

isomerization as evidence against an electron-transfer process is probably a more valid use of this test.

A test for an electron-transfer process based on the structural rearrangement of an initially formed anion radical appears to be useful with certain cyclopropyl enones. Provided the rate of rearrangement of the cyclopropyl ketone is sufficient, this experimental test offers compelling evidence for an anion-radical intermediate. Since this experimental probe also provides information about the lifetime of a radical-anion intermediate, hopefully a series of cyclopropyl ketones can be found whose anion radicals rearrange at sig-

nificantly different rates. Finally, the use of an enone whose anion radical is capable of eliminating an anionic substituent also offers compelling evidence for the presence of an intermediate formed by initial electron transfer.

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Magnetism and Magnetic Transitions of Transition-Metal Compounds at Low Temperatures

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A paramagnetic transition-metal compound contains ions with unpaired electron spins. It is attracted into a magnetic field, whereas diamagnetic compounds have filled shells and are repelled by a field. Quantitative measurement of this effect is convenient for diagnosis, since the degree of attraction into a field, the susceptibility, is proportional to the number of unpaired electrons. Thus, magnetic properties at high temperatures (that of liquid nitrogen and above) are often used in a subsidiary fashion in order to help characterize a transition-metal compound.

Paramagnetism is a single-ion effect in that, given the electronic structure of the constituents, the susceptibility may be calculated exactly by straightforward thermal averaging procedures.¹ The interactions between ions are negligible.

A simple model of a paramagnet suggests that the field aligns the spins parallel to it, while thermal agitation opposes this alignment, and leads¹ to the Curie law, which says the susceptibility is inversely proportional to temperature. The Hamiltonian used is the usual Zeeman one,

$$\mathcal{H} = g\mu_B S_z H_z \quad (1)$$

where g is a splitting constant, characteristic of a given system, μ_B is the Bohr magneton, H_z is the magnitude of the field, and S_z is the usual spin operator. The Curie law is then found¹ as

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$$\chi = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} \quad (2)$$

where N is Avogadro's constant, S is the spin of the ion, and k is the Boltzmann constant.

The magnetic susceptibility of a typical Curie law paramagnet, manganese Tutton salt, is illustrated in Figure 1a. This is the behavior typical of all isotropic materials at temperatures high with respect to any magnetic interactions, such as magnetic exchange, between the ions. Other substances, such as copper salts, obey the Curie law but with susceptibilities anisotropic because of g -value anisotropy. In order to observe this effect it is necessary to measure oriented single crystals, especially since there is more than one source of magnetic anisotropy, as we shall see.

A more important paramagnetic anisotropy arises when zero-field splittings occur,¹ that is, when the ground state may not be described only by the total spin, S . When the ground state of a system has spin degeneracy, such as with the 3A_2 state of vanadium(III), an axial distortion described by the spin Hamiltonian,

$$\mathcal{H} = D[S_z^2 - \frac{1}{3}S(S+1)] \quad (3)$$

where D is the zero-field splitting parameter, can resolve the system into a doubly degenerate $m = \pm 1$ state, separated D/k in energy from the $m = 0$ state. Note that D/k not only has magnitude, but also sign.

As is illustrated in Figure 1b, at temperatures high with respect to D/k the susceptibilities are Curie-like, but susceptibilities measured parallel and perpendicular to the axis of quantization at temperatures comparable to D/k are different and quite unlike Curie behavior. A representative system with be-

(1) R. L. Carlin, *J. Chem. Educ.*, **43**, 521 (1966).

havior like this² is $[\text{C}(\text{NH}_2)_3]\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The only parameters required to fit such data are the g values and the zero-field splitting.

As the temperature decreases, the magnetic interactions generally become more important, the exact temperature of concern varying with the particular compound. The discussion of this Account is restricted to transition-metal complexes for which effects arising from magnetic exchange may be observed in the region below 20 K. Other compounds exist for which the temperature region where magnetic interactions are important covers the whole accessible scale of temperature.

A major reason for investigating magnetic systems at lower temperatures is that the magnetic contribution to the particular effect being measured is generally much larger. Exchange interaction is usually measured by a parameter called the exchange constant, J , conveniently expressed as J/k , in units of degrees. When the ratio $J/kT \approx 1$, then the sample is in the temperature region where exchange is important.

A well-known example is copper acetate monohydrate,³ the prototype of a common behavior in copper salts. A dimer is found, and the two unpaired spins, one on each of the two metal ions, interact with one another antiferromagnetically. This means that the spins pair in the ground state, which is then a spin-singlet, and there is a spin-triplet $-2J/k$ in energy above the singlet. The factor of -2 is used to follow convention,¹ and in $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ the triplet is some 408 K or 285 cm^{-1} above the ground state. The observable result is that the susceptibility has a broad maximum at about 255 K, and falls to zero as the temperature decreases further.

The Hamiltonian in general use for spin-spin interaction may be written in the form

$$\mathcal{H} = -2J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4)$$

where \mathbf{S} is the spin on each ion i and j that interact. Even in extended or three-dimensional lattices, nearest-neighbor interactions usually predominate. This notation allows for antiferromagnetic (AF) interaction ($J < 0$) or ferromagnetic interaction ($J > 0$). As illustrated above with copper acetate, AF interactions cause spins on adjacent sites to align oppositely giving, to a first approximation, a completely ordered ground state with no net magnetic moment at 0 K.

In a ferromagnetic system the spins are also ordered, but in a parallel fashion that results in a large net moment in the ordered state. It is important to note that ordering is a spontaneous effect in zero magnetic fields, independent of all external conditions except temperature.

