Two-dimensional Antiferromagnetism and Weak Ferromagnetism in Some Anilinium Salts of the Types A_2MnCl_4 and A_2FeCl_4

By **Antony B. Blake,*** Department of Chemistry, University of Hull, Hull HU6 7RX
William E. Hatfield, Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514, U.S.A.

Magnetic susceptibility measurements have been made between 4.2 and 160 K on the powdered salts $(4\text{-}XC_6H_4NH_3)_2MnCl_4$ (X = F, Cl, Br, or Bu^n). These compounds have layer structures of the K_2NiF_4 type, with inter-layer spacings of 15.8, 16.6, 18.8, and 23.5 Å, respectively. Broad susceptibility maxima are observed at *ca.* 70 K, and can be fitted on the assumption of a two-dimensional exchange interaction of Heisenberg ($-2J\mathbf{S}_i \cdot \mathbf{S}_j$) form, with $-J/k$ = 4.25, 4.50, 4.00, and 3.75 (±0.1) K, respectively. All four compounds show weak ferromagnetism below the Néel temperature (T_N *ca.* 40 K), which is attributed to spin canting in the antiferromagnetically ordered state. The transition temperature is practically independent of the layer spacing. Measurements on a single crystal of the 4-chloro-compound indicate a canting angle of *ca.* 0.06°, and show that the resulting magnetisation lies in the layer plane. Powder susceptibility measurements on $(4\text{-}ClC_6H_4NH_3)_2FeCl_4$ indicate that this compound is also a two-dimensional antiferromagnet, with $-J/k = 10.7 \pm 0.5$ K (T_N *ca.* 87 K) and a canting angle *ca.* 0.8° in the ordered state. Below T_N the magnetic behaviour shows unusual dependence on the thermal and magnetic history of the sample, possibly due to a nearly degenerate magnetostrictive distortion.

SALTS of the type A_2MCl_4, where A is a univalent cation and M is a bivalent metal of the first transition series, generally crystallise with either discrete tetrahedral $[MCl_4]^{2-}$ anions, or infinite two-dimensional layers of corner-sharing octahedra, $[(MCl_2Cl_{4/2})_n]^{2n-}$, separated by layers of cations.[1] The layer structure, which is analogous to that of K_2NiF_4, is favoured by primary ammonium cations, and a number of compounds of this type with M = Cr, Mn, Fe, or Cu have been studied in recent years.[2-10] These compounds, like the layer fluorides, are of magnetic interest because they approximate to systems having magnetic interactions localised in two dimensions.[11,12] Thus, the manganese compounds all show a broad maximum in the susceptibility at *ca.* 80 K, which is typical of a two-dimensional antiferromagnetic interaction with spin correlation but no long-range order. If the exchange interaction is of the isotropic Heisenberg ($-2J\mathbf{S}_i \cdot \mathbf{S}_j$) type, as would be expected in first order for Mn^{2+}, and the layers are magnetically isolated, long-range order is known to be impossible above absolute zero temperature.[12,13] In practice these compounds invariably show a transition to a three-dimensionally ordered magnetic state at a relatively high critical temperature (*ca.* 45 K for the manganese salts), as a result either of interlayer interactions or of anisotropy in the exchange or single-ion Hamiltonian.[4-7,11,12] The iron compounds have been less thoroughly studied, but they seem to show similar behaviour at somewhat higher temperatures.[9]

In this paper we report the results of a magnetic investigation of the salts $(4\text{-}RC_6H_4NH_3)_2MnCl_4$ (R = F, Cl, Br, or Bu^n), in which the interlayer separation varies from 15.8 to 23.5 Å, and of $(4\text{-}ClC_6H_4NH_3)_2FeCl_4$ which was found to display unusual behaviour in the ordered state.

EXPERIMENTAL

Materials.—The salts $MnCl_2{\cdot}4H_2O$ and $FeCl_2{\cdot}4H_2O$ were AnalaR grade. The substituted anilines were reagent grade, and were converted into anilinium chlorides by crystallisation from 6 mol dm^{-3} HCl after boiling with active charcoal.

