

Field-Dependent Magnetic Phenomena

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Virtually every chemistry laboratory today contains one or more magnets. These are frequently incorporated into an NMR or EPR spectrometer or into an instrument for the measurement of the static magnetic susceptibility. In each of these cases, the response of the system to the applied field is to resolve some of its degenerate energy levels. That is, an electron spin $S = 1/2$ system has a degenerate ground state corresponding to $m_s = \pm 1/2$, and an external field H_a splits this state into two levels, separated by an amount $g\mu_B H_a$, where g is a factor characteristic of each particular system and μ_B is the Bohr magneton. This so-called Zeeman splitting leads in turn to a paramagnetic susceptibility or an EPR signal, depending on the measurement being performed. A similar phenomenon occurs with nuclear spin systems, and this in turn results in NMR absorption. An earlier Account¹ reviewed several aspects of the magnetic properties of transition-metal complexes. Zero-field splittings, the Zeeman term, and magnetic exchange interactions were discussed, and several typical examples of magnetic ordering phenomena were described. The bulk of the discussion concerned chemical systems and their spontaneous interactions in the absence of a large external magnetic field.

It is widely recognized that an applied field causes the destruction of ferromagnetism. That is, the field causes the electronic spins in a ferromagnet to align with the field, overcoming the spontaneous exchange interaction between the spins. This is called saturation. It is not as generally realized by chemists that an applied magnetic field can perturb a system so strongly as to cause a phase transition. The ratio of $g\mu_B H_a/k_B T$ is generally the quantity of interest, because it measures the competing tendencies of the applied field to align the spin system with it vs. the thermal agitation caused by increasing the temperature. Thus, field-dependent magnetic phenomena are most conveniently explored at high fields and low temperatures. One example of a system which is very sensitive to external fields is an antiferromagnet, which is a system in which the moments on different sublattices are spontaneously opposed, leading to zero net moment at low temperatures.

Richard L. Carlin, a native of Massachusetts, has been associated with two universities. He began his study of chemistry at Brown and continued it at the University of Illinois at Urbana. He returned to Brown in 1960, this time on the faculty, and then returned to Illinois in 1967, but in this case to the University of Illinois at Chicago Circle. His research concerns the electronic structure of transition-metal complexes, and he is editor of the review series, "Transition Metal Chemistry". He spent the 1973-1974 year on sabbatical leave at the University of Leiden and continues to collaborate with the members of the Kamerlingh Onnes Laboratorium.

A. J. van Duynveldt has been associated with the Kamerlingh Onnes Laboratorium since 1965. His research concerns the study of magnetic phenomena, including relaxation, at low temperatures.

The direction in the crystal which is parallel to the direction of spin alignment is called the preferred or easy axis. Cooling a paramagnet in zero applied field leads to a phase transition to an antiferromagnetic state at some temperature, T_c . This yields one point on the $H = 0$ axis of an H_a vs. T phase diagram (Figure 1) corresponding to the magnetic ordering or Néel temperature, $T_c(H_a = 0) \equiv T_c(0)$.

When a field is applied parallel to the preferred axis of spin alignment in an antiferromagnet, it tends to compete with the internal exchange interactions, causing $T_c(H_a)$ to drop to a lower value as H_a increases. Thus a phase boundary between antiferromagnetic (AF) and paramagnetic (P) states begins to be delineated on the H_a - T diagram, as is illustrated in Figure 1.

However, another phenomenon also can occur. When the system is in the antiferromagnetic state, i.e., at $T < T_c(0)$, and the field is again applied parallel to the preferred axis, a different kind of phase transition can occur. This is called spin flop, for when the field reaches a critical value, the moments flop perpendicular to the field (Figure 1). This is then the thermodynamically favored state, and the transition is first order. That is, there is a discontinuity in the magnetization (net alignment of spins) on crossing the AF-SF phase boundary. If the susceptibility of the system is measured at constant temperature as the field is increased, a peak is usually observed on crossing this boundary. As the field reaches high enough value, there is finally a transition from the spin-flop state to the paramagnetic state.

By contrast, the AF-P and the SF-P transitions are continuous or second-order transitions, as is implied by the moving of the moments in the SF phase suggested in Figure 1. The magnetization changes continuously as the boundary is crossed, and the susceptibility at constant temperature only exhibits a change in slope at the phase transition field.