It is convenient to consider a three-dimensional AF as consisting of (at least) two interpenetrating lattices on each of which all the spins are aligned similarly, but oppositely to those on the other sublattice. The direction in the crystal which is parallel to the direction of spin alignment is called the preferred axis. Most of our discussion of ordered systems will

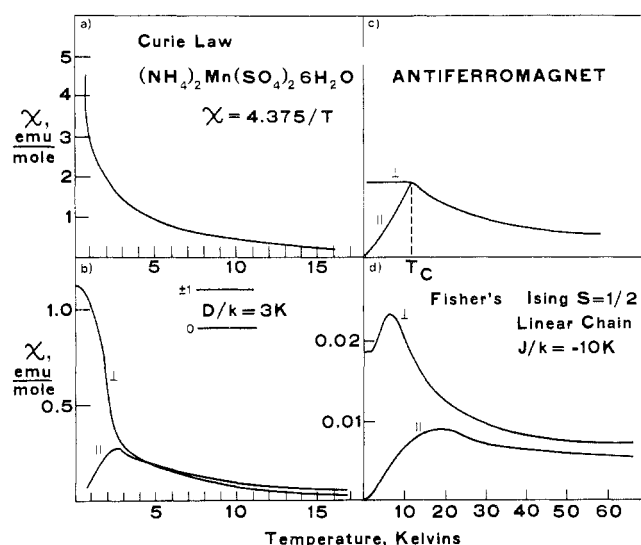


Figure 1. (a) Susceptibility of a Curie law magnet; (b) typical parallel and perpendicular susceptibilities for a zero-field splitting of 3 K; (c) typical susceptibility behavior of an antiferromagnet; (d) typical susceptibilities, parallel and perpendicular to the axis of spin alignment, of a linear chain antiferromagnet.

be limited to AF ones.

In contrast to paramagnetism in insulators, antiferromagnetism is a cooperative phenomenon. This many-body problem has made theoretical investigation of the phenomena associated with AF ordering difficult until recently. The transition from paramagnetic behavior at high temperatures to an AF or long-range ordered spin structure at some lower temperature, T_c , often called a Néel or critical temperature, is in fact a phase transition which occurs over a very small temperature interval. A variety of anomalies are associated with this phase transition, and some are discussed below. For reasons of space, our discussion is limited to information derived from specific heats and susceptibilities, but other techniques such as NMR and neutron diffraction illuminate further details of spin structures in ordered materials.⁴

Much of the recent interest in magnetism at low temperatures arises from a more basic interest in the general phenomenon of phase transitions. Many of these seem to have similar characteristics, whether the transition is a magnetic one, solid-liquid, order-disorder in an alloy, or so on. Detailed calculations on observable phenomena close to the critical point have been carried out recently for a variety of models, some of the variables being the dimensionality of the interactions, the degree of anisotropy of both the single contributing particles as well as of the interactions, and also the sign of the interactions. Since magnetic systems often offer the most convenient circumstances for the testing of such model calculations, ferromagnetic and antiferromagnetic long-range orderings are perhaps the best known examples of cooperative behavior.

The Hamiltonian of eq 4 may be used to characterize anisotropic exchange in the following fashion, beginning by an expansion of the dot product as

$$\mathcal{H} = -2 \sum_{i,j} \{J_z S_i^z S_j^z + J_{xy} (S_i^x S_j^x + S_i^y S_j^y)\} \quad (5)$$

(2) J. N. McElearney, R. W. Schwartz, S. Merchant, and R. L. Carlin, *J. Chem. Phys.*, **55**, 466 (1971).

(3) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952); B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

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

The highly anisotropic coupling obtained in the limit of $J_{xy} = 0$ is called the Ising model, while the case $J_z = J_{xy}$ corresponds to the isotropic Heisenberg model. The anisotropic model obtained with $J_z = 0$ is called the XY system. Most calculations have been carried out on one of these three extreme models. Most real systems fall somewhere in between. The choice of the appropriate model to apply to a set of experimental data is sometimes a case of trial and error, though ions with isotropic g values usually provide Heisenberg systems, while highly anisotropic g values often imply Ising behavior. Only a few XY magnetic systems have as yet been discovered. Note that the discussion thus far ignores the dimensionality of the interactions.

The third type of common susceptibility behavior, that representative of an AF transition in a three-dimensional lattice, is illustrated in Figure 1c. At temperatures high with respect to the ordering temperature, T_c , the susceptibilities are Curie-like. As T_c is approached from above, short-range ordering of spins occurs, and the susceptibility begins to round off and then splits into two anisotropic susceptibilities that diverge dramatically just above T_c . Susceptibilities parallel to the preferred or easy axis fall to zero as $T \rightarrow 0$ K, and the perpendicular susceptibility remains constant.

The subject of short-range order or lower dimensionality is introduced by the curves in Figure 1d. The term "short-range order" is often applied when magnetic exchange occurs in isolated clusters such as copper acetate, or in only one or two dimensions such as would occur, respectively, with isolated chains or planes of magnetic ions. These phenomena, long thought to be merely an interesting theoretical construct, have recently been shown to occur⁴ over wide temperature intervals in a variety of magnetic crystals. In the curve illustrated, an Ising system of spin $\frac{1}{2}$, anisotropic non-Curie behavior occurs. Examples have been given elsewhere⁴ of the behavior to be expected as a function of lattice dimensionality, spin value, and exchange anisotropy. Note that while exchange causes the particular behavior described here, the system remains in the paramagnetic region.