$(4\text{-}RC_6H_4NH_3)_2MnCl_4$ (R = F, Cl, Br, *or* Bu^n).—A filtered solution of $MnCl_2{\cdot}4H_2O$ (0.01 mol) in hot absolute ethanol (5 cm^3) was mixed, with stirring, with a hot, almost saturated solution of the anilinium chloride (0.02 mol) in ethanol, and the mixture was allowed to stand for 0.5—2 h. The products crystallised as pale salmon-pink square plates, which were filtered off and washed with anhydrous diethyl ether containing 10% of ethanol, then with ether alone. (The ether must be free from peroxide.) Yield 35—55%. The products were recrystallised from absolute ethanol. Single crystals (R = Cl) were grown by slow evaporation of an ethanol solution. Analytical results, in the form (R)% Found (% Calc.), were as follows: (F) C 34.05 (34.25), H 3.30 (3.35), Cl 33.8 (33.7), Mn 13.1 (13.05), N 6.60 (6.65); (Cl) C 31.75 (31.75), H, 3.10 (3.10), ionisable Cl 31.4 (31.3), Mn 12.15 (12.1), N 6.15 (6.15); (Br) C 26.7 (26.55), H, 2.75 (2.60), Cl 26.3 (26.1), Mn 10.2 (10.15), N 5.00 (5.15); (C_4H_9) C 48.45 (48.3), H 6.50 (6.50), Mn 11.1 (11.05), N 5.80 (5.65).

Compounds with R = H, I, and OCH_3 were prepared similarly, but the samples deteriorated, with formation of paramagnetic impurities, before magnetic measurements were complete. Attempts to prepare compounds with R = CH_3, C_2H_5, OC_2H_5, and NO_2 by the above method did not yield the desired products.

$(4\text{-}ClC_6H_4NH_3)_2FeCl_4$.—All operations were performed in a dry nitrogen-filled glove-box and the ethanol used as solvent was refluxed under nitrogen. Hot solutions of $FeCl_2{\cdot}4H_2O$ (0.02 mol) and of the anilinium chloride (0.04 mol) in ethanol (25 cm^3 each) were mixed, and the resulting solution was evaporated to *ca.* 15 cm^3 and allowed to cool. The almost colourless (faintly greenish-grey) leaflets were filtered off, washed well with anhydrous peroxide-free diethyl ether, and sucked dry (Found: C, 31.8; H, 3.05; N, 6.35. Calc.: C, 31.7; H, 3.10; N, 6.15%).

Analysis.—The C, H, N, and Cl microanalysis was by Galbraith Laboratories. Ionisable Cl was determined by the Mohr method, and Mn by ethylenediaminetetra-acetate titration using Fisher-certified manganese powder as standard.

Apparatus.—Magnetic susceptibility measurements were made on finely powdered samples or single crystals between

4.2 and 150 K on a model 155 vibrating-sample magnetometer (Princeton Applied Research Corporation), as described previously.[14]

RESULTS

Structures of the Compounds.—The K_2NiF_4 layer structure has been established in $(CH_3CH_2CH_2NH_3)_2MnCl_4$: although the unit cell is orthorhombic (a = 7.29, b = 7.51, c = 29.94 Å), the Mn atoms form a nearly tetragonal face-centred array, layers of corner-sharing $MnCl_6$ octahedra perpendicular to the c axis being separated by double layers of propylammonium ions, with the NH_3 groups hydrogen-bonded to Cl atoms.[15] The anilinium salts are assumed to have a similar structure: their crystals closely resemble those of the tetragonal methylammonium salt, and their X-ray powder photographs are similar to those of the latter compound,[3] although with evident deviations from exactly tetragonal symmetry. All show a strong line indexed as 004, from which the interlayer spacings $c/2$ were determined (see Table). Precession photographs of the 4-chloroanilinium salt show a primitive orthorhombic unit cell, Laue symmetry *mmm*, with a = 7.21, b = 7.28, c = 33.2 Å, and a two-fold screw axis parallel to c. The crystal faces developed are (001), (110), and ($\bar{1}10$). The corresponding iron compound gave an almost identical powder photograph.

