

Magnetochemistry of Ions in the 4A_2 Electronic State

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Electronic spectroscopy samples the excited states of a material. These states are, as a rule, not populated. The magnetic properties of a transition metal complex, in contrast, are determined by the thermally occupied electronic states.

Magnetic ordering in ferromagnetic metals and alloys has long been known and a variety of models involving itinerant electrons has been proposed to explain the existence of ferromagnetism. Recently, there have been studies of

Summary. Each of the following ions with spin $S = 3/2$, octahedral chromium(III), five-coordinate iron(III), and tetrahedral cobalt(II), possesses a 4A_2 ground state. The theory describing their paramagnetic properties is therefore the same, though some of the parameters change appreciably from ion to ion. This theory is described along with examples of experimental data. The implications of the paramagnetic properties for the magnetic ordering phenomena exhibited by complexes of these ions are also described.

The thermal energy available at room temperature is about 300 K or 200 cm^{-1} , so the magnetic susceptibility measured at room temperature is largely that of the ground state. At temperatures of about 4.2 K, only the ground state determines the value of the susceptibility. Conversely, the measurement of a complex ion's magnetic susceptibility at low temperatures allows the determination of the ground state of the central metal ions. This is important because this state defines energy-level separations that must be explained by theory. The ground state also determines the nature of the cooperative magnetic interactions among the ions. At low temperature, it is also possible to measure the magnetic contribution to the specific heat of a substance, which is often masked by the specific heat of the lattice at higher temperatures.

insulators, especially transition metal complexes, which undergo spontaneous long-range magnetic ordering. The magnetic electrons are more localized in these molecules.

One of the major goals of recent research in magnetochemistry has been to find experimental examples of the theoretical models for magnetic interactions. It is the ground state of the constituent ions that controls the cooperative magnetic ordering that a material undergoes. Metal ions with spin $S > 1/2$ can undergo zero-field splittings (ZFS) ranging in magnitude from about 0.1 K to about 25 K. Both the sign and magnitude of the ZFS are determined by the combined action of the spin-orbit coupling and the axial crystalline fields, and they vary strikingly from metal to metal, as well as from one compound to another. The ZFS of a particular compound determines the electronic ground state, which is the state involved in magnetic ordering at

low temperatures. The ZFS can therefore be said to control the nature of the magnetic ordering.

Three metal ions have a similar electronic structure, octahedral chromium(III), tetragonal-pyramidal iron(III), and tetrahedral cobalt(II). All have a 4A_2 ground state, which is well isolated from the excited states and which is nondegenerate orbitally but fourfold degenerate in spin. The spin degeneracy can be resolved in part by an axial crystalline electric field and spin-orbit coupling into the spin components, $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$; the energy separation between these levels is denoted $2D/k$, where k is Boltzmann's constant and D is the axial zero-field splitting. This ZFS has both sign and magnitude and will be given here in units of Kelvin. A positive value for D/k places $|\pm 1/2\rangle$ energy level below the $|\pm 3/2\rangle$ energy level. Only an applied magnetic field can resolve the remaining degeneracy. The ZFS increases in the order $\text{Cr(III)} < \text{Fe(III)} < \text{Co(II)}$, following the increase in spin-orbit coupling. Since the electronic structure of these ions may be treated by the same theory, it is convenient to discuss them together. They illustrate many of the phenomena currently of interest in magnetochemistry; and, increasingly, the relevance of magnetochemistry to biological problems is being recognized in the biochemical literature.

Theory

Zero-field splittings affect the lowest temperatures that can be reached by adiabatic demagnetization procedures using paramagnetic cooling salts (1). The magnetic specific heat of two doubly degenerate energy levels separated by $2D/k$ is

$$C = \frac{R(2D/kT)^2 \exp(2D/kT)}{[1 + \exp(2D/kT)]^2} \quad (1)$$

where R is the gas constant and T is temperature. This curve, which is an even function of D/k , gives rise to a broad maximum, usually called a Schottky anomaly. Note that only one parameter, $|D|/k$, enters into Eq. 1. Fit-

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ting experimental data to this expression is the most definitive procedure for determining the magnitude of the ZFS. An example is provided by the specific heat measurements from Cs_2CoCl_4 (Fig. 1), which exhibit a second broad maximum (at lower temperatures) due to the antiferromagnetic linear chain behavior of this compound (2). A magnetic linear interaction is found when the interaction occurs in only one dimension. The small peak at even lower temperatures is due to the onset of long-range antiferromagnetic order.