Before completing the discussion of spin-flop phase diagrams and the information which can be gained from the study of them, it will be instructive to consider a separate topic, that of level-crossing experiments. In these, the applied field not only splits a degenerate energy level (in a paramagnetic system) but it can also cause levels which are close in energy to mix with one another in certain situations. Degeneracy can, for example, be driven into the ground state by the applied field. In systems which meet certain requirements described below, this can even lead to a new phenomenon, field-induced magnetic ordering. This is contrary to the usual effect of a magnetic field, as we have al-

(1) R. L. Carlin, *Acc. Chem. Res.*, 9, 67 (1976).

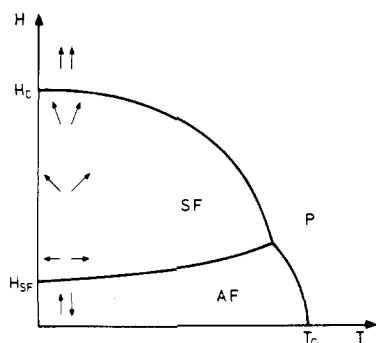


Figure 1. Phase diagram (schematic) for a typical antiferromagnet with small anisotropy with the external field applied parallel to the preferred axis of spin alignment. The point marked T_c is the Néel temperature, $T_c(H_a = 0)$. The bicritical or triple point is found where the three phase boundaries meet.

readily seen that an external field destroys ferromagnetism or may cause spin flop in an antiferromagnet.

It should be clear from the above that the first problem to be faced in characterizing a magnetic system is the determination of the magnetic properties and spin structure in zero applied field. This usually requires¹ the measurement of both the specific heat and the magnetic susceptibility. The most reliable method for measuring a susceptibility is by the ac mutual inductance zero applied field procedure. A sample is placed within a coaxial set of coils and a low-frequency signal is applied. The change in mutual inductance (coupling) between the coils is proportional to the magnetic susceptibility and can be calibrated in order to derive absolute values. This method has the advantage that the ac magnetic field imposed is generally only a few oersted and can be made very small if necessary. By insertion of this coil system within a solenoid magnet, the susceptibility can then be measured as a function of applied field. Portions of a typical installation are illustrated in Figure 2.²

Level Crossing Experiments

In a typical paramagnet the Zeeman interaction, $g\mu_B H S_z$, causes a small separation of the magnetic energy levels to occur, and it is the differing population among these levels caused by the Boltzmann distribution which gives rise to the normal paramagnetic susceptibility.^{1,3} However, consider the situation in an $S = 1$ system as provided by either vanadium(III) or nickel(II) in octahedral coordination with energy levels as illustrated in Figure 3. The experiment to be described requires an oriented single crystal. Indeed, we require a uniaxial crystal system so that the local crystal field or molecular (z) axes are *all* aligned parallel with respect to a crystal axis. This is a particularly stringent condition. It is also necessary that the energy separation D have the sign indicated, which is typical of V(III) compounds but happens randomly with compounds containing Ni(II). Then, in zero external field, typical paramagnetic susceptibilities which have been illustrated frequently elsewhere¹⁻⁵ are obtained, with χ_{\parallel} (the

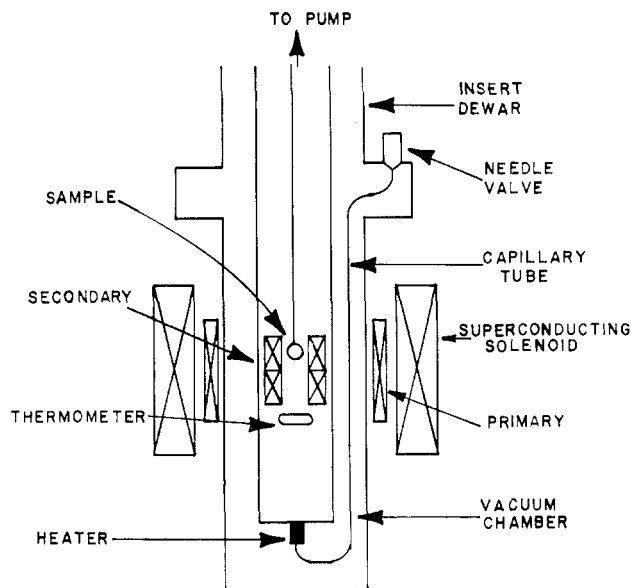


Figure 2. Experimental arrangement (not to scale) of magnet and coil systems for measuring field-dependent susceptibilities. This entire system is within a dewar and is surrounded by liquid helium. (Reproduced with permission from ref 2. Copyright 1979, The Institute of Physics.)

