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Magnetic Properties of Ammonium, Sodium, and Lithium Pentafluoromanganates(III)

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The magnetic susceptibility of ammonium pentafluoromanganate(III) has been determined in a temperature range of 4.2–300°K. The observed susceptibility *vs.* temperature curve shows a broad maximum at 58°K due to antiferromagnetic interactions within –Mn–F–Mn– chains and an additional sharp peak at 5.8°K attributable to weak ferromagnetic interaction between chains. Sodium and lithium pentafluoromanganates(III) are isostructural with the ammonium salt and show magnetic susceptibility *vs.* temperature curves resembling that of the ammonium salt except that the low-temperature peak is not observable above the liquid helium temperature.

Introduction

Theoretical calculations have been performed for the magnetic susceptibility of one-dimensional lattices.[1–3] The treatment is mathematically simpler and more rigorous than that for two- or three-dimensional lattices. Accordingly, a number of observations and calculations have been carried out on various types of linear magnetism and have given significant results for studying magnetic interactions. In our previous paper,[4] we have reported that dichloro(1,2,4-triazole)copper(II) shows magnetic properties corresponding to one-dimensional Ising spins. The present investigation has been undertaken in order to obtain some information about the magnetic properties of –Mn–F–Mn– linear chains. The X-ray crystal analysis of ammonium pentafluoromanganate(III)[5] has shown that the crystal is orthorhombic, $D_{2h}{}^{16}$-Pnma, that each manganese atom has a distorted coordination octahedron consisting of six fluorine atoms, and that the octahedral groups are linked by sharing their vertices to form an infinite linear chain along the *b* axis. This presents a good example for studying a linear magnetic chain composed of paramagnetic ions having four unpaired electrons. Therefore, we have determined the magnetic susceptibilities of ammonium pentafluoromanganate(III) and related compounds over a temperature range of 4.2–300°K.

Experimental Section

Ammonium pentafluoromanganate(III) was prepared by a method described by Christensen.[6] A solution of ammonium hydrogen fluoride was added in excess to a solution of manganese(III) oxide hydroxide, MnO(OH), in 20% hydrofluoric acid. When the mixed solution was concentrated by gentle heating, red-purple crystals separated. They were recrystallized from a concentrated ammonium hydrogen fluoride solution. Chemical analysis was carried out by the following method. A sample was dissolved in a 3% hydrogen peroxide solution acidified in advance with a few drops of hydrochloric acid. On adding ammonia to the solution, a precipitate was formed. It was heated to 900° and weighed as Mn_3O_4. From the filtrate, calcium fluoride was precipitated by adding a calcium chloride solution in excess. Fluorine was determined by the back-titration of calcium ions with EDTA. *Anal.* Calcd for $(NH_4)_2MnF_5$: Mn, 29.5; F, 51.2. Found: Mn, 29.4; F, 50.5.

Sodium and lithium pentafluoromanganates(III) were synthesized in a similar manner. *Anal.* Calcd for Na_2MnF_5: Mn, 28.1; F, 48.5. Found: Mn, 27.7; F, 48.4. Calcd for Li_2MnF_5: Mn, 33.5; F, 57.9. Found: Mn, 33.0; F, 58.1.

The magnetic susceptibility was determined by the Gouy method and the Faraday method using a magnetic balance described previously.[4]

The molar susceptibility has been corrected for the diamagnetic contribution of all ions involved: NH_4^+, 11.5×10^{-6}; Li^+, 0.6×10^{-6}; Na^+, 5×10^{-6}; Mn^{3+}, 10×10^{-6}; F^-, 11×10^{-6} emu.[7]

Discussion

The curve of susceptibility, χ, *vs.* temperature observed for ammonium pentafluoromanganate(III) exhibits maxima at 58 and 5.8°K, as shown in Figure 1.

In discussing the magnetic properties of this crystal in relation to its structure, the possibility of phase transitions presents a serious problem, because the magnetic measurements cover a wide temperature range, whereas the X-ray analysis was carried out at room temperature. However, the curve in Figure 1 is continuous, suggesting a change in magnetic interactions rather than changes in crystal structure. Therefore, it is assumed that the crystal structure observed at room temperature persists at low temperatures, except for thermal contraction.