The Curie law, which is the magnetic analogue of the ideal gas law, states that magnetic susceptibility χ varies inversely with temperature. This behavior is frequently found at higher temperatures. More complex behavior is found at lower temperatures, especially when the ZFS begins to affect the susceptibility. Thus, the susceptibilities parallel and perpendicular to the z axis for the 4A_2 state are

$$\chi_{\parallel} = \frac{Ng_z^2 \mu_B^2}{4kT} \cdot \frac{1 + 9 \exp(-2D/kT)}{1 + \exp(-2D/kT)} \quad (2)$$

$$\chi_{\perp} = \frac{Ng_{\perp}^2 \mu_B^2}{kT} [1 + \exp(-2D/kT)]^{-1} + \frac{3Ng_{\perp}^2 \mu_B^2 \tanh(D/kT)}{4D} \quad (3)$$

where N is Avogadro's number and μ_B is the Bohr magneton. The susceptibilities depend strongly on the sign of D ; but more importantly, there is a departure from Curie behavior when kT/D becomes less than 2. This deviation is due to the depopulation of the higher of the two energy levels of the 4A_2 state and the consequent decrease in its contribution to the susceptibility. Only one com-

pound, which will be discussed below, has been found to which these relationships have been applied.

There is another source of non-Curie behavior. Deviations from the ideal gas law are found when the pressure of a gas is increased or the temperature lowered. Departures from the Curie law are also found when the temperature of a magnetic system is decreased because the magnetic moments begin to interact with one another.

Equations 2 and 3 describe only the behavior of isolated or independent spins; and they must be corrected, if necessary, for exchange interactions between such spins. This is characterized by the spin Hamiltonian

$$H = -2J \sum_{i,j} S_i \cdot S_j$$

which is usually used in expanded form,

$$H = -2 \sum_{i,j} [J_{xy}(S_{x,i}S_{x,j} + S_{y,i}S_{y,j}) + J_z S_{z,i}S_{z,j}] \quad (4)$$

where the sum is over nearest neighbor magnetic ions i and j . The J 's are exchange constants which measure the strength of the magnetic interactions between the ions. The limiting cases that have been analyzed most thoroughly are the Heisenberg model, which sets $J_z = J_{xy}$, and the Ising model, which sets $J_{xy} = 0$. The case with $J_z = 0$ is called the XY model.

Just as gases will condense when the temperature is lowered enough, most solids containing ions that are paramagnetic will become ordered at some temperature. We turn now to the way in which the ZFS controls magnetic ordering phenomena (3). Magnetic ions can interact with each other through the in-

tervening ligands by a mechanism called superexchange interaction. This mechanism is quite similar to that which gives rise to electron-mediated spin-spin coupling in nuclear magnetic resonance (NMR) spectroscopy, and it causes a correlation of the magnetic moments of ions on neighboring lattice sites. Polarizable ligands often provide the most efficient superexchange paths. When the exchange becomes strong enough with respect to kT , it can bring about a transition to an ordered state. This process is a phase transition, just as is the freezing of water; and the nature of the ordering depends on the constituent ions, their arrangement in space, and the disposition of the ligands. When magnetic moments on neighboring sites are oppositely aligned, the ordered state is called antiferromagnetic. A sharp peak called the λ -anomaly is observed in the specific heat at the critical temperature, as is seen at 0.22 K in Fig. 1.

Magnetic ordering occurs spontaneously in many compounds, whenever the exchange interaction is larger than the ZFS (3). Such ordering is typical of manganese(II) salts, which have a 6A_1 ground state and therefore usually display only small ZFS values. The sign and magnitude of the ZFS are then irrelevant. Field-induced magnetic ordering can sometimes take place in materials with ions of spin $S = 1$ when the ZFS is larger than the exchange interaction (3, 4).