Magnetic Results and Evaluation of Exchange Parameters.—*Manganese compounds.* The molar susceptibilities were corrected for diamagnetism by use of Pascal constants.[16] The corrected data are available as Supplementary Publication No. SUP 22622 (16 pp.).* Figure 1 shows the susceptibilities of powdered samples of the four compounds at $\mu_0H = 1$ T. † The broad maximum at 70—80 K is typical of two-dimensional antiferromagnetism, which we assume to be of Heisenberg form. For a square, two-dimensional magnetic lattice with nearest-neighbour interaction $-2J\mathbf{S}_i \cdot \mathbf{S}_j$ the high-temperature susceptibility has been calculated by Rushbrooke and Wood [17] in the form of the series expansions (1), where $\chi_0 = Ng^2\mu_0\mu_B{}^2S(S+1)/3kT$ and $\theta = kT/|J|$. These authors give polynomial expressions for b_n (n = 1—6) in terms of S. An expression

$$\chi = \chi_0 \sum_{n=0}^{\infty} a_n\theta^{-n} = \chi_0\left(\sum_{n=0}^{\infty} b_n\theta^{-n}\right) \qquad (1)$$

for a_7 has also been given,[18] from which we have obtained the value of b_7 by inverting the second of equations (1), adding the a_7 term, and inverting again. The coefficients b_n for $S = \frac{5}{2}$ have the values 1, 23.333 33, 147.777 8, 405.481 5, 8 171.312, 64 967.81, 158 110.0, and 461 192.6 for

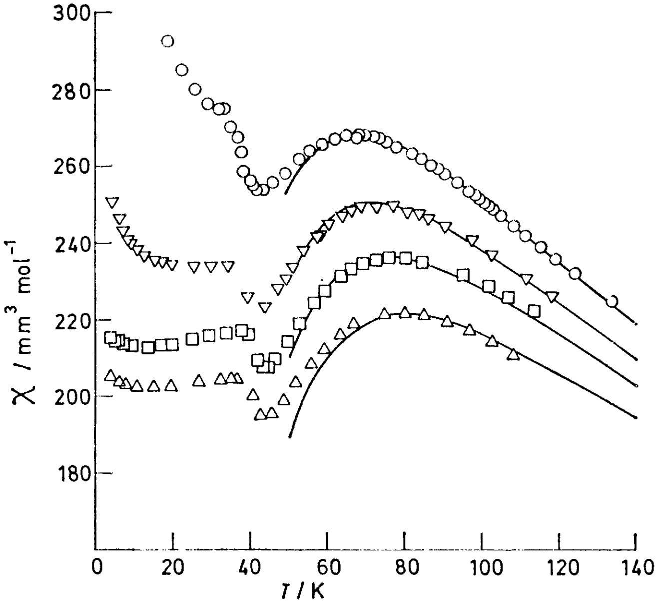

FIGURE 1 Magnetic susceptibilities of $(4\text{-}XC_6H_4NH_3)_2MnCl_4$ in powder form at μ_0H = 1.0 T, with X = F (□), Cl (△), Br (▽), or Bu^n (○)

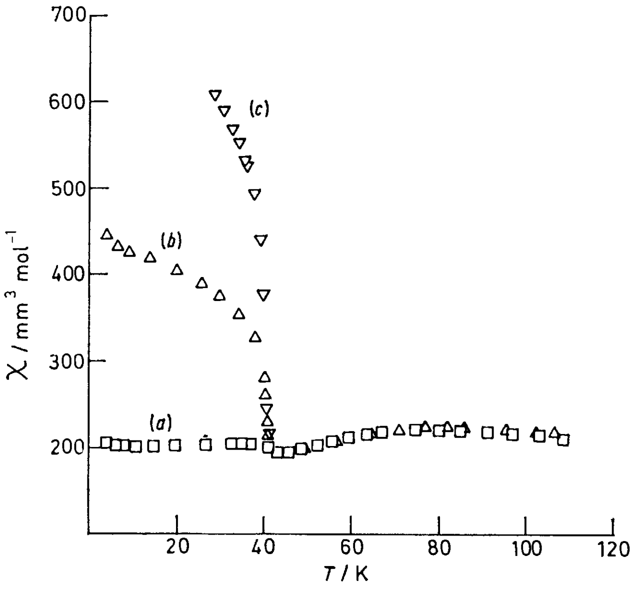

FIGURE 2 Field dependence of the average susceptibility of $(4\text{-}ClC_6H_4NH_3)_2MnCl_4$. Values of μ_0H are (a) 1.0, (b) 0.1, and (c) 0.05 T