The broad maximum at the higher temperature is undoubtedly due to a short-range antiferromagnetic interaction within a –Mn–F–Mn– linear chain. A theoretical equation has been proposed for the susceptibility of a one-dimensional array of Ising spins $S = {}^1/_2$[1]

$$\chi = \frac{Ng^2\beta^2}{4kT}e^{J/kT} \tag{1}$$

Here, N is the Avogadro number, g is the electronic g factor, β is the Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, and J is the ex-

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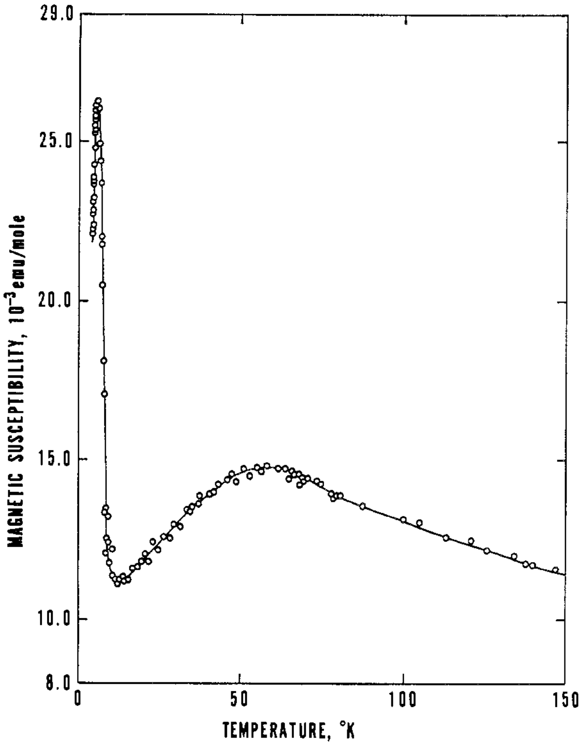

Figure 1.—Temperature dependence of the magnetic susceptibility corrected for diamagnetic contributions of ammonium pentafluoromanganate(III).

change energy. For the total electron spin S of an atom greater than $^1/_2$, no explicit equation is available for the susceptibility of a one-dimensional lattice. Suzuki, *et al.*,[3] have numerically calculated the susceptibility of Ising spins for $S = 1$ and $S = {}^3/_2$. The magnetic susceptibility of an infinite one-dimensional Heisenberg spin lattice has been calculated for $S = {}^1/_2$.[2] However, no calculation has been performed for $S \geq 1$.

Formally, eq 1 can be written as

$$\chi = \frac{Ng^2\beta^2S(S+1)}{3kT}e^{J'/kT} \qquad (2)$$

where J' is a parameter related to the exchange energy. This equation can be derived if it is assumed that a "reduced" spin magnetic moment defined as

$$\mu = \frac{1}{2}\left(\frac{S(S+1)}{3/4}\right)^{1/2} g\beta \qquad (3)$$

takes only two (parallel and antiparallel) orientations. Then one has

$$J' = \frac{S(S+1)}{3/4}J \qquad (4)$$

Accordingly, eq 2 may be used as a reasonable empirical formula. Therefore, log $[(3k/N\beta^2)\chi T]$ was plotted against $1/T$ in Figure 2. The curve is linear above about 80°K. The intercept of the straight line, $g^2S(S+1)$, yields a magnetic moment of 4.76 BM, which is reasonable for a manganese(III) ion having $S = 2$. This suggests that eq 2 is a fairly good expression for $S > {}^1/_2$ as in the case of linear antiferromagnetic coupling in ammonium pentafluoromanganate(III) at high temperature. The slope of the straight line gives the energy J' for the fictitious spins capable of orienting only in two directions. The value of J' is shown in Table I. It has some significance for comparing exchange interaction among different manganese(III) compounds.