The theory of paramagnetic susceptibilities is in such good condition that not only must a fit of experimental data illustrate the correct qualitative behavior, but quantitative agreement of experiment and theory must be found. An example is offered by $\text{Ca-Cu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$, a system of interest because it contains isolated chemical chains, and the copper atoms are eight-coordinate. The susceptibilities over the temperature range 80–300 K were interpreted on the basis of Fisher's linear chain Ising model, with a value of the exchange parameter $J/k = -1.4$ K. An examination⁵ of the susceptibilities in the temperature region 1.5–20 K, a temperature interval where an exchange contribution of this magnitude should make a more significant contribution to the total susceptibility, in fact showed that exchange (linear chain or otherwise) is not important above 1.5 K.

Experiments in the author's laboratory⁶ are carried

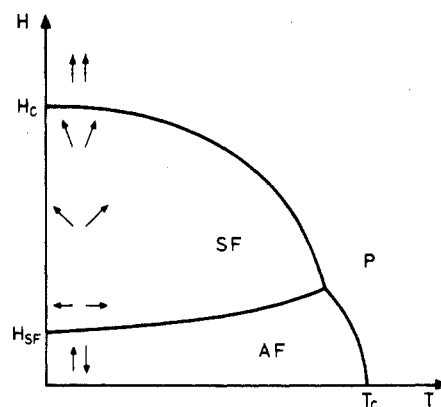


Figure 2. Phase diagram for a typical antiferromagnet.

out at zero external magnetic field ("zero field") before they are continued in the presence of a (magnetic) field. The reasons for this are several, an important one being that most of the thermodynamic theory which one uses for the analysis of these data has been obtained in the limit of zero field. But, as soon as the cooperative phenomenon of magnetic ordering becomes of concern (and it can scarcely be avoided at low temperatures), it becomes imperative to have zero-field data. For example, since ferromagnetically aligned spins are already strongly magnetized spontaneously, application of an external field causes the net magnetic moment to follow the field readily, thus aligning the spins with the field and destroying the paramagnetic (P) to ferromagnetic (F) transition.

Or consider the phase diagram in the magnetic field-temperature plane illustrated in Figure 2 for a typical antiferromagnet with weak exchange anisotropy. The critical temperature T_c at $H = 0$ is simply the Néel temperature already referred to. As the strength of the external field increases from zero, the spins tend to align more with the field, and so, in order to offset this effect by decreasing thermal agitation, the long-range ordering temperature usually decreases. The result is a boundary between the AF and P states.

A third region, called the spin-flop (SF) phase, will also be noted on the diagram. When the magnetic field is applied parallel to the preferred axis of the antiferromagnet, the SF phase occurs at a certain critical field, when the spins change their orientation (flop) from parallel to the field to perpendicular. This occurs because the free energy of an ordered system is lower when the spins are aligned perpendicular to the magnetic field and when the field is strong enough to overcome the exchange energy between the spins. Since there is also a boundary between the SF and P regions, there is also a triple or *bicritical* point.⁴

In other words, when the external field is stronger than all of the internal fields (e.g., exchange, single-ion anisotropy) the system reverts to a saturated paramagnetic one where the spins are aligned (non-cooperatively) by the effect of large external field and low temperature. Such phase diagrams have been obtained recently for a number of systems and point to the hazards involved in the determination of magnetic properties without due consideration for the effects of the field. One of the compounds discussed below undergoes a magnetic transition at 64 Oe,

(5) J. N. McElearney, D. B. Losee, S. Merchant, and R. L. Carlin, *J. Chem. Phys.*, **54**, 4585 (1971).

(6) J. N. McElearney, D. B. Losee, S. Merchant, and R. L. Carlin, *Phys. Rev. B*, **7**, 3314 (1973).

while $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ undergoes a transition⁷ at a mere 6 Oe!

It is usually useful if a magnetic investigation can be carried out on a series of related compounds, or, preferably, a series of isomorphous compounds. Magnetic ions in identical surroundings will have their own idiosyncrasies, such as varying degrees of single ion anisotropy. The investigation of a series allows a more complete characterization of the magnetic phenomena.

Typical Specific Heat Behavior

An investigation of a magnetic system is not complete without a companion measurement of the specific heats. Since the magnetic contribution to the specific heat is often masked by the lattice contribution at high temperatures, this phenomenon provides further justification for limiting the examination of magnetic compounds to those which exhibit magnetic effects only at low temperatures. Examples of typical phenomena appear in Figure 3.

We begin with a discussion of the measured⁸ specific heat of aluminum alum, a diamagnetic compound that offers an example of a lattice specific heat. Of necessity, the lattice (i.e., nonmagnetic) vibrational part always contributes in a magnetic system, and must be separated in some fashion in order to obtain the more interesting and relevant magnetic contribution. Aluminum alum and many other substances obey a T^3 limiting law for the specific heat at low temperatures, and this often facilitates its evaluation. A procedure often used when the magnetic and lattice parts seriously overlap is to find a nonmagnetic compound isomorphous to the magnetic compound of interest, and to use the measured specific heat of the nonmagnetic compound to calculate the lattice contribution of the magnetic compound by means of a corresponding states procedure such as first introduced by Stout and Catalano.⁹

Concentrating only on the magnetic contribution, Figure 3b illustrates the specific heat anticipated for an $S = 1$ system with zero-field splitting. A broad maximum is found, with the value of C_p at the maximum depending only on the relative degeneracies of the states involved. The temperature at which the maximum in this curve, which is often called a Schottky anomaly, occurs in turn depends on the magnitude of the splitting. Thus, one parameter alone (the parameter D/k , with both sign and magnitude) is required to fit the data. An example was supplied by another compound containing trivalent vanadium,¹⁰ $\text{V}(\text{urea})_6 \text{Br}_3 \cdot 3\text{H}_2\text{O}$.

