Inorg. Chem. **1996,** *35,* 2853−2857

Magnetic Properties of $(NH_4)_2FeF_5 \cdot H_2O$: Influence of a Structural Phase Transformation and Relevance of Ambient Temperature Structure Determinations to the Interpretation of Low Temperature Magnetic Behavior

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Received January 10, 1996⊗

Low temperature magnetic properties of $(NH_4)_2FeF_5 \cdot H_2O$ have been investigated via iron-57 Mössbauer spectroscopy and ac susceptibility measurements. The high temperature ac susceptibility data can be fitted to a Curie−Weiss law with $C = 4.22 \pm 0.05$ emu K mol^{-1} and $\Theta = -3.9 \pm 0.5$ K while the fit of the low temperature data to a Heisenberg linear-chain model yields $g = 1.97 \pm 0.02$ and an intrachain constant $J/k_B = -0.40 \pm 0.02$ K. At lower temperatures $(NH_4)_2FeF_5 \cdot H_2O$ exhibits a crossover to three dimensional magnetic ordering with $T_c = 2.2 \pm 0.05$ K and 1.61 ± 0.05 K from Mössbauer spectroscopy and ac susceptibility, respectively. Differential scanning calorimetry measurements suggest a first-order structural phase transition centered at $T_s = 139 \pm 1$ K on heating and $T_s = 125 \pm 1$ K on cooling for $(NH_4)_2FeF_5 \cdot H_2O$. No such transformation is suggested by scanning calorimetry studies of the corresponding K^+, Rb^+ and Cs^+ analogues. The limiting internal hyperfine field, H_n(0 K), is 45 T, indicating some 25% zero point spin reduction consistent with significant 1-d magnetic behavior. All the experiments reported here have been performed following varied and careful thermal treatments. A particularly interesting result is the observation of a persistent rapidly relaxing fraction that the Mössbauer spectra of $(NH_4)_2FeF_5 \cdot H_2O$ clearly exhibit below T_c but which is not seen in previous studies of the K^+, Rb^+, and Cs^+ compounds. A probable explanation for this is the loss of magnetic equivalence of the Fe^{3+} sites as a result of the structural phase transition. This behavior further calls into question the still common practice of interpretation of low temperature magnetic phenomena largely on the basis of ambient temperature structure determinations.

Introduction

Previous studies of the rich variety of magnetic behavior of high-spin Fe^{3+} complex fluorides with isolated $[FeF_6]^{3-}$ and $[FeF_5 \cdot H_2O]^{2-}$ polyhedra include $K_2[FeF_5 \cdot H_2O]$,[1,2] a 3d antiferromagnet with $T_c \sim 0.85$ K; β-Li_3FeF_6,[3] a 3d ferromagnet with $T_c \sim 1.1$ K; $[Cr(NH_3)_6][FeF_6]$,[3] a 3d ferrimagnet with $T_c \sim 0.6$ K; and $[Co(NH_3)_6][FeF_6]$, $Na_3[FeF_6]$, and $(NH_4)_3[FeF_6]$[3] all rapidely relaxing paramagnets to as low as ∼0.30 K. The magnetic exchange interactions between the $[FeF_6]^{3-}$ or $[FeF_5 \cdot H_2O]^{2-}$ octahedra of these systems can occur via hydrogen bonding and/or close $F^- \cdots F^-$ contacts. There are no formal covalent Fe···F···Fe bridging superexchange pathways.

The linear chain arrangement exhibited by the nearest neighbor Fe^{3+} ions in the $AFeF_5 \cdot H_2O$ (A = K,NH$_4$,Rb,Cs) series,[4−7] clearly determines the 1-d magnetic behavior of these compounds. A crossover to long range magnetic ordering occurs at lower temperatures due to the enhancement of the magnetic interactions between adjacent chains as the temperature is decreased. The K, Rb, and Cs derivatives have been described as antiferromagnetics below $T_c = 0.85$, 4.0 and 2.7 K, respectively.[1,2,8] A preliminary Mössbauer study indicated that $(NH_4)_2FeF_5 \cdot H_2O$ remains paramagnetic to 4.2 K.[5] The behavior of this compound is pontentially complicated due to the presence of the NH_4^+ ion which is well-known to undergo a variety of structural phase transformations.

We report here on the magnetic properties of $(NH_4)_2FeF_5 \cdot H_2O$ studied via Mössbauer spectroscopy and ac susceptibility with both conventional and SQUID detection. A structural phase transition is indicated by DSC experiments for $(NH_4)_2FeF_5 \cdot H_2O$ but is absent for the corresponding K^+, Rb^+, and Cs^+ compounds. The persistence of a rapidly relaxing phase below T_c, detected by Mössbauer spectroscopy, is also discussed.