Layer spacings and magnetic properties of some A_2MnCl_4 and A_2FeCl_4 salts

	$\frac{1}{2}c$/Å	$-Jk^{-1}$/K	g	T_N/K	Ref.
Rb_2MnCl_4	8.1	6.2 ±0.2		57	12, 27
Cs_2MnCl_4	8.5	5.0 ±0.2		52	12, 27
$[NH_3(CH_2)_3NH_3]MnCl_4$	9.5	4.6 ±0.2	2.00	43.6	7, 8
$(CH_3NH_3)_2MnCl_4$	9.7	4.6 ±0.2		45	3—6
$(4\text{-}FC_6H_4NH_3)_2MnCl_4$	15.8	4.25 ±0.1	1.96	40.4	This work
$(4\text{-}ClC_6H_4NH_3)_2MnCl_4$	16.6	4.5 ±0.1	1.95	39.5	This work
$(4\text{-}BrC_6H_4NH_3)_2MnCl_4$	18.8	4.0 ±0.1	1.96	38	This work
$(4\text{-}Bu^nC_6H_4NH_3)_2MnCl_4$	23.5	3.75 ±0.1	1.98	38	This work
$(CH_3NH_3)_2FeCl_4$				95	9
$(C_3H_7NH_3)_2FeCl_4$				90	9*a*
$(4\text{-}ClC_6H_4NH_3)_2FeCl_4$	16.6	10.7 ±0.5	2.15	87	This work
$(C_6H_5CH_2NH_3)_2FeCl_4$				72	9*a*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

† $\mu_0 = 4\pi \times 10^{-7}$ T m A^{-1} (1 T = 10^4 G). Note that in this paper susceptibility always means M/H, rather than $\partial M/\partial H$, where M is the molar magnetisation and H is the magnetic field strength.

$n = 0 - 7$, respectively. {They are related to the constants c_n, defined by Lines,[19] by $c_n = 3b_n[2S(S+1)]^{-n}$.} We have fitted equation (1) to the four sets of data above 60 K by the method of least squares with g and J as parameters. The calculated curves (Figure 1) fit the data well in the region where the expansion is expected to be valid.

Below *ca.* 40 K, weak ferromagnetism appears, causing the susceptibility to increase sharply and become field-dependent (Figure 2). (At the highest field strength, the susceptibility displays a maximum just below the transition temperature, especially in the F and Cl compounds, but this is absent at lower fields.) The temperature at which the derivative of the susceptibility with respect to temperature is a maximum, which we assume to be close to the critical temperature T_N for the onset of long-range antiferromagnetic order, is given in the Table. Measurements on a single crystal (*ca.* 5 × 5 × 1 mm) of the 4-chloro-compound showed that the weak ferromagnetism is highly anisotropic, the magnetisation measured at 4.2 K with $\mu_0H = 0.05$ T perpendicular to the layer plane being only about one fifth of that measured with the field parallel to the layer plane. Extrapolation to zero field of the in-plane crystal magnetisation at 4.2 K gives a net moment per Mn^{2+} ion of *ca.* 0.005 B.M.* in the ordered state.

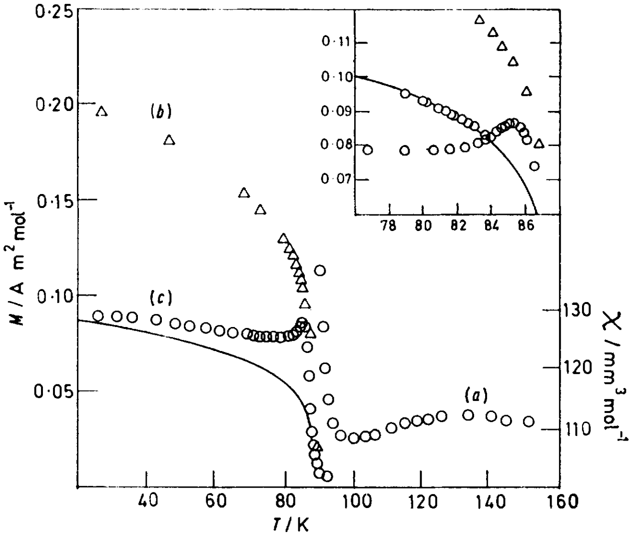

FIGURE 3 Magnetic susceptibility and magnetisation of $(4\text{-}ClC_6H_4NH_3)_2FeCl_4$ in powder form. (*a*) Susceptibility at $\mu_0H = 1.0$ T. (*b*) Magnetisation at 0.05 T with sample temperature decreasing. (*c*) Magnetisation at 0.05 T of a sample previously cooled from above 100 K in zero field, with temperature increasing; the solid curve represents a fit to data (*b*) scaled by 0.43. Inset: as in (*c*), but at *ca.* 84 K the temperature was progressively decreased to *ca.* 79 K and then increased again; the solid curve represents a fit to data (*b*) scaled by 0.72