Perhaps most familiar is the λ -shaped curve (Figure 3c) which is found at a long-range order transition temperature. This curve is generally very sharp, and the exact shape of it very close to the transition temperature has interested solid-state physicists.¹¹

The specific heat calculated for a one-dimensional Ising lattice is illustrated in Figure 3d, where it will be noticed that, although a broad maximum occurs,

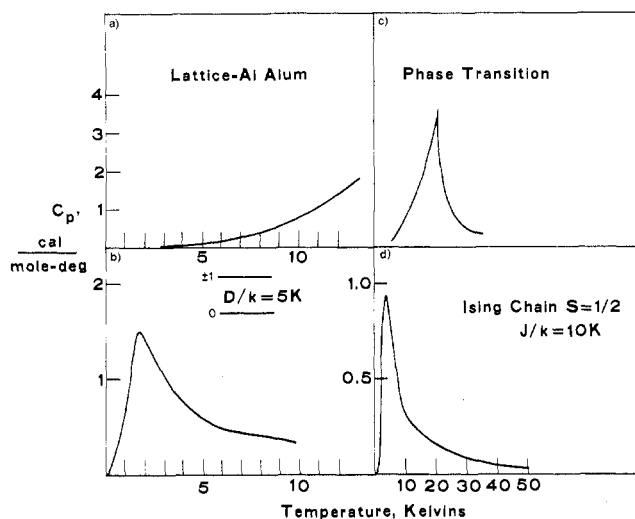


Figure 3. Typical specific heat behavior.

there is no sharp λ -like behavior: a one-dimensional magnet can undergo long-range order only at 0 K. Or, to put it differently, all the entropy of ordering is acquired in the paramagnetic region. The classic calculation of Onsager¹² for a rectangular Ising lattice with varying degrees of anisotropy showed that a sharp spike occurs in the specific heat whenever there is any interchain exchange introduced within a system of magnetic chains.

Examples have been given elsewhere⁴ of the behavior of the specific heat of a magnetic system as a function of lattice dimensionality, spin value, and exchange anisotropy. It is noteworthy that the value of the lattice dimensionality (1, 2, or 3) is more important for changes in the specific heat than is the structure of the particular lattice.

Nickel Chloride Tetrahydrate

Several of the phenomena discussed above are illustrated⁶ by $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$. This crystal, which is little known because it must be grown at 50 °C, is isomorphous at room temperature to the well-known $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, which is monoclinic and contains relatively distorted cis octahedra. The temperature-dependence of specific heat of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ is illustrated in Figure 4. Its most prominent feature, the λ -like peak at 2.99 K, suggests the onset of long-range order at that temperature.

The drop-off of the specific heat above the transition is not as sharp as in most λ -type transitions and indicates the presence of a Schottky anomaly in that region. The specific heat could be fit adequately above T_c , assuming contributions from three sources: (a) a lattice term proportional to T^3 ; (b) a magnetic term (fall-off of the λ peak, due to unspecified short-range order effects) proportional to T^{-2} ; and (c) a Schottky term resulting from the splitting of the 3A_2 ground state of the nickel ion. For a spin -1 system, the magnetic ordering process and Schottky term involve a total entropy change of $\Delta S = R \ln(2S + 1) = R \ln 3$. Integration of the magnetic portions of the heat capacity should, and in this case does, add up to the correct calculated value of the entropy.

The three orthogonal susceptibilities of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ are shown in Figure 5. One important feature is

(7) R. D. Spence, *J. Chem. Phys.*, **62**, 3659 (1975).

(8) D. G. Kapadnis and R. Hartmans, *Physica*, **22**, 173 (1956).

(9) J. W. Stout and E. Catalano, *J. Chem. Phys.*, **23**, 2013 (1955).

(10) J. N. McElearney, R. W. Schwartz, A. E. Siegel, and R. L. Carlin, *J. Am. Chem. Soc.*, **93**, 4337 (1971).

(11) R. F. Wielinga, *Prog. Low Temp. Phys.*, **6**, 333 (1971).

(12) L. Onsager, *Phys. Rev.*, **65**, 117 (1944).

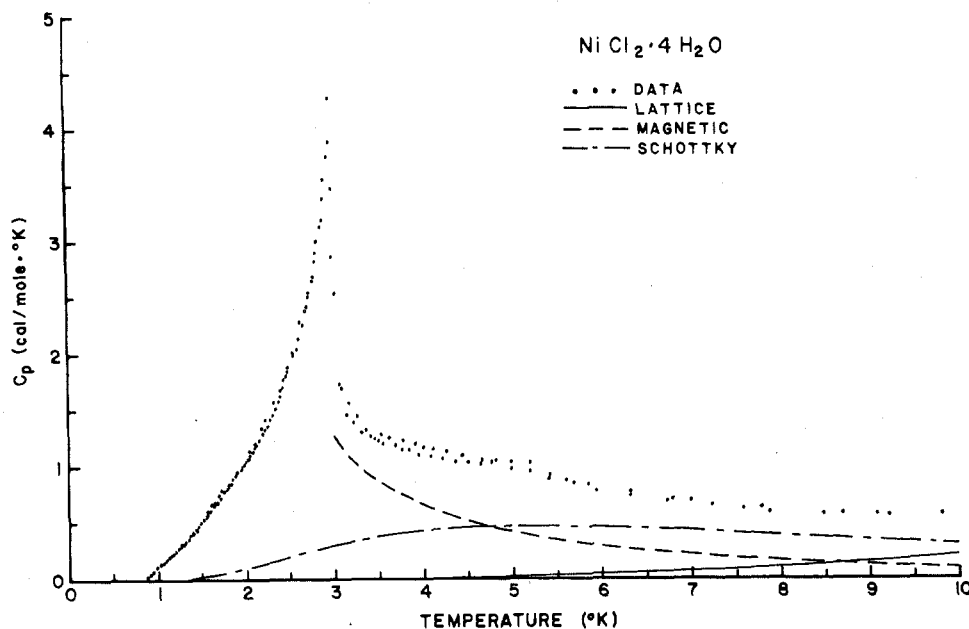


Figure 4. Specific heat of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$.⁶

