1.1. The separation between adjacent levels, ΔE , varies with field, and is easily calculated as $\Delta E = g\mu_B H = 2\mu_B H$. In a small field of 1 kG,

$$\Delta E = 2\mu_B H = 2 \times 9.27 \times 10^{-21} \times 10^3 \approx 2 \times 10^{-17} \text{ erg}$$

while at a temperature of 1 K,

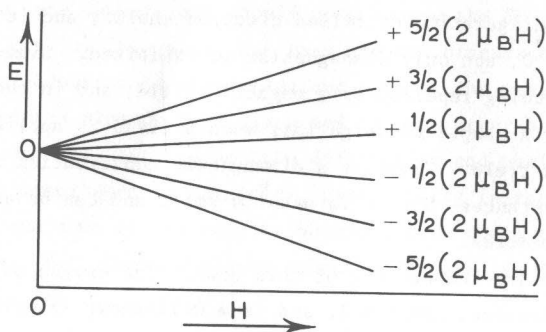


FIGURE 1.1 *Splitting of the lowest energy level of manganese(II) by a magnetic field into six separate energy levels.*

$$kT = 1.38 \times 10^{-16} \times 1 \approx 1.4 \times 10^{-16} \text{ erg.}$$

Thus, at $H = 1 \text{ kG}$ and $T = 1 \text{ K}$, $\Delta E < kT$, and the resulting levels are populated almost equally, as may be found by calculating the distribution of magnetic ions among the various states from the Boltzmann relation,

$$N_i/N_j \propto \exp(-\Delta E_i/kT),$$

ΔE_i being the energy level separation between levels i and j .

Since each state corresponds to a different orientation with regard to the external magnetic field, the net magnetic polarization or magnetization M of the substance would then be very small. Or, the field tends to align the spins with itself, but this is opposed by thermal agitation.

On the other hand, in a large field of 20 kG , $\Delta E = 4 \times 10^{-16} \text{ erg}$, and at 1 K , $\Delta E > kT$. Then, only the state of lowest energy, $-Jg\mu_B H$, will be appreciably populated, having about 95% of the total. This corresponds to the ions lining up parallel to the external field, and the magnetization would almost have its largest or saturation value, M_{sat} . Real crystals that have been shown to exhibit behavior of this sort include chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and manganese Tutton salt, $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Each of the magnetic ions in these salts is well separated from the other magnetic ions, so it is said to be magnetically dilute. The behavior then is almost ideal-gas-like in the weakness of the interactions. The statistical mechanics of weakly interacting, distinguishable particles is therefore applicable. This means that most

properties can be calculated by means of the Boltzmann distribution, as already suggested.

At low temperatures, the vibrational energy and heat capacity of everything but the magnetic ions may be largely ignored. The spins and lattice do interact through the time-dependent phenomenon of spin-lattice relaxation, a subject which will be introduced below. The magnetic ions form a subsystem with which there is associated a temperature which may or may not be the same as that of the rest of the crystal. The magnetization or total magnetic moment M is not correlated with the rest of the crystal, and even the external magnetic field has no effect on the rest of the crystal. Thus, the working hypothesis, which has been amply justified, is that the magnetic ions form a subsystem with its own identity, describable by the coordinates H , M , and T , independent of everything else in the system.

This model provides a basis for a simple derivation of the Curie law, which states that a magnetic susceptibility varies inversely with temperature. Although the same result will be obtained later by a more general procedure, it is useful to illustrate this calculation now. Consider a mole of spin-1/2 particles. In zero field, the two levels $m = \pm 1/2$ are degenerate, but split as illustrated in Figure 1.2 when a field $H = H_z$ is applied. The energy of each level is $mg\mu_B H_z$, which becomes $-g\mu_B H_z/2$ for the lower level, and $+g\mu_B H_z/2$ for the upper level; $\Delta E = g\mu_B H_z$, which for a g of 2, corresponds to about 1 cm^{-1} at 10000 gauss.

Now, the magnetic moment of an ion in the level n is given as $\mu_n = -\partial E_n / \partial H$; the molar macroscopic magnetic moment M is therefore obtained as the sum over magnetic moments weighted according to the Boltzmann factor.

$$M = N \sum_n \mu_n P_n = N \frac{\sum_{m=-1/2}^{1/2} (-mg\mu_B) \exp(-mg\mu_B H_z / kT)}{\sum_{m=-1/2}^{1/2} \exp(-mg\mu_B H_z / kT)}$$

where N is Avogadro's number and the summation in this case extends over only the two states, $m = -1/2$ and $+1/2$. Then,

$$\begin{aligned} M &= \frac{1}{2} N g \mu_B \left[\frac{\exp(g\mu_B H_z / 2kT) - \exp(-g\mu_B H_z / 2kT)}{\exp(g\mu_B H_z / 2kT) + \exp(-g\mu_B H_z / 2kT)} \right] \\ &= \frac{1}{2} N g \mu_B \tanh(g\mu_B H_z / 2kT), \end{aligned} \quad (1.2)$$