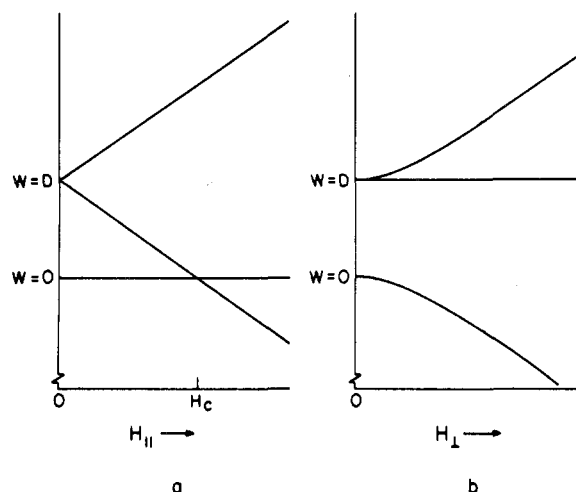


Figure 3. The lowest energy levels of Ni(II) and V(III) in uniaxial crystalline fields as a function of external magnetic field parallel (a) and perpendicular (b) to the principal molecular magnetic axes.

susceptibility measured with the oscillating field parallel to the z axis) having a broad maximum, and approaching zero at 0 K. Another way of saying this is that the magnetization for a small parallel field approaches zero at 0 K.

But, now, let a large magnetic field be applied parallel to the unique crystal axis as indicated in Figure 3a.⁶ One of the upper levels will descend in energy, and if the separation D is accessible to the available magnetic field, the two lower levels will cross and mix at some level crossing field, H_{lc} , and continue to diverge at higher fields as illustrated. In the absence of magnetic exchange interaction the separation is simply $g\mu_B H_{lc} = D$. In the presence of exchange interaction zJ , the field at which the levels cross becomes $g\mu_B H_{lc} = D + |zJ|$, where z is the magnetic coordination number and J measures the strength of the interaction between

(2) R. L. Carlin, K. O. Joung, A. Paduan Filho, C. J. O'Connor, and E. Sinn, *J. Phys. C*, **12**, 293 (1979).

(3) R. L. Carlin and A. J. van Duyneveldt, "Magnetic Properties of Transition Metal Compounds", Springer-Verlag, New York, 1977.

(4) R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *Inorg. Chem.*, **15**, 985 (1976).

(5) R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Am. Chem. Soc.*, **98**, 3523 (1976).

(6) K. M. Diederix, J. P. Groen, T. O. Klaassen, N. J. Poullis, and R. L. Carlin, *Physica B+C (Amsterdam)*, **97B**, 113 (1979).

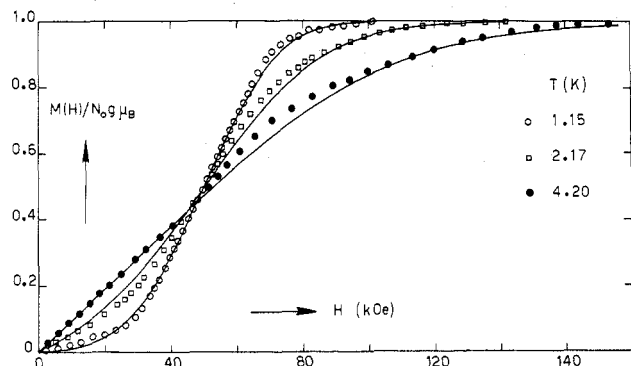


Figure 4. Pulsed-field magnetization curves of $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$. Solid curves have been calculated for isothermal behavior with $D/k_B = 6.51$ K, $zJ/k_B = -1.41$ K, and $g_{\parallel} = 2.32$, using the mean field approximation in eq 1. (Reprinted with permission from ref 7. Copyright 1977, North-Holland Publishing Co.)

neighboring ions. We are using a molecular field approximation here in which the individual interactions between the reference magnetic ion and the magnetic neighbors with which it is interacting are replaced by an effective internal magnetic or molecular field. The isothermal magnetization M (net alignment) with the applied field H_a parallel to all the z molecular axes is $M = N_0 g \mu_B \langle S_z \rangle$, with

$$\langle S_z \rangle = (e^h - e^{-h})(e^d + e^h + e^{-h})^{-1} \quad (1)$$

where $h = g_{\parallel} \mu_B H_e / k_B T$, $d = D / k_B T$, and k_B is the Boltzmann constant. The quantity H_e is an effective field $H_e = H_a + \lambda M$, where the molecular field approximation is used once again. Thus, λ is a molecular field constant, with value $\lambda = 2 |zJ| N_0 g_{\parallel}^2 \mu_B^2$, and N_0 is Avogadro's number. The magnetization calculated from eq 1 has a sigmoidal shape at low temperatures ($T \ll D/k_B$), and a typical data set⁷ of magnetization as a function of applied field for a system with large zero-field splitting is illustrated in Figure 4. The level-crossing field is determined by the inflection point, and is about 50 kOe for $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$.