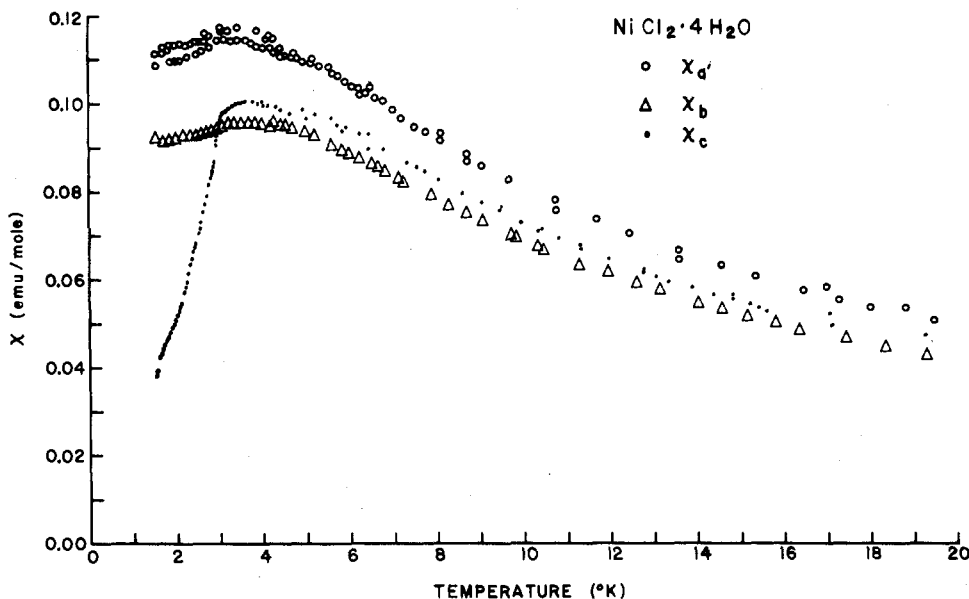


Figure 5. Magnetic susceptibilities of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$.⁶

the anisotropy which exists over the entire temperature region, indicating the same large zero-field splitting observed in the specific heat measurements. The second is the general relative behavior of the three curves: the leveling off of the susceptibility in two directions and its dropping in the third as the temperature falls below about 4 K. This behavior is typical of antiferromagnetic ordering and implies that the spin alignment is along the c axis. The inflection point in the c -axis (or parallel) data lies very close to the transition temperature observed in the heat capacity measurements. What is of especial importance is that the susceptibility data were fit with the same set of parameters as were found from analysis of the Schottky term in the specific heat. The large anisotropy in the paramagnetic region, in particular, was reproduced by the fitting process.

The significance of this investigation of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ is the following. It is isomorphic to $\text{MnCl}_2 \cdot$

$4\text{H}_2\text{O}$ (and, incidentally, also to $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$), which is one of the most widely investigated antiferromagnets. The introduction of the new material, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, allows the investigation of the effects of a change in spin and the addition of a large zero-field splitting on the magnetic ordering observed in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. For example, the transition temperature for the nickel compound is higher by a factor of 1.84 than that of the manganese compound, an increase that is just the opposite of the simple molecular field model prediction. However, if crystalline anisotropy and nearest and next-nearest neighbor exchange interactions are taken into account, an increase in crystalline anisotropy should increase the transition temperature when the exchange interactions are held constant.⁶