$(4\text{-}ClC_6H_4NH_3)_2FeCl_4$. The results of powder susceptibility measurements at 1 T are shown in Figure 3, curve (*a*). We have not attempted curve-fitting of the high-temperature data, but from the approximate co-ordinates χ_m, T_m of

$$\chi_m|J|/Ng^2\mu_0\mu_B^2 = 0.054\,7 \pm 0.000\,1 \qquad (2a)$$

$$kT_m/|J|S(S+1) = 2.07 \pm 0.01 \qquad (2b)$$

the broad maximum, and the relations (2) established by de Jongh [20] for the planar quadratic Heisenberg antiferromagnet with $S = 2$, we estimate the values of J and g given in the Table.

The onset of long-range three-dimensional order, accompanied by weak ferromagnetism, occurs at 87 K, and below this temperature the magnetic behaviour depends on the thermal and magnetic history of the sample, as shown in Figure 3, curves (*b*) and (*c*). When the magnetisation at 0.05 T was measured with the temperature decreasing from above T_N to 4.2 K the results followed curve (*b*). However, when the sample was first cooled from above T_N to 4.2 K in zero applied field and the magnetisation at 0.05 T was then measured with the temperature increasing, curve (*c*) was obtained. Similar results were obtained at $\mu_0H = 10^{-3}$ T, except that at this field strength the small maximum at 86 K in curve (*c*) was absent. At 10^{-3} T the average effective magnetic moment per Fe^{2+} ion (extrapolated to 0 K) was *ca.* 0.013 B.M. for a sample cooled in zero field and 0.028 B.M. for the same sample cooled in the field, a ratio of 0.48 : 1, while at 0.05 T the corresponding values were 0.016 and 0.037 B.M. (0.43 : 1).

Even more striking was the behaviour of a sample cooled in zero field when, in the course of susceptibility measurements at 0.05 T with the temperature increasing, the temperature was reduced by a few degrees just below T_N and then increased again (Figure 3, inset). During this thermal detour the magnetisation followed a curve similar to curve (*b*) in both directions, returning exactly to the original curve and then continuing as before. A possible interpretation of this behaviour (which was quite reproducible) will be offered presently.

DISCUSSION

The J/k values of the four manganese compounds, which are determined by the experimental data to within *ca.* ±0.1 K for the model assumed, are listed in the Table, together with those of some related compounds. The range of values presumably reflects variations in the Mn–Cl–Mn bond lengths (and angles), as discussed recently by de Jongh and Block.[21] An additional possible source of variation is the deviation of most of the organic salts from exactly tetragonal crystal symmetry.

In the case of the chloroanilinium salts we can compare the strength of superexchange in the $[(MCl_2Cl_{4/2})_n]^{2n-}$ layers for M = Mn and Fe.† In comparing the observed values $J/k = -4.50 \pm 0.1$ for Mn and -10.7 ± 0.5 K for Fe we note that the parameter J is in effect an *average* of all electron-pair exchange or superexchange contributions connecting a pair of neighbouring metal ions, and we must multiply J by n^2 (or, equivalently, by $4S^2$), where n is the number of unpaired electrons on the ion, in order to compare the sums of these contributions in the two cases. We find $(4S^2J)_{Fe}/(4S^2J)_{Mn} = 1.5 \pm 0.1$, which is close to the corresponding ratios for $BaFeF_4$ and

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m².

† Some caution is necessary because the anisotropy expected for Fe^{2+} makes the assumption of a Heisenberg interaction slightly questionable. However, in the cases of Rb_2FeF_4 and $BaFeF_4$ there is evidence that the Heisenberg model provides a more accurate description than the Ising for the purpose of estimating J/k from the high-temperature data.[22] The uncertainty of 0.5 K that we assign to the value of J/k for $(4\text{-}ClC_6H_4NH_3)_2FeCl_4$ includes the limitations of equation (2a) and the uncertainty in the location of χ_m and T_m but does not include any allowance for inaccuracy of the theoretical model.