Alternately, the measured isothermal susceptibility, $\chi_T = \partial M / \partial H_a$, increases with field and attains a maximum value at the crossing field.² Other systems which have recently been found to behave in this fashion are $[\text{C}(\text{NH}_2)_3]\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ⁷ and $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$.⁸ The analysis of the magnetization data has required the inclusion of the molecular field exchange interaction for all the nickel salts studied to date, but the exchange interaction has been found to be particularly weak in the vanadium salts.

If all the z molecular axes could not be oriented parallel simultaneously to the external field but some were, for example, because of the particular crystal structure, oriented perpendicular to the applied field, then the energy level scheme in Figure 3b would apply. In this case, the energy levels diverge, there is no level crossing, and only paramagnetic saturation occurs, at high fields. This has been observed by applying the external field perpendicular to the unique axis of $\text{Cs}_3\text{VCl}_6 \cdot 4\text{H}_2\text{O}$.⁸

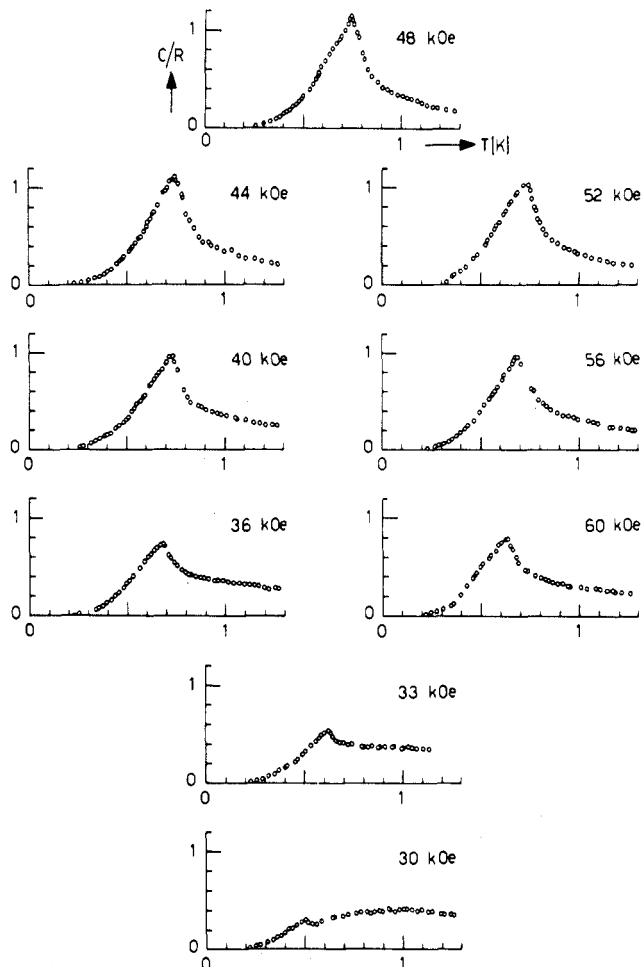


Figure 5. Specific heat of $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ as a function of temperature in various external fields applied parallel to the principal axis. (Reprinted with permission from ref 11. Copyright 1978, North-Holland Publishing Co.)

Special attention attaches to those systems, $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ and $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{NO}_3)_2$ being the best-known examples, in which the exchange interaction is subcritical but moderately strong ($zJ/k_B \sim -1.5$ K for both of these isostructural salts). These rhombohedral materials do not undergo magnetic ordering spontaneously in zero external field even as the temperature approaches 0 K, because D/k_B is about 6 K for both of these materials and that is much larger than the subcritical exchange interaction.^{2,5} Thus, the third law of thermodynamics is obeyed by single-ion processes, in which the total population lies in the $m = 0$ level at $T = 0$ K. But notice that a twofold spin degeneracy (effective spin $S' = 1/2$) has been induced (Figure 3a) at H_{lc} when a field equal to H_{lc} in magnitude has been applied as described above. Since the exchange interactions are not negligible, maintaining the sample at H_{lc} and then lowering the temperature ought to lead to a field-induced magnetic ordering. Such is indeed the case, as has been shown by both susceptibility^{6,9} and specific heat measurements on $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$.^{10,11} The latter measurements are illustrated in Figure 5. Molecular field theory says that in

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(10) H. A. Algra, J. Bartolome, K. M. Diederix, L. J. de Jongh, and R. L. Carlin, *Physica B+C (Amsterdam)*, **85B**, 323 (1977).

