

MAGNETIC TRANSITIONS AT LOW TEMPERATURES

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INTRODUCTION

In many crystalline substances there exists a pattern of electronic energy levels such that in the experimentally accessible range of temperature it is possible to pass from a low-temperature, completely ordered, form of essentially zero entropy to a higher temperature form where there is a nearly random distribution among several electronic states per molecular unit. There is, therefore, in the higher temperature form a substantial electronic contribution to the entropy of the crystal, of magnitude $R \ln n$ per mole, where n is the number of electronic states per molecular unit and R is the gas constant. Such a pattern of electronic energy levels is found in substances which the chemist would describe as having unpaired electrons and, in particular, in ionic crystals containing elements with partially filled d or f electronic shells. Because of the magnetic moment accompanying the spin and orbital angular momenta of the electrons, these substances are, in the higher temperature region, paramagnetic. The changes from the completely ordered low temperature form to a high temperature form where there is a random distribution among several electronic states may be called a magnetic transition. Such transitions always occur over an extended range of temperature and the increase in entropy of the electronic system (we shall for short call this the "magnetic entropy") is never found to occur discontinuously at a single temperature as happens in the more familiar first order transitions associated with melting, vaporization or the change from one crystal form to another.

In this paper we shall choose for more detailed discussion some examples of magnetic transitions in salts of divalent ions of manganese, iron, cobalt and nickel. No attempt will be made at a comprehensive survey of the considerable amount of experimental and theoretical information concerning magnetic transitions in ionic crystals which has become available in recent years, nor will the more complicated phenomena of ferromagnetism and antiferromagnetism in metals be discussed. There are several excellent recent review articles on antiferromagnetism¹⁻⁴ and ferromagnetism⁵. The examples, chosen from among substances in which the writer and his collaborators have an experimental interest, will be typical of many magnetic salts at low temperatures. The main emphasis in this paper will be on the thermal properties rather than the many interesting phenomena disclosed by measurements of magnetic susceptibility, of magnetic structure by neutron diffraction, and electronic and nuclear resonance measurements.

SINGLE ION ELECTRONIC STATES IN A CRYSTAL

If an ion having a d electron is situated at a point of cubic symmetry in a crystal, then the five orbital states, degenerate in the free ion, are split into two levels, one group of three $d\epsilon$ orbitals having a symmetry corresponding to the irreducible representation t_{2g} of the group O_h , and the other group of two $d\gamma$ orbitals having the representation⁶ e_g . If the positive ion is surrounded octahedrally by six negative ligands or by water molecules, as is usually approximately the case in ionic crystals of the iron group, then the $d\epsilon$ orbitals are lower in energy than the $d\gamma$ orbitals by the order of $10,000\text{ cm}^{-1}$. With the exception of a few tightly bound complexes usually involving triply charged ions, the electrostatic repulsion energy among the electrons in ions containing several d electrons is more important than the octahedral field energy and the lowest state is the one of maximum spin quantum number, S , consistent with the Pauli principle. In *Table 1*

Table 1. Electronic levels of some transition metal ions in an octahedral field

Free ion configuration	Octahedral field configuration	Spin	Orbital degeneracy	Divalent 3d ion
d^5	$d\epsilon^3 d\gamma^2$	$5/2$	1	Mn^{3+}
d^6	$d\epsilon^4 d\gamma^2$	2	3	Fe^{2+}
d^7	$d\epsilon^5 d\gamma^2$	$3/2$	3	Co^{2+}
d^8	$d\epsilon^6 d\gamma^2$	1	1	Ni^{2+}
d^9	$d\epsilon^6 d\gamma^3$	$1/2$	2	Cu^{2+}
d^{10}	$d\epsilon^6 d\gamma^4$	1	1	Zn^{2+}

are listed the ground state configurations in an octahedral field, the maximum spin quantum number, S , and the maximum possible orbital degeneracy of the ground level consistent with these. Because of the large energy required to promote an electron from a $d\epsilon$ to a $d\gamma$ orbital the excited states involving such a promotion are never thermally occupied at temperatures reached in heat capacity measurements. There is further a spin degeneracy of $2S + 1$ and the total number of low-lying states is the product of the spin and orbital degeneracies. These states are split by crystal fields of lower symmetry and by the spin-orbit interaction energy^{7, 8}. For the configurations d^5 and d^8 there is a single orbital state and consequently the maximum magnetic entropy that can be acquired at attainable temperatures is $R \ln (2S + 1)$. In the case of the remaining configurations (except the diamagnetic d^{10}) listed in *Table 1* it is possible to have orbital degeneracy in the ground state and the pattern of low-lying levels varies widely from one compound to another since it is critically dependent on the crystalline field of symmetry lower than cubic.

