TRANSITION METAL CHEMISTRY

A Series of Advances

EDITED BY
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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE
CHICAGO, ILLINOIS

VOLUME 7

1972
MARCEL DEKKER, INC., New York

MARCEL DEKKER, INC.
95 Madison Avenue, New York, New York 10016

LIBRARY OF CONGRESS CATALOG CARD NUMBER 65-27431

ISBN 0-8247-1082-7

PRINTED IN THE UNITED STATES OF AMERICA

TRANSITION METAL CHEMISTRY

Volume 7

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Chapter 1

MAGNETIC PHASE TRANSITIONS AT LOW TEMPERATURES

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PART 1

INTRODUCTION

I. SCOPE

A number of reviews of various aspects of magnetic phase transitions have been published in the past few years. Most of these papers either cover special topics, or attempt to give a concise review of the entire field of magnetism.

Recently, however, there has been renewed interest in the behavior of insulating magnetic compounds which order at relatively low temperatures. In particular, the behavior of antiferromagnetic compounds in magnetic fields can be studied in detail if the compound orders at reasonably low temperatures. Presently available laboratory magnets can produce magnetic potential energies comparable to, or greater than, the internal exchange and anisotropy energies in such compounds.

Molecular field and spin wave theories present a rather complete description of the behavior of antiferromagnetic compounds in external fields. Depending on the nature, and magnitude, of the various internal interactions, a number of field induced phases are predicted which may be experimentally investigated at low temperatures.

The present discussion is limited to magnetic insulators which order in, or near, liquid helium temperatures. The main aim is to review the area of field induced phase transitions. The best known systems which order at low temperatures are the iron group transition metal halides, a number of double salts containing transition elements, and certain rare earth compounds. Because of the diversity of crystal and magnetic structure of such compounds, they offer an interesting group to study.

In Part 2 a short review of static critical point phenomena will be presented with results for both ferromagnetic, as well as antiferromagnetic compounds cited for completeness. Several excellent reviews on the topic have been published in recent months, and the reader will be referred to these works for a complete survey of the current situation in this very fascinating area of research.

Part 3 contains the discussion of the behavior of antiferromagnetic compounds in magnetic fields. In Part 5 a list of a number of common magnetic insulators is given, together with a list of some of the more important magnetic parameters which have been determined for these substances.

II. SOME GENERAL PROPERTIES OF MAGNETIC PHASE TRANSITIONS AT LOW TEMPERATURES

A. Specific Heat and Entropy

In recent years a large number of insulating magnetic compounds have been discovered which order at low temperatures. Both ferromagnetic and antiferromagnetic order is observed, and in some cases a more complicated situation exists where antiferromagnetic order is followed at lower temperatures by ferromagnetic order. In zero applied magnetic field, the transition from the paramagnetic to the ordered state is characterized by a somewhat anomalous behavior of some of the thermodynamic properties of the material. The specific heat, for instance, usually shows a λ-type behavior at the transition temperature. An example shown in Fig. 1 is that of antiferromagnetic $NiCl_2 \cdot 6H_2O$ reported by Robinson and Friedberg [1]. The data given is the total specific heat which is the sum of the magnetic and the lattice contributions. When the lattice contribution is subtracted it is found that a sizable magnetic contribution still persists above the transition temperature. This has been interpreted as evidence that short range order persists even in the paramagnetic state. Further evidence of this interpretation can be obtained if one calculates the entropy of magnetic order. The relationship between the magnetic contribution to the specific

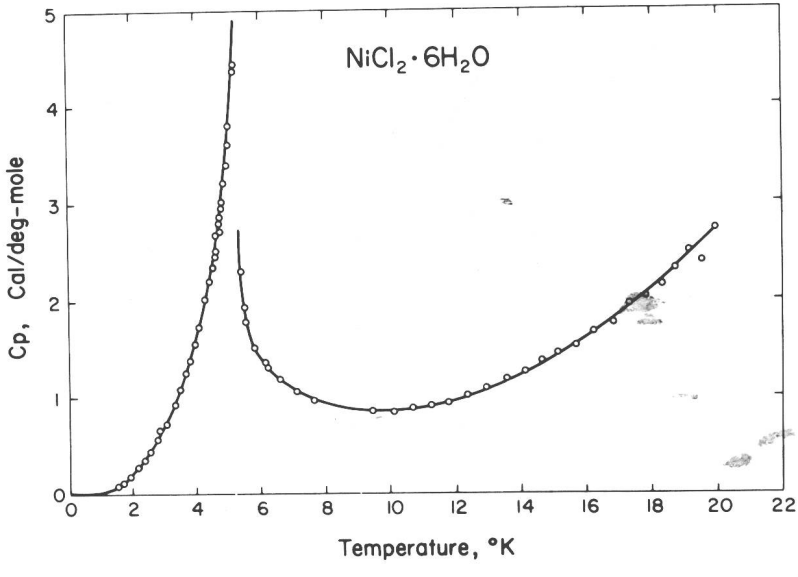

FIG. 1. Molar specific heat of $NiCl_2 \cdot 6H_2O$ as a function of temperature. (Reprinted from Ref. 1, p. 404, by courtesy of Am. Phys. Soc.)