(11) H. A. Algra, J. Bartolome, L. J. de Jongh, C. J. O'Connor, and R. L. Carlin, *Physica B & C (Amsterdam)*, **93B**, 35 (1978).

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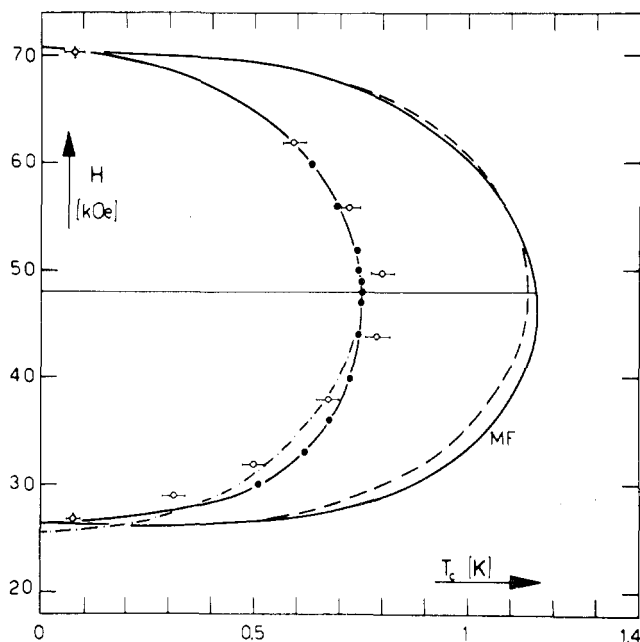


Figure 6. Magnetic phase diagram of $[\text{Ni}(\text{C}_6\text{H}_5\text{NO})_6](\text{ClO}_4)_2$. The points are experimental; the curve through them is calculated, taking into account the third component of the triplet state. The curves labeled MF ignore this level. The system is antiferromagnetic within the hemispherical region and paramagnetic without. (Reprinted with permission from ref 11. Copyright 1978, North-Holland Publishing Co.)

the field-induced ordered state the moments should lie in the plane perpendicular to the external field, that is the xy plane of the rhombohedron. This has indeed been found to be the case,⁶ and thus these systems are examples of the XY magnetic model.

Another feature of these results is that magnetic ordering is still observed even if the applied field moves away from the level crossing field. The levels diverge (Figure 3a) on either side of H_{lc} , of course, but if exchange is strong enough, ordering can still occur. However, the further H_a is from H_{lc} , the lower the ordering temperature, T_c , will be. This is also illustrated in Figure 5, where the loci of the specific heat maxima are tracing out a phase diagram in the H_a - T plane. The derived results are presented in Figure 6.

A similar phase diagram for tetragonal $[\text{Ni}(\text{thiourea})_4\text{Cl}_2]$ has recently been measured.¹² The zero-field splitting is larger in this salt than in the pyridine N -oxide systems, and the exchange interactions are also stronger. Thus, the antiferromagnetic phases are shifted to both higher temperatures and stronger fields for this system.

Spin-Flop Phase Diagrams

This type of phase diagram is more common. A hypothetical one was illustrated earlier (Figure 1), and the phase diagram¹³ of the well-known chemical $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ is illustrated in Figure 7 as an example. This type of behavior is typical of systems with small anisotropy, which is generally caused by zero-field splitting and magnetic dipole-dipole effects. Long-range antiferromagnetic order occurs¹³ in this compound at $T_c(0) = 1.25$ K at zero field. The bicritical

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(13) C. J. O'Connor, S. N. Bhatia, R. L. Carlin, A. van der Bilt, and A. J. van Duyneveldt, *Physica B+C (Amsterdam)*, **95B**, 23 (1978).