$BaMnF_4$ ($-J/k$ *ca.* 6.4 and 2.75 K, respectively [22]) and for FeO and MnO ($-J/k$ *ca.* 7.75 and 3.32 K, respectively [23]). It is also close to the ratio 1.56 : 1 calculated theoretically for the oxides by Nesbet [24] on the assumption that only the e_g electrons contribute to J (*via* the oxygen p orbital). The ratio observed in the layer fluorides and chlorides thus seems to be consistent with M–X–M superexchange by a σ pathway involving only the metal e_g electrons. This is in agreement with calculations on the fluorides A_2MF_4 (A = K, Rb, or Cs; M = Mn, Co, or Ni) by de Jongh and Block,[21] who were able to reproduce the observed ratios of J values using a simple three-centre, four-electron, superexchange model.

At *ca.* 40 K the anilinium tetrachloromanganates undergo a transition to long-range order. Although at short separations the critical temperature decreases somewhat with increasing interlayer separation, it becomes practically independent of the spacing when the latter exceeds *ca.* 15 Å, in accord with the accepted view that anisotropy in the two-dimensional Hamiltonian, rather than dipolar coupling or interlayer superexchange, is primarily responsible for the stability of the ordered state.[11,12]

Below the critical temperature we find that the anilinium compounds behave in moderate or weak magnetic fields as highly anisotropic, weak ferromagnets. The behaviour is similar to that reported for $(NH_3CH_2CH_2CH_2NH_3)MnCl_4$,[7] and, as in that case, we attribute it to spin canting in the antiferromagnetic state. The single-crystal measurements on $(4\text{-}ClC_6H_4NH_3)_2MnCl_4$ indicate that the resulting moment is directed in the layer plane, the preferred antiferromagnetic spin direction presumably being perpendicular to the layers as in other compounds of the types A_2MnF_4 and A_2MnCl_4.[3,6-8,25-27] On the basis of a simple two-sublattice structure, like that found in K_2NiF_4 and $(CD_3ND_3)_2MnCl_4$,[4,26] the small zero-field moment of *ca.* 0.005 B.M. per Mn^{2+} ion implies a canting angle of *ca.* 0.06°. For fields with $\mu_0H \leqslant 0.1$ T the resulting spontaneous magnetisation dominates the average susceptibility, but at 1 T it is small compared with the antiferromagnetic susceptibility, merely giving rise to a shoulder just below T_N, as in Figure 1. The slight peak which appears at high field strengths can probably be attributed to magnetically induced ordering: a sharp increase in the perpendicular (in-layer) component of the differential susceptibility near T_N is predicted to arise from this effect in weak ferromagnets with single-ion anisotropy, and has been observed in several such compounds.[5,9,28,29] At still lower temperatures the susceptibility increases again, possibly owing to the presence of a paramagnetic impurity or to surface effects; this increase was absent from the single-crystal data.

The low-temperature behaviour of $(4\text{-}ClC_6H_4NH_3)_2FeCl_4$ is broadly similar to that of the manganese compounds, and can likewise be accounted for in terms of canted-spin antiferromagnetism. There are, however, some significant differences. The spontaneous magnetisation in the iron compound is considerably greater, and on the basis of similar assumptions would imply a canting angle of *ca.* 0.8°. Moreover, the magnetisation of a powdered sample, measured at 4.2 K in the direction of a small applied field, was found to be approximately twice as great when the sample had been cooled from $T > T_N$ in the field as when it had been cooled in zero field.

A clue to the explanation of the latter observation can be found in the properties of Rb_2FeF_4. In this compound, and also in $(CH_3NH_3)_2FeCl_4$, it has been established that the preferred spin direction in the ordered state is within the layer planes (unlike that in the manganese compounds).[9,26] In Rb_2FeF_4 the spins lie along an axis in the layer plane, and there is no evidence of spin canting.[26] However, Mössbauer studies show that the transition to long-range order is accompanied by a small crystallographic distortion within the layer plane, which lowers the tetragonal symmetry of the crystal, and optical-rotation studies have revealed the presence of optically active domains with mutually perpendicular distortions when viewed along the c axis below T_N.[30] Since it increases with increasing sublattice magnetisation, this distortion seems to be at least partly magnetostrictive in origin.