$[(\text{CH}_3)_3\text{NH}]\text{MX}_3 \cdot 2\text{H}_2\text{O}$

This new series of compounds of the divalent met-

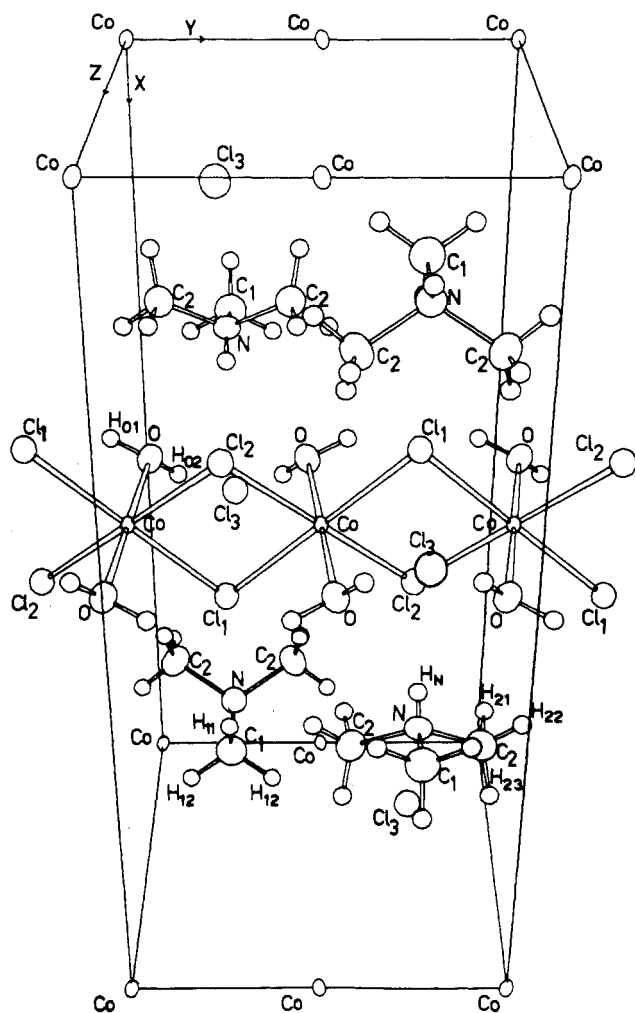


Figure 6. Crystal structure of $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$.¹⁴

als promises to provide a great deal of information on the magnetic properties of low-dimensional systems.¹³ The wide variety of behavior that is found here is shown by the fact that the Co-Cl compound is a spin $-\frac{1}{2}$ Ising system,^{14,15} the Cu-Cl system is a spin $-\frac{1}{2}$ Heisenberg system,¹⁶⁻¹⁸ and the Mn-Cl and Mn-Br systems are spin $-\frac{5}{2}$ Heisenberg systems;^{19,20} the nickel system²¹ has recently been prepared, and the characteristics of this spin -1 system remain to be explored.

All of these compounds have the same molecular, but not crystallographic, structure. The Co-Cl system is orthorhombic,¹⁴ the Cu-Cl system is monoclinic (though the angle β differs from 90° by only 2°),¹⁶ and the Mn-Cl system is also orthorhombic.¹⁹ The structure, illustrated in Figure 6, consists of dichloro-bridged cobalt atoms linked into infinite chains par-

allel to the crystallographic b direction; two trans water molecules complete the coordination sphere of each octahedral metal atom. A third chlorine atom lies between the chains, linking them into a planar structure by hydrogen bonding. It is this effect which gives to the chains the anisotropic two-dimensional magnetic structure of the compounds. The trimethylammonium groups lie between the planes and effectively isolate one from another.

The susceptibilities¹⁶ of the copper compound between 1.5 and 20 K show no unusual features and obey the Curie law, showing that this compound behaves as a simple paramagnet. The specific heat results are consistent with this, being featureless above 3 K, and are attributed to a lattice contribution alone. The specific heat begins to rise at low temperatures, and the λ peak has been observed at 0.165 ± 0.005 K.¹⁸ The susceptibilities¹⁷ below 0.45 K confirm that the system orders antiferromagnetically at $T_c = 0.157 \pm 0.003$ K. Large values of the peak susceptibility were observed and judged to be consistent with a strong two-dimensional ferromagnetic interaction above T_c . The data were fit with a Heisenberg model of this sort with $J/k = 0.28$ K and an interplanar exchange constant an order of magnitude smaller and of opposite sign. On the other hand, the specific heat is more characteristic of one-dimensional interaction,¹⁸ and the susceptibilities have been reinterpreted with this model.

What is surprising is how weak the exchange is in this salt, and that such a low transition temperature is observed. The compound $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($T_c = 4.36$ K) has chemical chains similar to those found in $[(\text{CH}_3)_3\text{NH}]\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$, and yet there the exchange constant has the value $J/k \approx -5.5$ K. The compound $\text{CuCl}_2 \cdot 2\text{py}$ ($T_c = 1.130$ K) exhibits²² a broad maximum at 17.5 K in the susceptibility which is characteristic of an antiferromagnetic linear chain. This compound, which also contains dichloro-bridged copper atoms but has two trans pyridine molecules, has an intrachain $J/k = -13.2$ K. The compound with the most structural asymmetry in the $(-\text{CuCl}_2-)$ unit, i.e., $\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, has the largest exchange, while the least asymmetric unit, $[(\text{CH}_3)_3\text{NH}]\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$, displays the least amount of exchange along the chemical chain.¹⁶ Thus, small changes in the coordination geometry are associated with profound changes in the exchange to the point where even the sign of the exchange has been reversed.

The Co-Cl compound is the best understood example in this series. It orders antiferromagnetically¹⁴ at 4.135 K, as determined from the specific heat curve. The evaluation of the lattice heat capacity above this temperature was carried out by a corresponding states procedure using the copper analog as the non-magnetic material; as was mentioned above, the specific heat of the copper compound through this temperature region is due to the lattice alone. The cobalt(II) ion is a spin $-\frac{1}{2}$ ion in the helium temperature region because of the resolution of its degeneracy by spin-orbit coupling. Upon integrating the specific heat in order to obtain the entropy, only 8% of

(13) J. N. McElearney, G. E. Shankle, D. B. Losee, S. Merchant, and R. L. Carlin, *ACS Symp. Ser.*, No. 5, 194 (1974).

(14) D. B. Losee, J. N. McElearney, G. E. Shankle, R. L. Carlin, P. J. Cresswell, and W. T. Robinson, *Phys. Rev. B*, 8, 2185 (1973).

(15) R. D. Spence and A. C. Botterman, *Phys. Rev. B*, 9, 2993 (1974).

(16) D. B. Losee, J. N. McElearney, A. Siegel, R. L. Carlin, A. A. Khan, J. P. Roux, and W. J. James, *Phys. Rev. B*, 6, 4342 (1972).

(17) C. R. Stirrat, S. Dudzinski, A. H. Owens, and J. A. Cowen, *Phys. Rev. B*, 9, 2183 (1974).