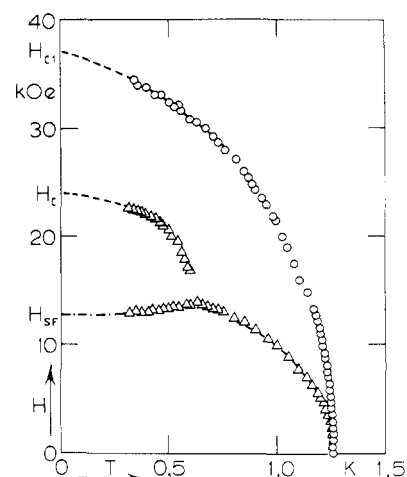


Figure 7. Magnetic phase boundaries of $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$. The triangles refer to measurements with the applied field parallel to the easy axis while the circles refer to a perpendicular orientation. (Reprinted with permission from ref 13. Copyright 1978, North-Holland Publishing Co.)

point is that point where the three phase boundaries meet. Below the bicritical point (0.62 K and 13.9 kOe in this case), increasing an applied field which is parallel to the easy axis^{1,3} causes the sublattice magnetizations to flop perpendicular to the external field as the AF-SF boundary is crossed. This is a first-order phase transition and is characterized by a readily observed sharp peak in the ac susceptibility as the boundary is traversed. The other boundaries, antiferromagnetic to paramagnetic and spin flop to paramagnetic, are second-order transitions, and the field-dependent susceptibility exhibits a change in slope from which one can determine T_c . Similar phase diagrams have also recently been observed for $\text{Cs}_2[\text{FeCl}_5(\text{H}_2\text{O})]$ ¹⁴ and $\text{K}_2[\text{FeCl}_5(\text{H}_2\text{O})]$.¹⁵

There are a number of reasons for studying such phase diagrams, not the least of which is that the shape of the phase boundaries as they meet at the bicritical point is of intense current theoretical interest.¹⁶ Furthermore, several of the magnetic parameters can be evaluated independently and with greater accuracy than from fitting the zero-field susceptibilities, for example. An anisotropy field, H_A , can be defined¹⁷ as the sum of all those (internal) factors which contribute to the lack of the ideal isotropic interactions in a magnetic system. The most important factors are single-ion or crystal-field anisotropy and dipole-dipole interactions; if zero-field splitting alone contributes, then $g\mu_B H_A = 2|D|(S - 1/2)$, where S is the spin of the magnetic ion. One may also define the exchange field, H_E , which is given by $g\mu_B H_E = 2z|J|S$, and the ratio $\alpha = H_A/H_E$ is a useful relative measure of the ideality of the isotropic exchange interaction. One can show by molecular field theory that $H_{SF}(0)$, the value of the antiferromagnetic to spin-flop transition field extrapolated to 0 K, is given

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(17) L. J. de Jongh and A. R. Miedema, *Adv. Phys.*, **23**, 1 (1974).

by $H_{\text{SF}}(0) = [2H_{\text{E}}H_{\text{A}} - H_{\text{A}}^2]^{1/2}$ and that $H_{\text{c}}(0)$, the field of the spin flop to paramagnetic transition extrapolated to 0 K, equals $2H_{\text{E}} - H_{\text{A}}$. Thus, observation to low temperatures of these boundaries allows a determination of these quantities. All of these parameters have been evaluated for $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$, and the anisotropy field of 6.8 kOe could entirely be assigned to the zero-field splitting of the nickel ion.¹³ Indeed, since $T_{\text{c}}(0) = 1.25$ K and $|D/k_{\text{B}}| = 1$ K in this system, this method provides an unambiguous determination of the magnitude of the zero-field splitting.

Unfortunately, $H_{\text{c}}(0)$ is often very high, so that it is difficult to measure directly; it is estimated to be about 150 kOe for $\text{Cs}_2[\text{FeCl}_5(\text{H}_2\text{O})]$, for example. In such cases, one can also make use of the relationship that $\chi_{\perp}(0)$, the zero-field susceptibility perpendicular to the easy axis extrapolated to 0 K, takes the value $\chi_{\perp}(0) = 2M_{\text{s}}/(2H_{\text{E}} + H_{\text{A}})$, where $M_{\text{s}} = N_0g\mu_{\text{B}}S/2$ is the saturation magnetization of one antiferromagnetic sublattice. This relationship, in combination with that for $H_{\text{SF}}(0)$, can be used to determine H_{A} and H_{E} .

If the applied field is perpendicular to the easy axis of spin alignment, then in a typical two-sublattice antiferromagnet there is simply a smooth boundary separating the antiferromagnetic and paramagnetic states. That is, there is of course no spin-flop phase, as illustrated in Figure 7. The boundary, extrapolated to 0 K, yields $H_{\text{c}}'(0)$, which is equal to $2H_{\text{E}} + H_{\text{A}}$.