The ZFS in many cases determines the magnetic model (1, 5) that is applicable to a particular compound. The Heisenberg model of exchange interaction is an isotropic one, whereas the Ising model is highly anisotropic; the XY model is intermediate between the two. A tetrahedral cobalt compound could behave as any one of these three models predicts, depending on the sign and magnitude of the ZFS. The reason for emphasizing which model a system follows, as de Jongh and Miedema show (5), is that the thermodynamic quantities measured for a compound depend not only on the lattice dimensionality but also on the particular magnetic model that is applicable. For example, the shape of the specific heat curve at a phase transition depends on whether the compound is Heisenberg-, XY -, or Ising-like. In recent years, much of the effort of chemists and physicists in this research area has been focused on the preparation and study of new compounds in the hope of finding the best possible example of each of these magnetic models; this goal has now largely been achieved.

Of the ions reviewed here, the ZFS is generally largest for tetrahedral cobalt-

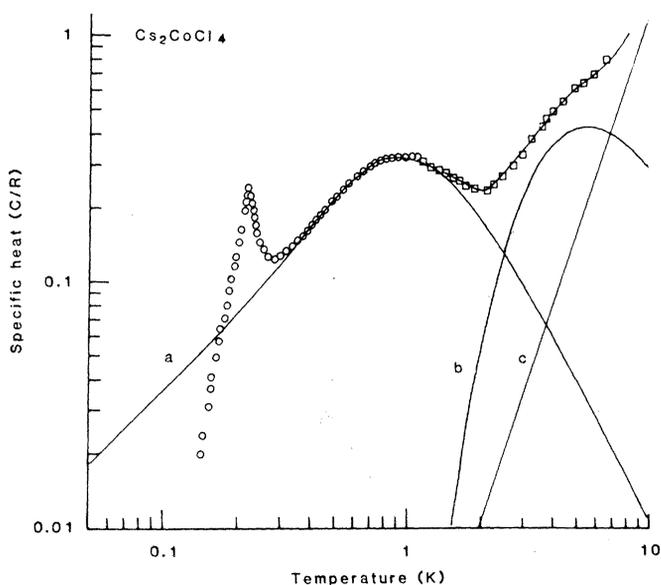


Fig. 1. The specific heat in dimensionless units (data points) of Cs_2CoCl_4 as a function of temperature. The drawn curves are fitted to the data. Curve b is the Schottky curve given by Eq. 1 with $2D/k = 13.5$ K. Curve a is that calculated for an XY linear chain, and c is the estimated lattice contribution. The long-range ordering peak is at 0.22 K. [From (2); courtesy of North-Holland Publishing Company]

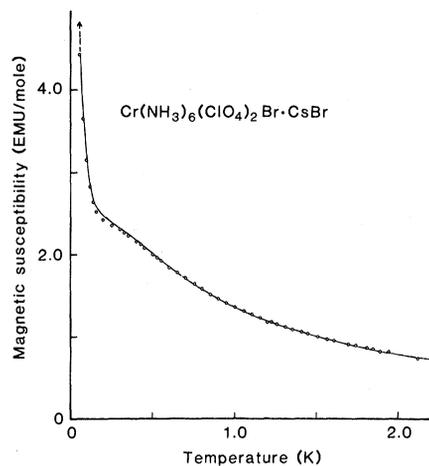


Fig. 2. The magnetic susceptibility measured parallel to the unique axis of $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_2\text{Br} \cdot \text{CsBr}$ at low temperatures. The points are experimental data, and the curve is fitted to the data with Eq. 2 along with a small correction for exchange interaction. [From (6); courtesy of the American Chemical Society]

(II) and that is why more is known about the effect of ZFS on the magnetic properties of cobalt compounds than the other ions discussed here. Since in this case only the lower doublet is involved in magnetic ordering, the cobalt(II) effectively acts as an ion with spin $S = 1/2$, the splitting factors, or g values, depending on which component of the 4A_2 state is the lower one. The ZFS in octahedral chromium(III), by contrast, is so small that its effect on magnetic ordering has scarcely been observed.

Octahedral Chromium(III)

Exchange interactions have been found to be relatively weak in chromium compounds, and there are only a few superexchange-coupled systems known.