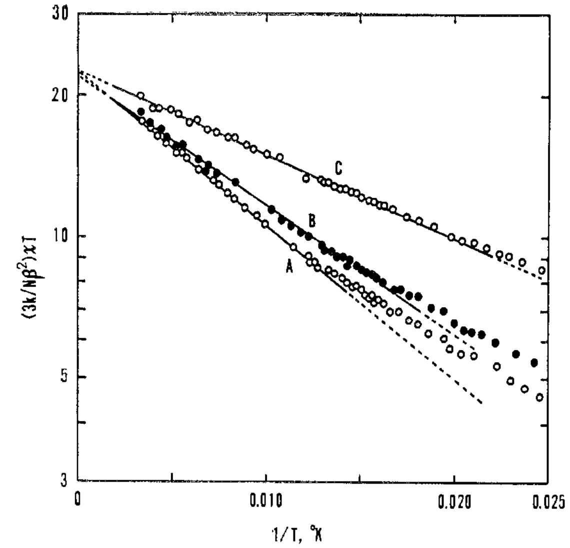

Figure 2.—Linear relation between log $[(3k/N\beta^2)\chi T]$ and $1/T$ for ammonium (A), sodium (B), and lithium (C) pentafluoromanganates(III).

Table I

The Magnetic Susceptibility χ Corrected for Diamagnetic Contributions, the Effective Exchange Energy J', and the Cell Dimensions of Ammonium, Sodium, and Lithium Pentafluoromanganates(III)

Compounds	$10^3\chi$, cgs emu	J'/k, °K	Cell dimensions, Å a	b	c
$(NH_4)_2MnF_5$	7.53 (298°K)	−75.6	6.20	7.94	10.72
Na_2MnF_5	7.93 (296°K)	−63.0	6.08	7.86	9.28
Li_2MnF_5	8.56 (299°K)	−40.8	5.46	7.78	8.81

In the series expansion method,[8] the reciprocal of the reduced susceptibility χ_r is expanded in ascending powers of the reciprocal of the reduced temperature $\theta = kT/|J|$

$$\frac{1}{\chi_r} \equiv \frac{Ng^2\beta^2}{|J|\chi} = \frac{3\theta}{S(S+1)}\sum_{n=0}^{\infty}\frac{b_n}{\theta^n} \qquad (5)$$

The coefficients b_n (n = 0–6) have been calculated by Rushbrooke and Wood[8] for Heisenberg model ferromagnetics. For the antiferromagnetic problem, the corresponding series is obtained by replacing b_n by $(-1)^nb_n$. We have calculated the first few coefficients b_n for the Ising model. For Heisenberg model antiferromagnetics, one has

$$\frac{1}{\chi_r} = \frac{3\theta}{S(S+1)}\left\{1 + \frac{2zS(S+1)}{3\theta} + \frac{2zS(S+1)}{3\theta^2}\left[\frac{2}{3}S(S+1) + \frac{1}{2}\right] + \ldots\right\} \qquad (6)$$

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where z is the number of nearest neighbors. For Ising model antiferromagnetics, the series expansion yields

$$\frac{1}{\chi_r} = \frac{3\theta}{S(S+1)}\left\{1 + \frac{2zS(S+1)}{3\theta} + \frac{2zS(S+1)}{3\theta^2}\left[\frac{2}{5}S(S+1) + \frac{1}{5}\right] + \ldots\right\} \quad (7)$$

The convergence of these series expansions is rather slow near the Néel temperature. However, because the coefficients are exact, the expressions are rigorous provided that the series convergence is confirmed. By use of the numerical value of b_n calculated by Rushbrooke and Wood, it was found that, for Heisenberg model antiferromagnetics, the series expansion of eq 6 gives practically the same value regardless of whether the series is terminated with $n = 6$ or $n = 2$ when $z = 2$ and $\theta > 6$. For the present case, both S and z are equal to 2. By choosing J and g properly, our experimental data can be fitted to the Heisenberg model as well as to the Ising model in the high-temperature region ($\theta > 6$) as shown in Figure 3. The values of J/k thus obtained are shown in Table II along with those calculated from eq 4.