We suggest that a similar situation exists in $(4\text{-}ClC_6H_4NH_3)_2FeCl_4$, but with the additional complication of a non-collinear spin arrangement in the ordered state. There are two ways in which this could account for behaviour like that illustrated in Figure 3. (*i*) It may be that, for reasons of crystallographic or magnetic symmetry, only one of the two mutually perpendicular distortions permits the spins to be canted. Provided the energy minima for the two modes of distortion are still approximately equal, a crystal cooled through T_N in the absence of an external field would consist of roughly equal volumes of four types of antiferromagnetic domains, of which two would have a net internal magnetisation. The alignment that allowed canting would, however, be favoured energetically by an external field, so that a crystal cooled through the ordering temperature in the presence of a field would consist largely of weakly ferromagnetic domains with distortions in the same crystallographic direction. The magnetisation induced in a powdered sample by a small field would then be about twice as great in the second case as in the first. (The picture is complicated somewhat by the fact that with such weak ferromagnetism the optimum domain size may well be larger than the individual particles in the powdered sample.)

Alternatively, (*ii*) it may be that both directions of distortion permit a non-collinear spin arrangement (so that a sample cooled in zero field would contain four types of weakly ferromagnetic domains), but that the internal strain and magnetostrictive energy associated with the distortion strongly inhibit the movement of 90° domain walls. Application of a magnetic field at low temperatures would then result in only such magnetisation as could be achieved (by 180°-wall movement) without significantly changing the relative volumes having the two types of distortions. On the other hand, cooling from above T_N in the presence of a field would result in a sample in which the distortion direction in each particle was predominantly that which placed the magnetisation vector nearest to the field direction. Assuming again that the two distortions are approximately equivalent energetically, we conclude that the magnetisation in the field direction in the second case would be between $2^{\frac{1}{2}}$ and 2 times greater (depending on field strength and coercivity effects) than that in the first.

A distinction between the above alternative interpretations, which are admittedly somewhat speculative at present, is not possible without further experimental work (*e.g.* Mössbauer spectroscopy, single-crystal magnetic experiments, or low-temperature *X*-ray analysis). They have in common, however, the idea of two types of domains, one capable of becoming magnetised in the direction of an applied field, the other not, with conversion from one into the other being favoured by an external field but inhibited by a crystalline energy barrier. We believe that this general picture can also account for the behaviour illustrated in the inset to Figure **3**. We note first that the magnetisation-temperature curve of a sample cooled in zero field, measured with the temperature increasing, ought to have the same shape (although only about half the vertical amplitude) as the curve measured with temperature decreasing from above T_N, provided that the ratios of the volumes of the two types of domains did not change with temperature. It is reasonable to suppose that, because of the barrier imposed by magnetostrictive distortion, these domains would not readily be interconverted as long as long-range order persisted. However, such order is perfect only at 0 K; the appearance of localised regions of disorder as the temperature approached T_N, and the accompanying relaxation of magnetostrictive forces, might well permit some growth of the magnetically favourable domains at the expense of the others, by rotation of the axis of distortion. Being driven by the applied field, this process would occur only to a small extent in very weak fields, and then only near T_N, but at moderate field strengths we should expect it to become evident at a lower temperature, and the extent of conversion to increase sharply just below T_N, causing the sample moment to rise to a maximum before its inevitable collapse at T_N. The solid line below (*c*) in Figure **3** is a curve fitted to the data points (*b*) and scaled by the factor 0.43 [so as to coincide at 0 K with an extrapolation of data (*c*) to absolute zero], and the progressive deviation of points (*c*) from this line can be regarded as measuring the growth of domains with a magnetically favourable direction of distortion. Note also that if, at some point a little below T_N, the temperature were reduced by a few degrees and then increased again, we should expect a portion of the complete $M(T)$ curve, scaled by the proportion of magnetically favourable phase then present, to be traced out in both directions, since no further domain conversion should take place during such a detour. This is in agreement with our observations: the 'detour' points in Figure **3** (inset) lie almost exactly on such a curve, the scaling factor indicating that at the temperature in question *ca.* 72% of the sample consisted of the magtically favourable phase.

Thus, the behaviour of this compound below its ordering temperature, which at first sight appeared rather bizarre, is seen, if our interpretations are on the right lines, to arise by conventional mechanisms from a particular combination of crystal symmetry and magnetic anisotropy occurring in a layer antiferromagnet. We may anticipate that similar behaviour will be found in other members of the A_2FeCl_4 series.

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