The ZFS in chromium(III) is generally best determined by electron paramagnetic resonance (EPR) methods. With an external field H_z applied parallel to the principal symmetry axis, the degeneracy of both the $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ energy levels is resolved. Transitions are allowed between the $|+1/2\rangle$ and $|-1/2\rangle$ spin energy states, which are separated by an energy $g_{\parallel} \mu_B H_z$, between $|+1/2\rangle$ and $|+3/2\rangle$, and between $|-1/2\rangle$ and $|-3/2\rangle$. The latter transitions are separated by $2D$ and therefore allow its determination. The magnitude of $2D$ is easily evaluated from the spectrum, but the sign is not easily established. This method, while very accurate, is usually limited to cases in which $2D/k$ is substantially less than 1 K.

I know of only two cases where the

ZFS has been determined by the measurement of magnetic susceptibilities and these involve the compounds $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_2\text{Br} \cdot \text{CsBr}$ (6) and $\text{Cs}_2\text{CrCl}_5 \cdot 4\text{H}_2\text{O}$ (7). In the first case, the compound remains paramagnetic at temperatures down to 40 mK. Since the substance is uniaxial, measurements parallel to the unique axis allowed the evaluation of the ZFS, using Eq. 2, as $2D/k = 0.53$ K. The data and fit are presented in Fig. 2. The shortest metal-metal separation in this material is close to 10 Å, and there are no important superexchange paths.

In the second compound, monoclinic $\text{Cs}_2\text{CrCl}_5 \cdot 4\text{H}_2\text{O}$, the determination of the ZFS was less-straightforward because of the low symmetry. Furthermore, the exchange interaction and the ZFS were comparable in energy, and there were important lower-dimensional magnetic interactions in this compound. Thus a model incorporating these features was proposed that could be fitted with the experimental data, and the ZFS was found to be $2D/k = -0.32$ K. The compound undergoes long-range antiferromagnetic order at 185 mK.

Several bimetallic coordination compounds of chromium have been investigated (8-10). They are substances such as $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$, and the exchange interaction is about 20 times greater in these materials than in analogous salts in which one of the chromium atoms is replaced isomorphously by diamagnetic cobalt(III). Nevertheless the exchange interaction is still quite weak, and magnetic ordering takes place in the Cr-Cr salts at temperatures well below 1 K. The ZFS values are so small in these salts that they appear to have no effect on the magnetic properties at temperatures down to 40 mK, and thus their behavior has been analyzed successfully in terms of an isotropic $S = 3/2$.

Five-Coordinate Iron(III)

Octahedral iron(III) usually has either a spin-free, $S = 5/2$, or spin-paired, $S = 1/2$, ground state. The existence of several five-coordinate iron(III) complexes that have a 4A_2 ground state has recently been discovered. This ground state is known to be important in some molecules in biological systems, but the most thoroughly studied example is chlorobis(diethyldithiocarbamate) iron(III), $\text{Fe}(\text{Cl})(\text{S}_2\text{CNET}_2)_2$ (11-13). The lattice consists of discrete pyramidal molecules with a 4A_2 ground state like that of octahedral chromium(III) and tetrahe-

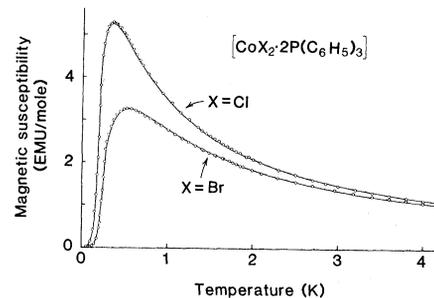


Fig. 3. Magnetic susceptibilities measured parallel to the c axis of $\text{CoCl}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{CoBr}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$. The broad, continuous curves are characteristic of materials with less than three-dimensional magnetic character. The points are experimental data, and the curves are fitted. [From (20); courtesy of the American Chemical Society]

dral cobalt(II). Zero-field splittings are then expected, and a critical analysis of the data (12) results in the evaluation of the ZFS parameters as $D/k = -3.32$ K and $E/k = -0.65$ K, where the rhombic parameter E describes distortions from axial symmetry. The rhombic term is significant, so the total ZFS of the 4A_2 state is calculated as $2(D^2 + 3E^2)^{1/2}$, or 7 K. The system orders ferromagnetically at 2.46 K.