Results

Differential Scanning Calorimetry. In order to detect the existence of any structural phase transitions as a function of temperature, DSC measurements have been performed at different cooling and heating rates: 2, 5, 10, and 25°/min. Figure 1a shows the experimental results on heating $(NH_4)_2FeF_5 \cdot H_2O$ at 5°/min. In all cases, a maximum in the heat flow is detected, suggesting the occurrence of a structural phase transition. The temperature at which the maximum of the peak

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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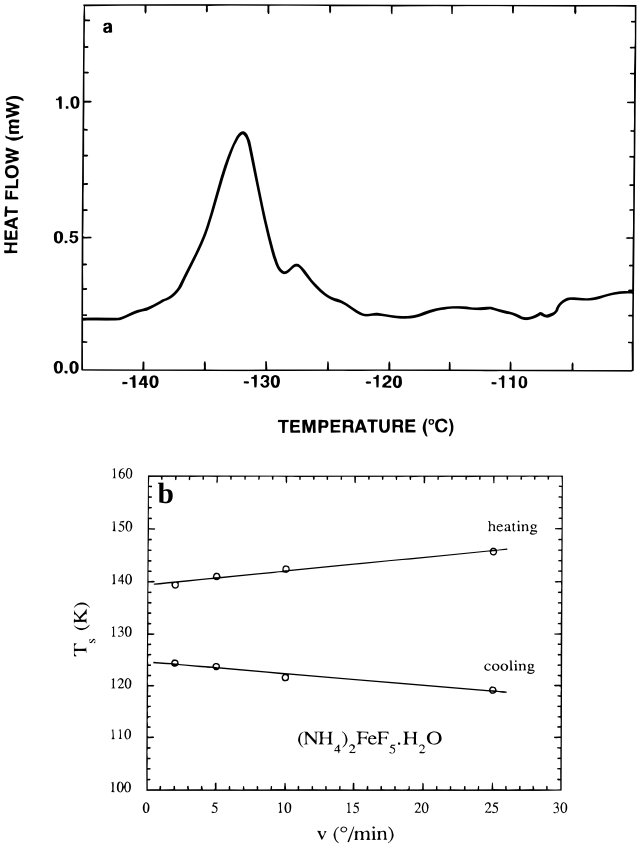

Figure 1. (a) Differential scanning calorimetry measurements performed on $(NH_4)_2FeF_5\cdot H_2O$ heating at 5°/min. (b) T_s vs sample cooling and heating rate. T_s represents the maximum of the peak detected by differential scanning calorimetry. The data are extrapolated to $v = 0$°/min.

arises, here defined as T_s, slightly increases/decreases with increasing the heating/cooling rate, as expected.

Through a plot of T_s vs the rate of heating or cooling of the sample, it is possible to calculate the value of T_s at a rate of 0°/min by extrapolation of the line obtained (see Figure 1b). Following this procedure, the temperature at which the structural phase transition takes place when heating the sample can be estimated as T_s(heating) $= 139 \pm 1$ K. Upon cooling the sample, this value moves to T_s(cooling) $= 125 \pm 1$ K. Therefore, a thermal hysteresis of about 14° is detected, suggesting a first-order phase transition.[9]

Further DSC experiments indicate that the appearance of the transition on heating is not dependent of the cooling rate, that is such a transition appears even if the sample has been quenched from room temperature to 110 K. Furthermore, no structural phase transformations are suggested by similar DSC measurements (heating or cooling) of K^+, Rb^+, and Cs^+ analogues.

The ac Magnetic Susceptibility. The temperature dependence of the ac susceptibility is shown in Figure 2 in reduced units. The sole paramagnetic ion present in the compound is $S = {}^5/_2$ high-spin Fe^{3+}. The fitting of the high temperature data, from 100 to 300 K, to a Curie–Weiss law yields $C = 4.22 \pm 0.05$ emu K mol^{-1}, $g = 1.97 \pm 0.02$ and $\Theta = -3.9 \pm 0.5$ K. We have used the convention for which a negative Θ value indicates antiferromagnetic interactions. As the temperature decreases, a broad maximum appears at 3.5 ± 0.1 K for the in-phase component of the magnetic susceptibility, χ'. This component then decreases leading to an inflection point at 1.61 ± 0.05 K. Along the whole range of temperature, the out-of-phase component of the susceptibility χ'' is 3 orders of magnitude smaller than the in-phase. The negligible value of χ'' indicates the absence of significant *net magnetic moments* confirming a three-dimensional antiferromagnetic ground state.