When there is an even number of electrons in an ion it is possible for the crystalline fields of symmetry lower than cubic, combined with the spin-orbit interaction, to remove all degeneracy of the electronic states. An example of such a case is $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ discussed below. When there is an odd number of electrons in an ion, however, a well-known theorem first formulated by Kramers⁹ states that under the influence of crystalline fields and spin-orbit coupling each energy level is at least doubly degenerate. The residual magnetic entropy of $R \ln 2$ in the lowest

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single-ion level, which by the third law of thermodynamics must vanish at the absolute zero, is lost through interactions between ions.

When the interionic interaction energies are weak compared with the splitting of the electronic levels by the crystal fields, then the magnetic entropy is lost gradually as the temperature is lowered. The magnetic heat capacity has the form of a Schottky curve, describable by a single-ion partition function. An example of such a case is that of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$, whose heat capacity¹⁰ in the range 1–12°K is shown in *Figure 1*. The observed heat capacity is the sum of a lattice heat capacity which will in this temperature region vary approximately as T^3 and a magnetic heat capacity derived from the partition function

$$Q = 1 + \exp(-\theta_1/T) + \exp(-\theta_2/T)$$

This partition function represents three states per Ni^{2+} ion, the two higher energy states having energies $k\theta_1$ and $k\theta_2$ above the ground state. The two parameters were chosen by a least-squares fit of the observed heat capacity data, after making a small correction for the lattice heat capacity, and the values $\theta_1 = 6.44 \pm 0.10$ deg and $\theta_2 = 7.26 \pm 0.10$ deg were obtained. The heat capacity curve calculated with these values of the parameters, shown as a solid line in *Figure 1*, agrees with an average deviation of 0.9 per cent with the twenty-four points between 1.1° and 5.8°K. The

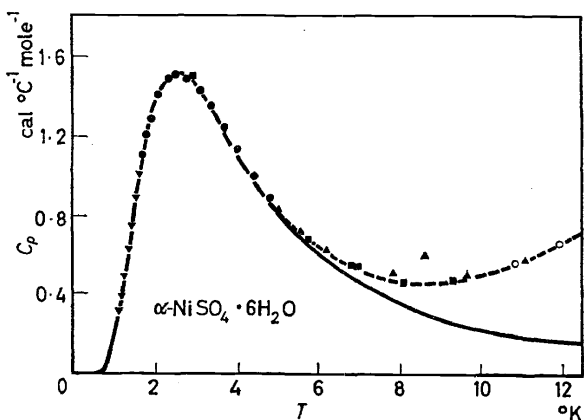


Figure 1

total magnetic entropy change agrees closely with the expected value of $R \ln 3$. Because of the very small lattice heat capacity of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ in the temperature range where the magnetic heat capacity is large, it is, in this substance, very easy to separate the magnetic and lattice contributions to the entropy. In many substances, however, there are similar gradual changes in magnetic entropy which occur at higher temperatures where the lattice heat capacity is large and there is appreciable magnetic heat capacity over a wide range of temperature. In such a case it is much more difficult to separate the magnetic and lattice contributions to the heat capacity and entropy.

INTERACTIONS BETWEEN MAGNETIC IONS

The interaction energy between different magnetic ions may be formally described as an exchange energy³,

$$\sum -2\mathcal{J}_{ij}\vec{S}_i \cdot \vec{S}_j$$

where \mathcal{J}_{ij} is the exchange integral between the i th and j th atoms and \vec{S}_i and \vec{S}_j are the respective spin angular momenta in units of \hbar . The exchange forces are short-range and act essentially only between near neighbours. In ionic crystals they are believed to be transmitted between positive magnetic ions *via* intervening closed-shell anions¹¹. A positive \mathcal{J} corresponds to a ferromagnetic interaction between two ions and a negative \mathcal{J} to an antiferromagnetic interaction (lowest energy for the antiparallel spin alignment of the two atoms). The long-range dipole interactions between magnetic ions are anisotropic and often determine the direction of alignment of the magnetic moments relative to the crystal axes. The dipole energies in magnetically concentrated compounds are of the order of magnitude of kT at 1°K which may become energetically important in compounds such