When the ZFS is negative, as in the present case, the $|\pm 3/2\rangle$ state needs to be examined. Since $\Delta m_s = 3$, the effective g_{\parallel} is $3g_{\parallel}$ or about 6; there are no matrix elements for the S_{\pm} operators that connect the two states, so g_{\perp} is zero to the first order. Since the exchange constant J is proportional to the magnetic moments of the ions, J is proportional to g^2 ; and the large anisotropy in the g values is reflected in highly anisotropic exchange. These are the conditions required for a system to behave as an Ising system, and that is precisely what has been found.

When the $|\pm 1/2\rangle$ state is the ground state the situation changes. Then, the effective g_{\parallel} is approximately the same as the real g_{\parallel} , about 2. The effective g_{\perp} is twice the real g_{\perp} , about 4. The ratio of exchange constants J_z and J_{xy} is proportional to the square of the ratio of the effective g values, $(g_{\parallel}/g_{\perp})^2$, about 1/4. This ratio indicates behavior consistent with the XY model. One must determine the g values from experiment to evaluate this ratio for any given system, and the smaller the ratio, the more closely is the XY model followed (14). The selenium analogue, $\text{Fe}(\text{Cl})(\text{Se}_2\text{CNET}_2)_2$, which apparently is isomorphous to the dithiocarbamate complex, also orders ferromagnetically, at 3.46 K. The sign of the ZFS changes, with the $|\pm 1/2\rangle$ state being lower; and the parameters are $D/k = 6.95$ K and $E/k = -0.14$ K. The total

ZFS is then 13.9 K, and therefore the $|±3/2\rangle$ state is depopulated at T_c . As a result, the magnetic anisotropies are smaller than in the dithiocarbamate compound, and behavior consistent with the XY model is found (15).

The five-coordinate chloro(*meso*-tetraphenylporphinate)iron(III) complex has a spin $S = 5/2$ and a 6A_1 ground state (16) unlike the compounds discussed above. A large ZFS is reported ($D = 6.9 \text{ cm}^{-1}$, or $D/k = 10 \text{ K}$).

Tetrahedral Cobalt(II)

The majority of magnetic data about 4A_2 systems is from tetrahedral cobalt(II). The best known species is the CoCl_4^{2-} ion, which is always distorted in its crystalline compounds. The distortion changes the ZFS. Thus for the ion as it occurs in Cs_3CoCl_5 (17), $2D/k = -12.4 \text{ K}$; whereas for CoCl_4^{2-} in Cs_2CoCl_4 , $2D/k = +13.5 \text{ K}$ (2, 14, 18, 19). The relationship between structure

and ZFS for cobalt has been discussed elsewhere (3).

Two other compounds have been studied recently (20), $\text{CoCl}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{CoBr}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$. The ZFS of each of these compounds is again large, but since the data were not measured above 4.2 K, only the sign (negative) but not the magnitude of the ZFS was determined. In any case, the ZFS is much larger than kT at 4.2 K.

The ZFS of cobalt ions has become a topic of study in biochemistry and biophysics. There have been studies of enzymes in which the natural diamagnetic zinc ions have been replaced by paramagnetic cobalt ions. The geometry around the metal is often not well defined, because cobalt may be four-, five- or six-coordinate, and the complex may be distorted as well. The magnetic properties of cobalt are sensitive to changes in its environment, so recent studies have used model compounds to identify and define the coordination environment of the metal.

Makinen and co-workers (21) have worked out an EPR method for determining the ZFS in biological materials and used it to assign the coordination geometry in cobalt-reconstituted enzymes. The method is an indirect one, depending on the temperature dependence of the continuous-wave microwave saturation (the Orbach process). Zero-field splitting values have been determined for a number of materials with this method, even when the ZFS is negative. Assignments of coordination geometry are based on an empirical relation of the magnitude of the ZFS in several compounds; the ZFS has not been determined directly in any of the five-coordinate cobalt compounds. The chemical $[\text{Co}(\text{2-picoline } N\text{-oxide})_5](\text{ClO}_4)_2$, with the uncommon coordination number of five, appears to have a 4A_2 ground state. A ZFS value of 25.3 cm^{-1} (36 K) has been determined by Makinen (21). This is a large value; and it has led to the suggestion that the hydrolysis of esters by carboxypeptidase A requires a five-coordinate metal ion.