(18) H. A. Algra, L. J. de Jongh, H. W. J. Blöte, W. J. Huiskamp, and R. L. Carlin, *Physica*, 78, 314 (1974).

(19) S. Merchant, J. N. McElearney, G. E. Shankle, and R. L. Carlin, *Physica*, 78, 308 (1974).

(20) P. R. Newman, J. A. Cowen, and R. D. Spence, *AIP Conf. Proc.*, No. 18, 391 (1974).

(21) J. N. McElearney, unpublished.

(22) K. Takeda, S. Matsukawa, and T. Haseda, *J. Phys. Soc. Jpn.*, 30, 1330 (1971); W. Duffy, Jr., J. E. Venneman, D. L. Strandburg, and P. M. Richards, *Phys. Rev. B*, 9, 2220 (1974).

the theoretical maximum entropy for a mole of cobalt ions has been acquired at the transition temperature. Thus, substantial short-range order persists in this compound above T_c and is an indication of the lowered lattice dimensionality of the magnetic spin system. This was suggested by the structure.

Because of the large anisotropy in the g values of cobalt, it is often an Ising ion at low temperatures. Since the crystal structure shows the compound to consist of sheets of cross-linked infinite chains, the magnetic specific heat of $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ was successfully fitted to Onsager's solution¹² for the specific heat of an anisotropic two-dimensional (anti-) ferromagnet. The exchange parameter $|J/k|$ equals 7.7 K, with a ratio of $|J/J'|$ of approximately 100.

Although Co(II) in an octahedral environment usually exhibits magnetic anisotropy, the single-crystal magnetic susceptibilities of $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ show an exceptional anisotropy, with dramatically different behavior of each principal axis susceptibility. At 4.33 K, just above T_c , the susceptibility measured along the chemical chain is approximately $1/500$ th of that measured perpendicular to the chain along the c axis. Below about 3 K much of the anisotropy disappears; χ_a and χ_b remain constant with decreasing temperature, while χ_c tends to zero. At least in the lowest temperature region, the susceptibility behavior appears similar to that of an antiferromagnet in the ordered state, with χ_c behaving as χ_{\parallel} and χ_a and χ_b as χ_{\perp} .

However, it was obvious upon consideration of the measured magnitudes of χ_a and χ_c at higher temperatures that the transition occurring in this compound is not a simple paramagnetic to antiferromagnetic one. Since the problem of calculating the susceptibility of an anisotropic two-dimensional magnetic system has not been solved yet, and since the specific heat results indicated exchange between the cross-linked chains in $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ to be relatively small, the susceptibility results were examined using equations based upon isolated, noninteracting Ising linear chains. It is remarkable that χ_b could be fit throughout the whole temperature region, and χ_c above the transition temperature, with the exchange constant determined independently from the specific heat results, $J/k = +7.7$ K. Note that the positive sign is now required for the interaction constant, implying that the material consists of ferromagnetically oriented chains. Confidence in the procedure is gained from an independent measurement of the g_c value and magnetic structure by NMR methods.¹⁵

The χ_a data were not as easily fit, and a clue to the reason was given by the behavior of χ_a below 4.3 K. A region of large, nearly constant susceptibility was observed, indicating the presence of a net moment along the a axis. Such behavior might well be expected for a canted spin system which is weakly ferromagnetic. In fact, behavior similar to that of χ_a in the paramagnetic region was predicted by Moriya,²³ by the introduction of an antisymmetric exchange term in the Hamiltonian.

The addition of this term allowed a satisfactory fit of the χ_a data, and allowed a postulation of the spin

structure¹⁴ which has been confirmed by NMR methods.¹⁵ The spin structure consists of ferromagnetically aligned chains which are weakly coupled antiferromagnetically. There is a weak moment in the ac plane, obtained by a canting along a . The source of the canting is the large g -value anisotropy, coupled with the tilting of the g -tensor axes with respect to each other. Deuteration to form $[(\text{CH}_3)_3\text{ND}]\text{CoCl}_3 \cdot 2\text{D}_2\text{O}$ causes a negligible change in the ordering temperature which is consistent with this spin structure.²⁴

Metamagnetism is a phenomenon that occurs in a highly anisotropic system, which causes the spin-flop region (Figure 2) to shrink to zero area. Application of a magnetic field then causes, at a certain critical field, an abrupt transition to a paramagnetic system. A field of only 64 Oe (below 2.5 K) has been found¹⁵ to cause such a metamagnetic transition in $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$, while a field of 120 Oe is required for the bromide.

Much the same story applies to the similar manganese compounds;¹⁹ a broad peak appears in the heat capacity at low temperatures, with some 80% of the magnetic entropy being obtained above the long-range ordering temperature. The susceptibilities become anisotropic at low temperatures, and a canted antiferromagnetic structure obtains. The Mn-Br system likewise becomes metamagnetic in a field of some 1200 Oe.²⁰ The analysis of the data in terms of exchange parameters is difficult because of the large spin value, but approximate values are available.¹⁹ A further problem concerns the canting and the strength of the Moriya interaction, which should be proportional to the g -value anisotropy, which is well known to be very small for manganese(II). Since the interaction is large here, these results suggest that a more complicated situation occurs.