heat, C_M, and the entropy of magnetic order, S_M, follows from the thermodynamic relation

$$C_M = T(\partial S_M/\partial T) \tag{1}$$

By integrating this we have

$$S_M = \int_0^T (C_M/T)\, dT \tag{2}$$

From statistical mechanics we have

$$S_M = k \log_e W_M \tag{3}$$

where k is the Boltzmann constant and W_M is the number of ways of achieving the same total energy for the macroscopic magnetic system by different microscopic arrangements of the elementary moments. In the perfectly disordered state there are 2S+1 quantum states of different orientation open to each ion, where S is the total spin quantum number for the ion. In the perfectly ordered state there is only one such state. Hence the difference in entropy between the perfectly ordered and the completely disordered states is, per mole

$$\begin{aligned} \Delta S_M &= Nk \log_e (2S+1) - Nk \log_e 1 \\ &= Nk \log_e (2S+1) \end{aligned} \tag{4}$$

where N is Avogadro's number. Figure 2 shows the result of such a calculation for $NiCl_2 \cdot 6H_2O$ by Robinson and Friedberg [1]. It is evident from this curve that some short range order persists well above the transition temperature.

Modern microscopic theories indeed predict such a short range order, whereas earlier molecular field models predicted a zero magnetic contribution to the entropy above the ordering temperature.

Although most magnetic transitions exhibit a λ-type anomoly in the specific heat where the asymptotic limit of the specific heat is singular on one or both sides of the transition, $GdCl_3$[2,3] appears to be an exception. The early work of Leask, Wolf and Wyatt [2] indicated that the specific heat was finite but had a simple discontinuity. More recent high resolution measurements of Landau [3] shown in Fig. 3 verify that the specific heat is finite on both sides of the transition, but that the derivatives are infinite. The asymptotic form for the specific heat is not singular, hence the transition appears to be of the type 2b, or diffuse, second order transition.

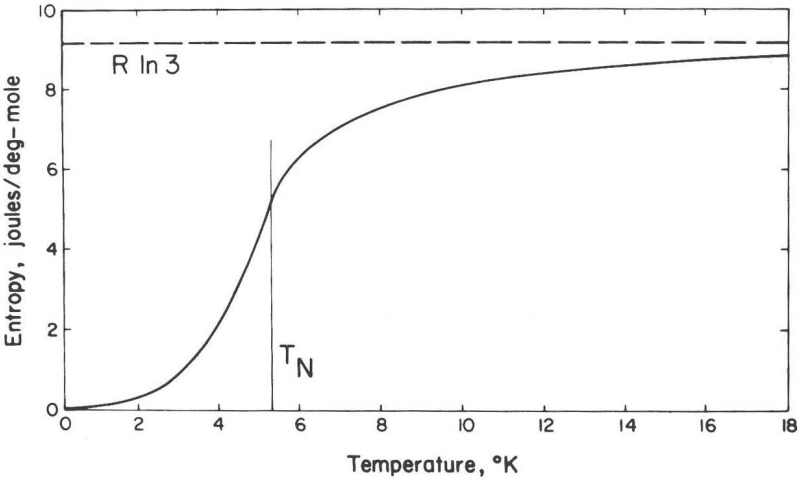

FIG. 2. Magnetic entropy as a function of temperature for $NiCl_2 \cdot 6H_2O$. (Reprinted from Ref. 1, p. 407, by courtesy of Am. Phys. Soc.)

B. Susceptibility and Magnetization

At temperatures well above the ordering temperature the magnetic susceptibility $\chi = dM/dH$, in the limit of zero external field, usually follows a Curie-Weiss behavior. Thus, well into the paramagnetic region one has $\chi = C/(T \pm \theta)$, where C is the Curie constant for the material and θ is a constant related to the energy of interaction between the spins. The minus and plus signs indicate ferromagnetic and antiferromagnetic order, respectively. In Fig. 4 the Curie-Weiss behavior is shown for, (a) the antiferromagnetic case, (b) the ferromagnetic case, and (c) the ideal noninteracting paramagnetic case.

Below the ordering temperature there exists a spontaneous magnetization. In the ferromagnetic case this magnetization is a maximum at T=0 and drops to zero at the ordering temperature. From molecular field theory one obtains

$$M_S = M_o B_J (\mu M_S/kT) \tag{5}$$

where $B_J (\mu M_S/kT)$ is the Brilluoin function of $\mu M_S/kT$, i.e.,

$$B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{1}{2J} x \tag{6}$$

The measured spontaneous magnetization of a number of ferromagnetic materials has a temperature dependence which closely resembles Eq. (5) (See, for instance, Ref. 3).