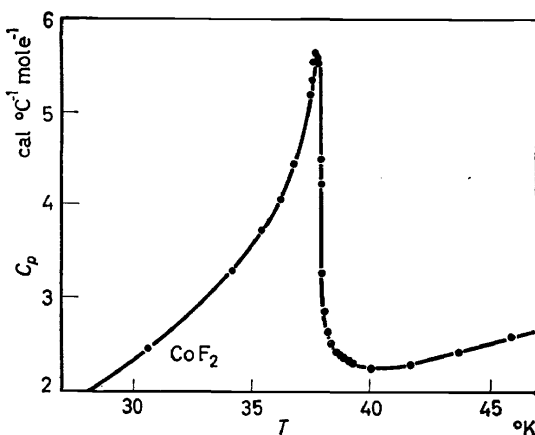


Figure 2

as MnBr_2 and MnCl_2 whose transitions occur in the helium temperature range. In many ionic crystals it is possible to divide the magnetic ions into two interpenetrating sub-lattices having opposite alignments of moments and arranged so that the neighbours of the ions of one sub-lattice belong to the other sub-lattice. Such an ordered arrangement was called antiferromagnetism by Néel¹² and an approximate statistical treatment equivalent to the Weiss molecular field approximation in ferromagnetism was given by Van Vleck¹³. According to this simple model the magnetic heat capacity and entropy in the antiferromagnetic state both increase with temperature until a critical temperature, called the Néel or Curie temperature, is reached. At this temperature the last trace of ordering among the magnetic ions disappears, the magnetic heat capacity drops abruptly to zero and the full magnetic entropy is acquired. Below the critical temperature the magnetic susceptibility of a single crystal measured

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perpendicular to the direction of alignment of the antiferromagnetically ordered atomic moments is independent of temperature, while the susceptibility parallel to the direction of alignment drops with decreasing temperature below the critical temperature.

The observed effects in antiferromagnetic substances, the variations in magnetic susceptibility^{3, 14}, the long-range ordered structure as seen by neutron diffraction¹⁵ and the observations of electronic¹⁶ and nuclear¹⁷ resonance in the ordered state are, for the anhydrous fluorides of manganese, iron, cobalt and nickel, in qualitative agreement with the simple model of Néel and Van Vleck. There is, however, quantitative disagreement, particularly in the neighbourhood of the critical temperature.

Typical heat capacity curves involving co-operative ordering of the magnetic moments are shown for CoF_2 (Figure 2)¹⁸; MnBr_2 (Figure 3)¹⁹; CoCl_2 (Figure 5)²⁰; and FeCl_2 (Figure 6)²¹. Similar heat capacity anomalies involving co-operative ordering have been observed in MnF_2 ²², FeF_2 ¹⁸, NiF_2 ²³, MnCl_2 ²⁴, NiCl_2 ²⁵ and many other compounds³ containing magnetic ions. The general features of these heat capacity curves are a rise to a sharp peak considerably higher than would be found in a Schottky curve, and an abrupt drop at temperatures above the peak. There is always considerable magnetic heat capacity in the short-range order region above the maximum. Such an effect is expected from more elaborate statistical theories²⁶ of the antiferromagnetic transition but there is as yet no statistical theory which agrees quantitatively with experiment.

NATURE OF THE CO-OPERATIVE TRANSITION

Ehrenfest²⁷ classified transitions as first, second, third, *etc.*, order according to whether a discontinuity first appears in the first, second, third, *etc.*, derivatives, with respect to temperature and pressure of the Gibbs free energy. With the possible exception of MnBr_2 none of the co-operative transitions discussed above shows any evidence of a latent heat as would be found in a first order transition. Experimentally it is very difficult to prove whether there exists a discontinuity in the heat capacity (second order transition) or whether the heat capacity is continuous but has a discontinuous derivative. In order to investigate this point it is necessary to take heat capacity measurements involving a very small temperature rise and since there is always some finite instrumental limit to the precision with which temperature may be measured, a decrease in the temperature rise of a point results in a decreased accuracy and consequent greater scatter. With platinum thermometers in the range above 20°K the practical lower limit to the temperature rise in a measurement is about 0.05°K. If there is a discontinuity in heat capacity there will always be one point in a series which spans this discontinuity and which will fall between the upper and lower values of heat capacity at the discontinuity. In CoF_2 (Figure 2)¹⁸ it was found that near the peak the heat capacity curve was definitely rounded at the top, involving a change in sign of the curvature of heat capacity *versus* temperature, and then appeared to drop very rapidly. In the other co-operative transitions listed above there is a similar rapid drop in heat capacity above the temperature of the maximum. It is not possible

to decide whether in this temperature region the heat capacity *versus* temperature curve has a mathematical discontinuity or merely has a rapidly varying but continuous shape. It is preferable to class the magnetic transitions along with the transition in liquid helium, that in ammonium chloride and order-disorder transitions in alloys as lambda-transitions²⁸ rather than try to decide the order in the Ehrenfest sense.