Manganese Chloride Dihydrate

This substance has a chemical or structural linear chain which exhibits, by chance, isotropic magnetic behavior. As with the trimethylammonium series described above, the compound consists of chains of edge-sharing $\text{trans-}[\text{MnCl}_4(\text{OH}_2)_2]$ octahedra. Specific heat measurements indicated a magnetic phase transition at 6.68 K and lacked magnetic linear chain characteristics, thus suggesting interchain and intrachain exchange to be of comparable magnitude. NMR measurements determined the spin structure, in which the chains are antiferromagnetically coupled. The magnetic susceptibility²⁵ confirms these results, for it exhibits behavior that is very similar to that of systems with isolated monomers in which there is little short-range magnetic order above T_c . The data were fit successfully, with the resulting parameters for intrachain and interchain exchange being indeed equal within experimental error.

Replacement of the trans water molecules by either pyrazole or pyridine ligands serves²⁶ to push the linear chains further apart and thus to increase the magnetic chain behavior. The intrachain exchange

(24) R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *Phys. Lett. A*, 50, 433 (1975).

(25) J. N. McElearney, S. Merchant, and R. L. Carlin, *Inorg. Chem.*, 12, 906 (1973).

(26) F. W. Klaaijzen, H. Den Adel, Z. Dokonpil, and W. J. Huiskamp, *Physica B*, 79, 113 (1975).

(23) T. Moriya, *Phys. Rev.*, 120, 91 (1960).

constant for $\text{MnCl}_2 \cdot 2\text{py}$ is within a factor of two of that for $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, but the ratio of $|J'/J|$ decreases from about 1 in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ to 1.5×10^{-2} in $\text{MnCl}_2 \cdot 2\text{py}$.

Discussion

Only a few problems have been touched upon here, in an attempt to show that there is a correlation between molecular structure and magnetic properties, especially magnetic exchange interactions. One of the serious remaining problems is to correlate exchange energies with such variables as the particular metal ion involved, the distance separating the metals, the nature of the intervening ligands, and the geometry of the metal-ligand-metal unit. Those topics fall within the theory of superexchange interaction, of which the most recent advance concerns the 180° superexchange in some iron series fluorides.²⁷ A correlation between the metal-ligand-metal bonding angle and the exchange interaction in a series of copper dimers has been noted.²⁸

More new model systems remain to be discovered, especially examples of the XY model, which requires a special anisotropy. The only one-dimensional XY magnet to date is²⁶ $(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2$, while $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ appear to be two-dimensional examples of this model.²⁹ Of great current interest is the recent discovery³⁰ that $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ is an example of the spin $-1/2$, simple-cubic, XY model magnet. Since it has been suggested³¹ that liquid helium is also a spin $-1/2$, XY model material near its λ transition, that would make the pyridine *N*-oxide compound a magnetic analog of liquid helium.

Several other comparisons may yet be made. For

example, one of the selection rules that allows canting of the spins is that the magnetic ion may not reside at a center of symmetry. Canting is allowed in $\text{CsCoCl}_3 \cdot 2\text{H}_2\text{O}$, which consists of chains of singly bridged $-(\text{Co}-\text{Cl})$ units, and it is found there,³² but the isostructural manganese analog, $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$, does not exhibit canting.³³ The argument that the canting must be small or zero for a manganese system is inapplicable, as shown by the results described above for the $[(\text{CH}_3)_3\text{NH}]\text{MnX}_3 \cdot 2\text{H}_2\text{O}$ series. It may well be that the single-ion anisotropy of manganese, which can also lead to canting, is much larger than anticipated in the trimethylammonium salt; after all, $|D/k|$ has been found²⁶ to be as large as 0.2–0.5 K in the chained MnX_2L_2 series ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{pyrazole}, \text{pyridine}$).³⁴

The intrachain exchange is antiferromagnetic for all the compounds, $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$, $[(\text{CH}_3)_3\text{NH}]\text{MnX}_3 \cdot 2\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 2\text{py}$ ³⁵ and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, but is almost an order of magnitude larger in the singly bridged cesium compound than in the others. Similarly, it is larger in $\text{CsCoCl}_3 \cdot 2\text{H}_2\text{O}$ than in either $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ ³⁶ but the intrachain exchange is ferromagnetic in the last two compounds and antiferromagnetic in the cesium compound. Ferromagnetic chains have also been found in $\text{CoCl}_2 \cdot 2\text{py}$,²² but single-crystal measurements are not yet available. It would be interesting to discover other ferromagnetic, insulating crystals that are amenable to the procedures discussed here.

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(32) A. Herweijer, W. J. M. de Jonge, A. C. Botterman, A. L. M. Bongaarts, and J. A. Cowen, *Phys. Rev. B*, **5**, 4618 (1972).

(33) H. Kobayashi, I. Tsujikawa, and S. A. Friedberg, *J. Low Temp. Phys.*, **10**, 621 (1973).

(34) This indeed seems to be the case. Using the calculations of Blöte (H. W. J. Blöte, *Physica B*, **79**, 427 (1975) we estimate $D/|J|$ is at least as large as -1 .

(35) P. M. Richards, R. K. Quinn, and B. Morosin, *J. Chem. Phys.*, **59**, 4474 (1973).

(36) A. Narath, *Phys. Rev. A*, **136**, 766 (1964); **140**, 552 (1965).

(27) L. J. de Jongh and R. Block, *Physica*, in press.

(28) W. E. Hatfield, *ACS Symp. Ser.*, No. 5, 108 (1974).

(29) J. W. Metselaar, L. J. de Jongh, and D. de Klerk, *Physica B*, **79**, 53 (1975).

(30) R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Am. Chem. Soc.*, **98**, 685 (1976); H. A. Algra, L. J. de Jongh, W. J. Huiskamp, and R. L. Carlin, to be published.

(31) D. D. Betts and J. R. Lothian, *Can. J. Phys.*, **51**, 2249 (1973).