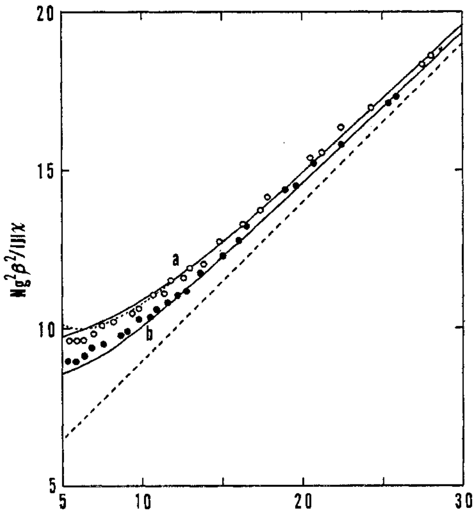

Figure 3.—The inverse reduced susceptibility, $\chi_r^{-1} = Ng^2\beta^2/|J|\chi$, of ammonium pentafluoromanganate(III) plotted against the reduced temperature, $\theta = kT/|J|$, for (a) the Heisenberg model (series terminating with $n = 6$ for the solid curve and $n = 2$ for the dotted curve) and (b) the Ising model ($n = 2$). The broken straight line represents the Curie–Weiss law, which corresponds to the first two terms of eq 6 and 7 ($n = 1$). Observed values are fitted to the Heisenberg model curve and the Ising model curve by proper choice of J and g.

TABLE II

EXCHANGE ENERGY J/k IN DEGREES KELVIN EVALUATED BY VARIOUS METHODS OF CALCULATION[a]

	Series expansion		
Compounds	Heisenberg	Ising	Reduced spin
$(NH_4)_2MnF_5$	−10.6 (1.99)	−11.5 (2.00)	−9.45 (1.94)
Na_2MnF_5	−9.2 (1.97)	−10.2 (1.99)	−7.88 (1.92)
Li_2MnF_5	−5.6 (1.97)	−6.1 (1.98)	−5.10 (1.94)

[a] g values are given in parentheses.

Below about 80°K, the observed points lie above the straight line in Figure 2, indicating that the Ising model based on the reduced spins yields susceptibility data smaller than the observed values. Presumably, this is because spin components perpendicular to the field direction can no longer be ignored at low temperatures as is done in the Ising theory. Although this suggests that the Heisenberg model is adequate,[2] it is difficult to conclude from the series expansion method which model is more appropriate, because the results of calculation by the series expansion are not valid in the limit of $T = 0$°K (see Figure 3). In addition, the effect of three-dimensional magnetic interaction among the chains discussed below is surely present in this temperature range of increasing susceptibility.

Another maximum of susceptibility at low temperature is attributable to a three-dimensional long-range ordering that exists below this temperature owing to interaction between chains. The magnetic behavior below 10°K is distinguished from the paramagnetic increase of the magnetic susceptibility of dichloro-(1,2,4-triazole)copper(II)[4] and other copper(II) compounds having a linear-chain structure[9,10] in that a distinct maximum was observed. The following mechanisms are conceivable for this behavior. At high temperature, the magnetic interaction within the linear chain is dominant, leading to linear antiferromagnetism. However, at very low temperature, the interaction between the resultant or residual moments of linear chains is not negligible. If the residual moments couple ferromagnetically with one another, the susceptibility increases sharply with decreasing temperature, and passes through a maximum at a transition to an antiferromagnetic state. An alternative effect is conceivable. The susceptibility shows a paramagnetic dependence on temperature owing to the presence of the end effect and decreases with decreasing temperature below a transition to an ordered state, because the end effect is not appreciable in the three-dimensional ordered state.

The magnetic susceptibilities of sodium and lithium pentafluoromanganates(III) resemble that of the ammonium salt, as shown in Figure 4, but the second maximum was not observed in the temperature range investigated. However, the lithium salt showed an incipient rise of magnetic susceptibility with decreasing temperature below about 5°K, suggesting the appearance of the second peak at a still lower temperature.