A change in the nature of the ground state has been found to alter the nature of the magnetic ordering that the different substances go through (1, 22). The compounds of tetrahedral cobalt that are known to undergo magnetic ordering have two characteristics in common. First, the magnetic exchange is weak, and thus the substances are found to order at temperatures below 1 K. Second, the ZFS values are all relatively large, on the order of 10 to 15 K. That means that the state involved in the

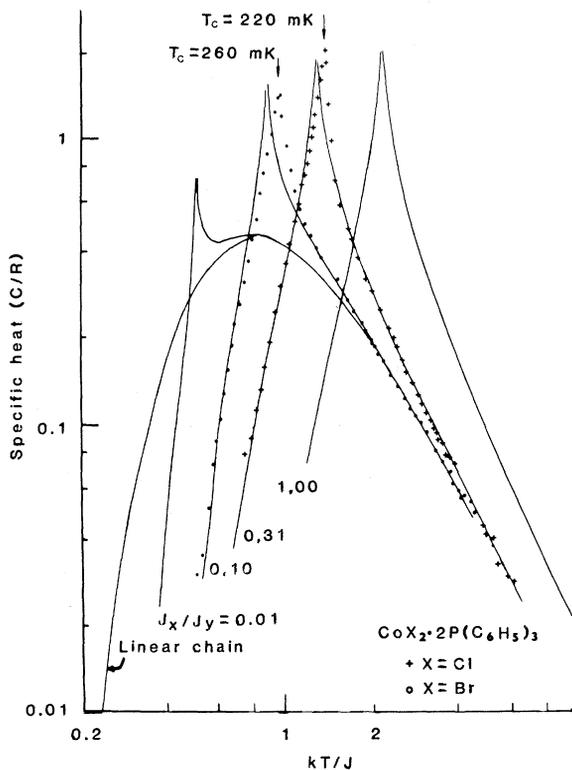


Fig. 4. The measured specific heats of $\text{CoX}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$, $\text{X} = \text{Cl}^-(+)$ and $\text{Br}^-(\circ)$. The interaction constants, J , used in obtaining the relative temperature scales are defined by $|J| = |J_z^{(0)}|$. [From (20); courtesy of the American Chemical Society]

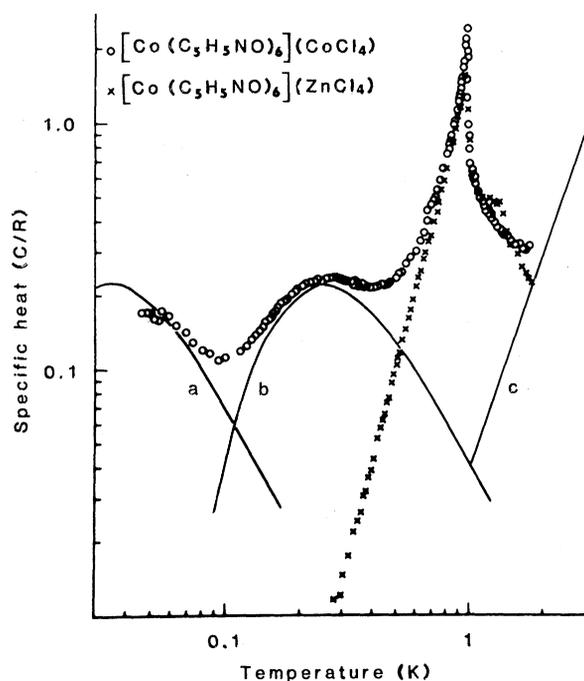


Fig. 5. Specific heat of $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{CoCl}_4)$ (\circ) and $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{ZnCl}_4)$ (\times). Curves a and b are the Schottky curves. Curve c is the estimated lattice contribution. [From (25); courtesy of North-Holland Publishing Company]

ordering is but one doublet of the 4A_2 ground state, and this doublet is relatively isolated from the one of higher energy. If the ZFS value were much smaller than the transition temperature, then the cobalt would order as an ion with spin $S = 3/2$ and would follow the Heisenberg magnetic model. Also, the g values would be nearly isotropic, with values of 2.2 to 2.4. No such example has yet been found.