It is interesting that, although all the boundaries in the H - T plane for a three-dimensional Heisenberg magnet generally lie at temperatures below $T_{\text{c}}(H = 0)$, this does not appear to be true for a linear-chain system. The zero-field behavior of Heisenberg one-dimensional systems has been described elsewhere.^{1,3,17} Consider the phase diagram of $[(\text{CH}_3)_2\text{NH}_2]\text{MnCl}_3 \cdot 2\text{H}_2\text{O}$, a linear chain system¹⁸ with $T_{\text{c}}(0) = 6.4$ K and $J/k_{\text{B}} = -3.7$ K. The phase boundaries above the bicritical point (at 6.0 K and 14.7 kOe) bulge out to temperatures nearly 2 K above $T_{\text{c}}(0)$. This behavior is common in linear chain systems¹⁹ and is due to the characteristic susceptibility behavior of the individual isolated chains. This is true even though the phenomenon being measured is the three-dimensional transition temperature, that is, the long-range ordering temperature describing the interaction between the chains. Anisotropy, which is probably due to dipole-dipole interactions favoring spin orientation perpendicular to the chain axis, causes the phase boundaries to differ for each orientation of the sample with respect to the field.

Metamagnets

Antiferromagnets with a large anisotropy do not show a spin-flop phase, but instead they may undergo a first-order transition toward a phase in which there exists a net magnetic moment. Such compounds are usually referred to as metamagnets and are among the more complicated ones in analyzing the field-dependent ac susceptibility.²⁰ Let us emphasize this topic by discussing the relatively simple example, $[(\text{CH}_3)_2\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$.²¹ This metamagnet²² was reviewed earlier

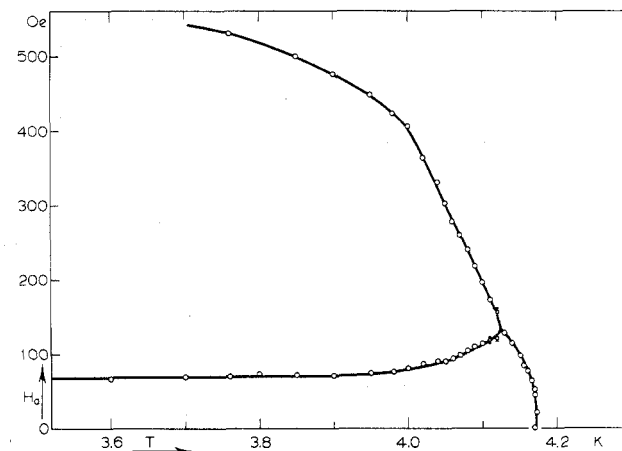


Figure 8. Phase diagram of the metamagnet, $[(\text{CH}_3)_2\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$. The ordinate indicates the applied field. (Reprinted with permission from ref 23. Copyright 1980, North-Holland Publishing Co.)

as far as its zero-field susceptibility was concerned.¹ It was concluded that ferromagnetically coupled chains of cobalt ions along the b axis ($J_0/k_{\text{B}} \approx 15.4$ K) are coupled by a ferromagnetic interaction $J_1/k_{\text{B}} \approx 0.17$ K in the c direction. Then, these ferromagnetically coupled planes order antiferromagnetically below $T_{\text{c}} = 4.18$ K due to a weak interaction between the bc planes ($J_2/k_{\text{B}} \approx -0.007$ K). If an external magnetic field is applied parallel to the easy axis of antiferromagnetic alignment, then at a certain field value the antiferromagnetic arrangement is broken up. The system exhibits a first-order phase transition toward a ferromagnetic state and the transition field (extrapolated to $T = 0$ K) is in fact a direct measure for J_2 . For $[(\text{C}_2\text{H}_5)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ examining $\chi(H)$ for $H \parallel c$ leads to a phase diagram as shown in Figure 8.²³ The figure shows three distinct regions, which meet at a temperature of 4.13 K. This diagram resembles strongly the examples given above, but the phase lines have a completely different meaning. This difference in meaning is as follows.

With ferromagnets, the net internal magnetic moment is large and acts to repel the external field. This is described by means of a sample-shape-dependent demagnetizing field which tends to counteract the external field, causing the internal field to differ from the external field.