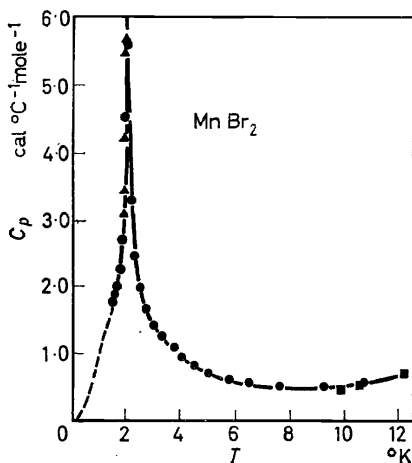


Figure 3

In MnBr_2 (Figure 3)¹⁹ short points near the peak were measured which gave values as high as $30 \text{ cal mole}^{-1} \text{ }^\circ\text{C}^{-1}$ for the heat capacity. In these points it was also observed that the approach to equilibrium was slow and the points did not fall on a smooth curve. In all the other magnetic transitions listed above there was no slowness in equilibrium near the peaks and no evidence of thermal hysteresis. It is probable that in MnBr_2 there is a latent heat or that the real heat capacity rises to extremely high values. The transition is not like the usual first order one, however, since the major part of the entropy change does not occur isothermally but is spread out over a large temperature interval.

ENTROPY CHANGES ASSOCIATED WITH THE CO-OPERATIVE TRANSITIONS

In the case of MnCl_2 ²⁴ and MnBr_2 ¹⁹ the transitions occur in the liquid helium range and it is easy to make a sufficiently accurate correction for the small lattice contribution to the heat capacity. In both of these manganous salts the total magnetic entropy change is found to be $R \ln 6$ in agreement with that expected for six closely spaced single-ion states coming from the spin of $5/2$. In MnBr_2 half of this entropy change occurs in the region of short-range order at temperatures above the heat capacity maximum. MnCl_2 ²⁴ is unusual in that there are two peaks in the heat capacity curve, and approximately one-third of the total magnetic entropy is acquired at temperatures above the upper peak. In the case of the other compounds the transitions occur at a sufficiently high temperature

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so that the lattice contributions to the total entropy and heat capacity form an important fraction of the total and must be estimated with considerable accuracy in order to calculate the magnetic contributions to these thermodynamic quantities. Stout and Catalano²⁹ used data on the isomorphous diamagnetic compound ZnF_2 , together with a corresponding states argument, to estimate the lattice contributions to the entropy and heat capacity of MnF_2 , FeF_2 , CoF_2 and NiF_2 . The total magnetic entropy change in MnF_2 , FeF_2 and NiF_2 is $R \ln(2S + 1)$. This indicates that in these salts there is a single low-lying orbital state and the splitting of the $2S + 1$ spin states by the crystalline field is small compared with kT at the transition temperature. In MnF_2 , FeF_2 , and NiF_2 between 70 and 90 per cent of the total magnetic entropy is acquired at the temperature of the heat capacity maximum. The variation with temperature of the magnetic entropy in these three fluorides is shown in *Figure 4*. In CoF_2 , on the other

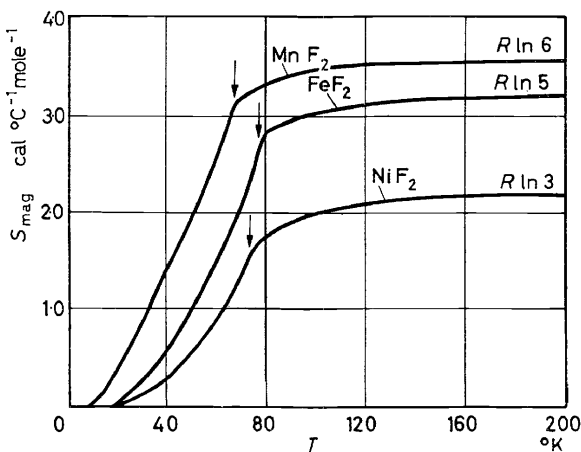


Figure 4

hand, the entropy acquired in the antiferromagnetic transition is $R \ln 2$, indicating that the ground state in the crystalline field is a Kramers doublet and that the energy difference to the next excited state is large compared with kT at the transition temperature of $37\text{--}70^\circ\text{K}$. This structure of electronic levels in MnF_2 , FeF_2 and CoF_2 is consistent with the more detailed information given by paramagnetic resonance experiments³⁰ on dilute solutions of these salts in isomorphous ZnF_2 .