Because the ground state of Cs_3CoCl_5 is the fairly well isolated $|\pm 3/2\rangle$ doublet, Ising magnetism is to be expected, and the data are consistent with this (17, 23). Ising behavior is also found in $CoX_2 \cdot 2P(C_6H_5)_3$ complexes where $X = Cl^-$ or Br^- . These compounds order, respectively, at 0.21 K and 0.25 K; and both exhibit broad maxima in the susceptibility data from the "easy axis," which is characteristic of compounds with substantial short-range order. (The easy axis is that crystal axis parallel to which the magnetic moments are aligned.) These are layered materials, and there is little magnetic interaction between the layers. That result is illustrated by the susceptibility data in Fig. 3. The susceptibility measured parallel to the principal molecular axis is more than an order of magnitude larger than those measured perpendicular to the principal axis at the transition temperature, which suggests that the Ising model should be applicable here. This hypothesis is confirmed by the successful fitting of not only the magnetic susceptibility data but also of the measured specific heats of both compounds (20) with equations applicable to the Ising model. The data are illustrated in Fig. 4, where the specific heats of both compounds are presented. The solid curves represent the calculated specific heats for rectangular Ising systems having different $J_z^{(x)}/J_z^{(y)}$ values, according to the theory of Onsager, where x and y denote directions in the lattice. Curves for the linear chain and the two-dimensional, quadratic planar, lattice are also illustrated. The ratios $J_z^{(x)}/J_z^{(y)} = 0.31$ (Cl^-) and 0.10 (Br^-) give good fits to the data, except near the critical point. This is due to weak interactions through the third dimension of the crystal in materials that are primarily two dimensional in their nature.

As stated above, the nature of magnetic ordering changes when the $|\pm 1/2\rangle$ state is the ground state. Only one experimental example of this state is

known, and that is found in Cs_2CoCl_4 . The analysis of the magnetic data for this compound was complicated by the substantial short-range ordering this material exhibits. In fact, it is the only experimental example of antiferromagnetic material with spin $S = 1/2$ and properties consistent with the XY and linear-chain models that is available in single-crystal form. Because of the peculiar crystallography of this compound, only the transverse susceptibility can be measured. In order to fit the measured data, Oitmaa and his colleagues first had to calculate the expected theoretical behavior. There was excellent agreement between the theoretical behavior and the experimental data (19). The optimum value of J_z/J_{xy} was found to be 1/4, as was derived from the analysis of the heat capacity data (2).

The $CoCl_4^{2-}$ ion is also found in the salt with the stoichiometry $Co(C_5H_5NO)_3Cl_2$, where C_5H_5NO is pyridine N -oxide. This material should be formulated as $[Co(C_5H_5NO)_6][CoCl_4]$ (24, 25), and it contains two independent magnetic subsystems, that of the octahedral ions and that of the tetrahedral ions. The octahedral subset orders magnetically at 0.95 K, but the tetrahedral ions do not order at all. Actually the internal magnetic field established by the ordered lattice of the octahedral ions resolves the degeneracy of the 4A_2 state and gives rise to Schottky anomalies that are resolved at very low temperatures. This is illustrated in Fig. 5, where it will be observed that $[Co(C_5H_5NO)_6](CoCl_4)$ and $[Co(C_5H_5NO)_6](ZnCl_4)$ order at precisely the same temperature. The replacement of the magnetic $CoCl_4^{2-}$ anion with the isomorphous, nonmagnetic $ZnCl_4^{2-}$ anion has no effect on the long-range ordering of the octahedral ions.

Conclusions

Zero-field splittings are important not only for their intrinsic interest, such as their empirical reflection of the structural environment in a material, but also for the ways in which they control magnetic ordering. A magnetically ordered substance is made up of single ions, and they determine the way that the system as a whole behaves. At this time, one cannot predict in advance nor control the ZFS. Once it is known, however, the nature of the collective behavior of a system can

be predicted. The important part of research in this area has been the preparation of new samples and the exposition of their properties in comparison with theory. For the future, it would be especially useful if more examples of substances which follow the XY model could be found. Finally, small values of the ZFS can be easily determined from alternating-current susceptibility measurements at frequencies smaller than the spin-lattice relaxation rate. Cross relaxation between the doublets is then observed. Such experiments are easily performed (26), but there has been no sustained effort to perform them.

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