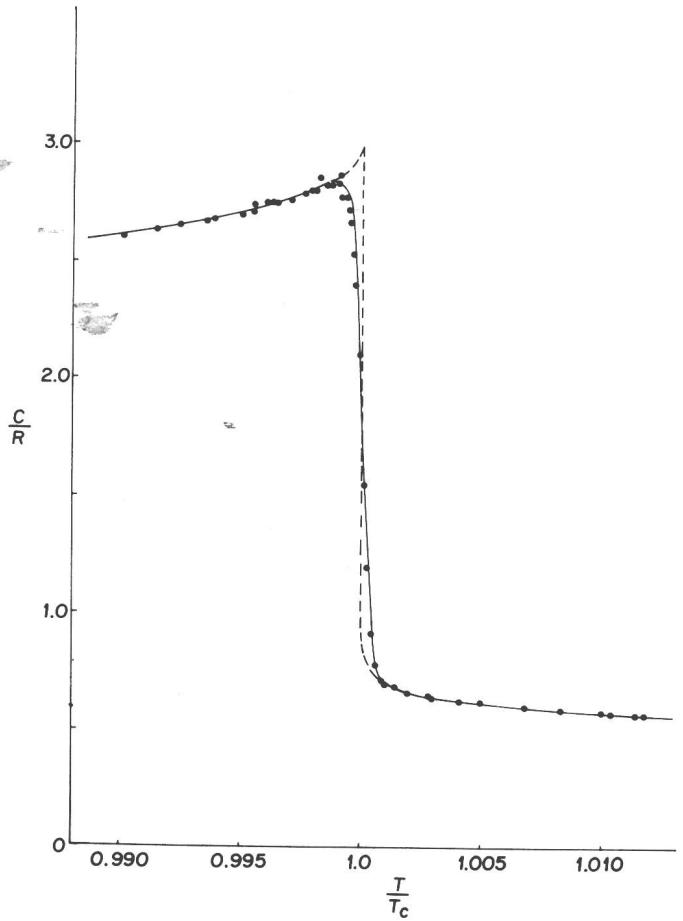

FIG. 3. Specific heat of $GdCl_3$ vs. T/T_c. Experimental results . . . , asymptotic unrounded critical behavior ---, rounded result from Gaussian distribution with half-width Γ = 1.5 mK (Reprinted from Ref. 3, p. 916, by courtesy of La Societé Francaise de Physique.)

In the antiferromagnetic case the situation is complicated by the antiparallel alignment. However, in most cases one can view this case in terms of several interpenetrating sublattices. Within each sublattice there exists a spontaneous magnetization, which according to molecular field theory, should follow Eq. 5. In the case of a simple two sublattice model the spontaneous magnetization of one sublattice is aligned antiparallel to that of the other sublattice. Anisotropy effects lead to a preferred direction for the alignment.

If the susceptibility of a single crystal is measured along this preferred

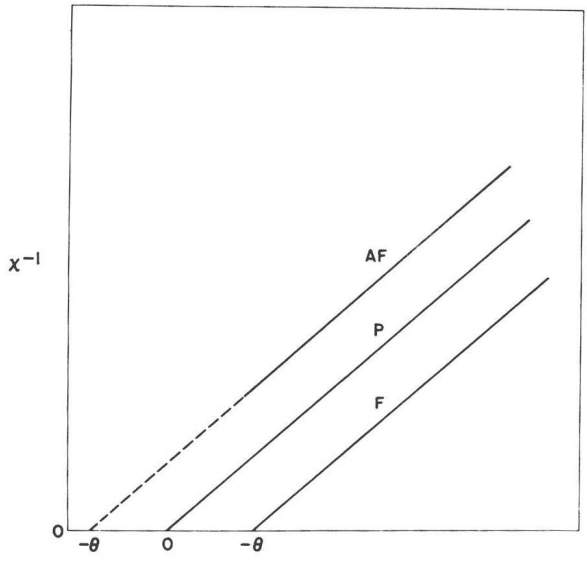

FIG. 4. Inverse magnetic susceptibility against temperature for paramagnetic (P), ferromagnetic (F), and antiferromagnetic (AF) materials according to the Curie-Weiss theory.

direction, one finds, as the temperature is reduced through the ordering temperature, that the susceptibility goes through a maximum (near T_c) and then decreases to zero as T approaches zero. In a direction perpendicular to the preferred direction the susceptibility remains almost independent of temperature below ordering temperature.

C. Field Induced Phase Transitions

In the case of a simple two sublattice antiferromagnet with anisotropy Fig. 5 shows a typical H-T phase diagram with the field along the preferred direction. At zero field T_N separates the paramagnetic state from the ordinary antiferromagnetic state. As the field is increased from zero a second order phase boundary, CD, results. At temperatures below T_t at a critical field H_{cl} there is a first order transition to the spin flop state. As the field is increased still further there is a second order transition to the paramagnetic state.

It is possible to give a simple argument to determine which state is stable at a given temperature and field by considering the free energy of the system. For a field parallel to the preferred direction the magnetic potential energy is given by

$$E = -(1/2)\,\chi_{||}\,H^2 \qquad (7)$$