No crystal data have been reported for these two salts. Therefore, we have taken powder patterns by means of a Norelco X-ray diffractometer. The diffraction patterns indicate that these compounds are isostructural with the ammonium salt, suggesting that –Mn–F–Mn– chains are formed in the crystals. Figure 2 shows linear relation between log $[(3k/N\beta^2)\chi T]$ and $1/T$ in the high-temperature region. The g value of 1.93 (1.94 for the ammonium and lithium salts and 1.92

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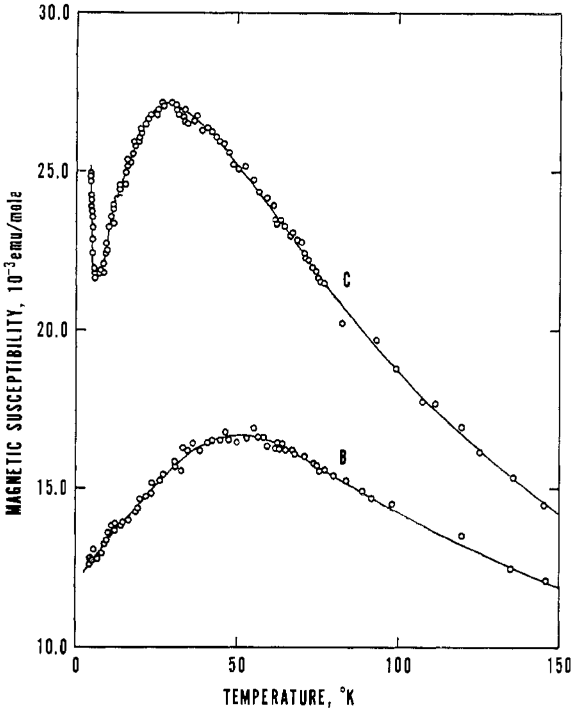

Figure 4.—Temperature dependence of the magnetic susceptibilities corrected for diamagnetic contributions of sodium (B) and lithium (C) pentafluoromanganates(III).

for the sodium salt) as calculated from the intercepts of the three straight lines in Figure 2 is reasonable for a manganese(III) ion having a less than half-filled 3d shell. These facts indicate that the susceptibility can be expressed by eq 2 or that a strong linear antiferromagnetic coupling exists within the chain. The J' values estimated from eq 2 are shown in Table I. The exchange energies evaluated by various methods are given in Table II. The agreement between the data evaluated by different methods is good, especially as regards the relative values of different compounds.

The Mn–Mn distance, which is equal to half the cell dimension along the *b* axis, decreases in the order of the ammonium, sodium, and lithium salts as shown in Table I. Contrary to a simple expectation, the absolute value of J decreases in the same order. This indicates that superexchange interaction depends to a marked extent on the Mn–F–Mn angle rather than the Mn–Mn or Mn–F distance, the direct interaction being of minor importance. The sign of superexchange interaction has been determined from the symmetry relation of atomic orbitals involved.[11] In the case of a d^4–d^4 interaction, the sign and the magnitude of exchange energy depend to a great extent on the path of superexchange interaction for the following reasons. The electronic configuration of a Mn^{3+} ion in its high-spin state is $d\epsilon^3 d_{z^2}$. When Mn–F–Mn is linear, partial σ bonds are formed by the p_z orbital ($p\sigma$ orbital) of fluorine and the d_{z^2} orbital of manganese. Because these orbitals are nonorthogonal or bond forming, antiferromagnetic coupling results between the two manganese ions in accordance to the mechanism of simultaneous partial bonds.[11,12] The d_{xz} orbital of a manganese ion forms a π bond with the p_x orbital of fluorine. The d_{yz} orbital also can form an equivalent bond. The resulting π-contribution to the superexchange should be antiferromagnetic for the same reason as above. With decreasing angle Mn–F–Mn, the antiferromagnetic interactions decrease owing to the decrease in the overlap of orbitals involved. Superexchange interactions due to the higher order perturbations (*e.g.*, d_{xz}–d_{xy} interaction) are ferromagnetic (Anderson mechanism)[13] and are presumed to be less dependent on the Mn–F–Mn angle. In general, antiferromagnetic coupling is dominant when the interaction takes place between two cations through an anion with a cation–anion–cation angle of 180°, whereas ferromagnetic interaction is favored for 90° cation–anion–cation interaction.[11] At a critical angle between these extreme cases, the antiferromagnetic coupling changes into ferromagnetic interaction. The Mn–F–Mn bond angle is 139° in the ammonium salt. Presumably, it is smaller in the sodium and lithium salts because of reduction in the cell dimension along the *b* axis. Therefore, it is reasonable to expect that the extent of antiferromagnetic exchange interaction within a chain increases in the increasing order of the cell dimension along the *b* axis.

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