In the compounds FeCl_2 , CoCl_2 and NiCl_2 the magnetic ions are at positions of point symmetry D_{3d} and the threefold orbital degeneracy present in Fe^{2+} and Co^{2+} in a field of octahedral symmetry is partially removed, giving one doubly degenerate level and a singly degenerate one. Kanamori³¹ has calculated the expected energy level pattern in FeCl_2 and concluded that if, as seems indicated by experiments, the doublet level lies lowest in energy, the total of ten low-lying electronic states will be split by the spin-orbit coupling into five pairs separated from one another by the magnitude of the spin-orbit coupling constant (100 cm^{-1} in the free ion). We have made use of heat capacity data on MnCl_2 ²⁰ and ZnCl_2 ²¹ to estimate by the corresponding states method the entropy changes involved

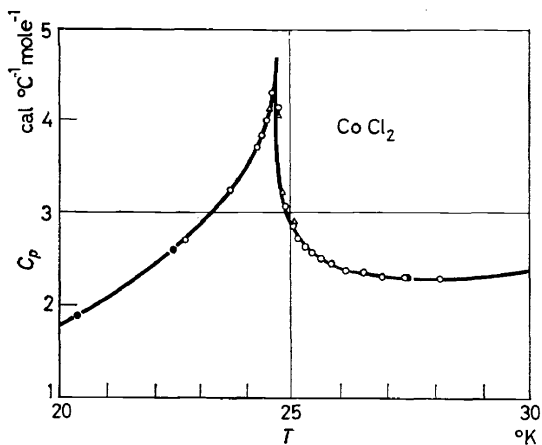


Figure 5

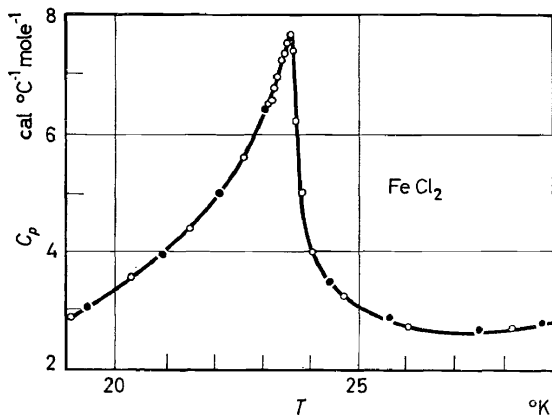


Figure 6

in the co-operative transitions. These are listed, together with the temperatures of transition and the corresponding data on the fluorides, in *Table 2*. The entropy change of $R \ln 2$ in FeCl_2 is consistent with

Table 2. Data on magnetic transitions in some anhydrous fluorides and chlorides

Substance	Temp. of C_p max(°K)	Entropy change of co-operative transition	$2S + 1$
MnF_2	66.5	$R \ln 6$	6
FeF_2	78.35	$R \ln 5$	5
CoF_2	37.70	$R \ln 2$	4
NiF_2	73.22	$R \ln 3$	3
MnCl_2	1.81, 1.96	$R \ln 6$	6
FeCl_2	23.6	$R \ln 2$	5
CoCl_2	24.7	$R \ln 2$	4
NiCl_2	52.35	$R \ln 3$	3

Kanamori's calculation³¹ of the electronic energy level pattern. One would expect additional heat capacity, of the Schottky type, at temperatures above the observed anomaly (*Figure 6*) and extending up to several hundred degrees. At present it does not seem possible to estimate the lattice heat capacity of FeCl_2 at higher temperatures with sufficient accuracy to permit a reliable experimental estimate of this additional magnetic entropy which should amount in total to $R \ln 5$. The entropy change of $R \ln 2$ in CoCl_2 indicates that the lowest Kramers doublet is separated from the first excited level by an energy greater than kT at the transition temperature. Here also, one expects additional magnetic entropy gradually to be acquired at higher temperatures through the excitation of additional low-lying crystal field levels. In NiCl_2 ²⁵ there is a single orbital level and the splitting between the three spin states is small compared with the interaction energy between ions, giving an entropy change of $R \ln 3$ associated with the co-operative transition.

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