In the weakly anisotropic systems that exhibit spin flop, demagnetizing effects are often small enough to be ignored, and one can equate the applied field H_{a} with the more relevant internal field $H_{\text{i}} (= H_{\text{a}} - NM, N$ being the demagnetizing factor). This is generally not possible with metamagnetic systems, however, as ΔM at the first-order transition is no longer negligible. For such a system it is not possible for all spins to change orientation at the value of H_{a} where H_{i} reaches its critical value, because as soon as a number of spins are reoriented, H_{i} is reduced and no further transitions are possible. As a result there will be a region of H_{a} , of magnitude $N\Delta M$, where the phase transition takes place and where H_{i} remains constant at its critical value. Thus, the isothermal susceptibility, χ_{T} , over the

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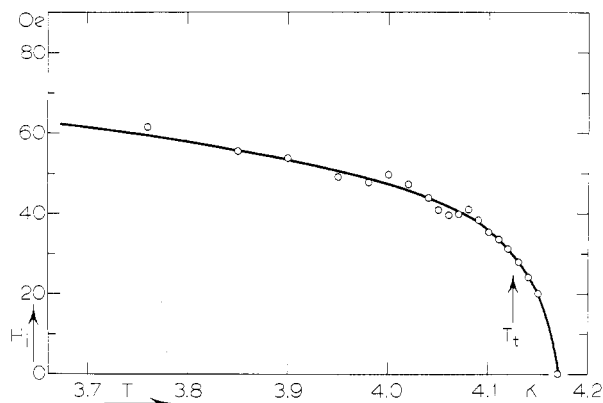


Figure 9. Magnetic phase diagram of $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$. The ordinate is the internal field, in orientation parallel to the c axis of the crystal. The tricritical point is indicated. (Reprinted with permission from ref 23. Copyright 1980, North-Holland Publishing Co.)

“seemingly spin-flop” phase in Figure 8 remains constant at the value $1/N$, and this phase is in fact a mixed (paramagnetic and antiferromagnetic) phase in which the transition takes place gradually with increasing H_a . This discontinuity in the magnetization disappears at the tricritical temperature T_t , and the mixed phase of Figure 8 joins the second-order antiferromagnetic-paramagnetic boundary at this temperature (4.13 K).

If plotted vs. the internal field, the phase diagram appears as a single smooth curve (Figure 9), consisting of a line of first-order points at temperatures below T_t , going over to a line of second-order points above T_t . Tricritical points have been of enormous interest recently to both theorists and experimentalists. The latter group should be aware that in the above it is assumed that the ac susceptibility equals χ_T , the isothermal susceptibility, which is often not true. In the above-mentioned experiments large relaxation effects occurred in the mixed-phase region and the experimental determination of χ_T becomes very difficult.

Concluding Remarks

Our thesis is simple: external magnetic fields can perturb a magnetic system. In a magnetic measurement, especially at high fields, the external field can even change the magnetic behavior of a system. This is especially true when the sample is ordered.

There are a number of other studies that require the application of an external field. The description provided above of antiferromagnets was limited to two-sublattice systems. There are a number of materials which consist of more than two magnetic sublattices.

For example, different spin arrangements have been proposed²⁴ for $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ for the external field parallel to the easy spin direction, depending on the strength of the field lying between the values 0 and 12 kOe, 12 and 32 kOe, 32 and 56 kOe, or higher than 56 kOe. Different transitions were also observed when the orientation of the external field was varied.

Or, the specific heat of $\text{Cs}_2[\text{FeBr}_5(\text{H}_2\text{O})]$ exhibits²⁵ magnetic ordering peaks in zero external field at 14.06 and 12.92 K. This implies that there is a spin reorientation: one type of magnetic order sets in at the higher temperature and changes to some other spin arrangement at the lower temperature. Field-dependent studies such as described above will be required in order to determine the nature of the ordered states.

Few magnetic phase diagrams have been determined below 1 K, simply because of experimental difficulties. Our recent measurement²⁶ of the susceptibilities of $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{NO}_3)_2$ ($T_c = 430$ mK), the only example²⁷ of the $S = 1/2$ three-dimensional XY antiferromagnet, have been difficult to interpret because the susceptibility measured in the XY plane does not go to zero as we anticipated as the temperature goes to zero. The determination of the field-dependent phase diagram should help to unravel this question.

Finally, a problem of current theoretical and experimental interest concerns the tetracritical point which occurs in antiferromagnets which are homogeneous mixtures of different ions (such as Mn^{2+} and Fe^{2+}) of competing spin anisotropies. Composition thus becomes a variable on the phase diagram, as well as temperature and applied field. Though neutron diffraction is an important element in the study of such phenomena, susceptibility studies have also been important. One system studied in detail to date is $\text{K}_2\text{Mn}_{1-x}\text{Fe}_x\text{F}_4$.²⁸

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