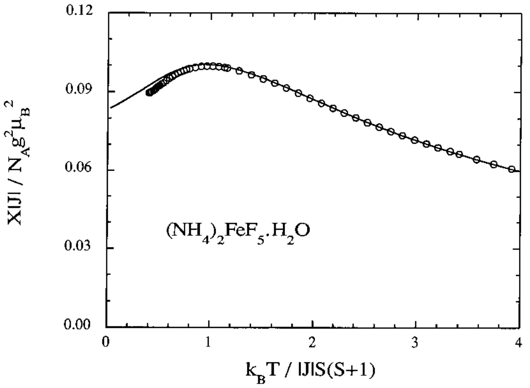

Figure 2. The ac magnetic susceptibility vs temperature in reduced units for $(NH_4)_2FeF_5\cdot H_2O$. The continuous line represents the fit of the experimental data to a Heisenberg linear-chain $S = {}^5/_2$ model (see text).

Owing to the structural phase transition suggested by the DSC experiments and the relevance of the thermal history of the sample reported for similar compounds,[10-12] it is appropriate to mention that two sample cooling rates have been used to decrease the temperature from ambient to 5 K. The first consists of liquid helium quenching for about 15 s. The temperature is slowly decreased over about 3 h in the second procedure. From 5 K to the lowest reached temperature, the cooling rate was the same for both procedures. After the sample was cooled, the experimental points were taken on heating back to room temperature. The two experimental curves obtained after the two rounds lie exactly one on top of the other. Thus, it can be deduced that the ac magnetic susceptibility of $(NH_4)_2FeF_5\cdot H_2O$ as a function of temperature is not influenced by the sample cooling rate.

The $A_2FeX_5.H_2O$ series ($X = Cl^-$) exhibits an isotropic magnetic behavior with values for α between 10^{-2} and 10^{-3}, where α is the ratio of the anisotropy field to the exchange field.[13] Hence, a Heisenberg Hamiltonian has been used for data analysis of the present system. Moreover, zigzag chains of $[FeF_5(H_2O)]^{2-}$ octahedra linked by O–H···F hydrogen bonds suggest a chain-like superexchange path in $(NH_4)_2FeF_5\cdot H_2O$ (see Figure 3).[5] As a result of the comments presented above a linear-chain model has been used to fit the experimental points.[14] This theoretical model fits the experimental data from room temperature to 2.6 K with an error less than a 1% yielding $g = 1.97 \pm 0.02$ and an antiferromagnetic intrachain constant $J/k_B = -0.40 \pm 0.02$ K (see Figure 2).

As temperature is decreased below 2.6 K, interchain interactions become significant and a long range magnetic ordering occurs at $T_c = 1.61 \pm 0.05$ K. The critical temperature has been estimated as the point at which $(d\chi'/dT)$ exhibits a maximum. A value of $R = |J'/J| = 0.05$, where J'/k_B represents the interchain interaction, can be obtained following Green's function method used by Oguchi[15] together with observed T_c

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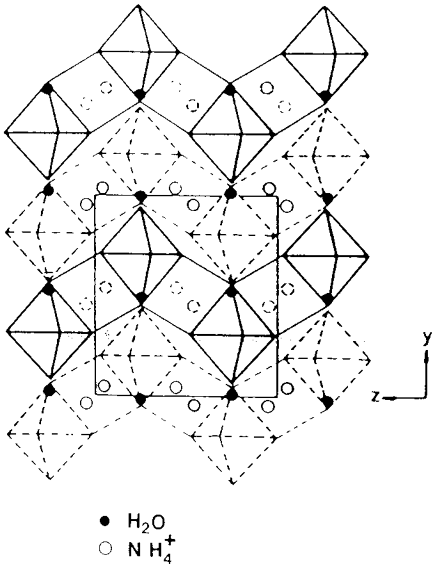

Figure 3. Crystal structure of $(NH_4)_2FeF_5 \cdot H_2O$: projection on (100) plane.

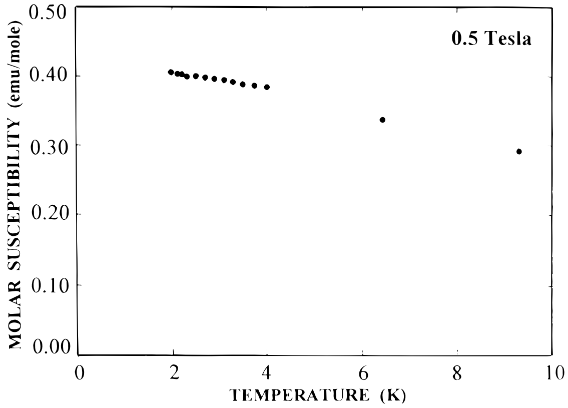

Figure 4. The dc magnetic susceptibility of $(NH_4)_2FeF_5 \cdot H_2O$ as a function of temperature at 0.5 T. The same temperature evolution is found at external applied fields of 1.5 and 1.9 T.

and J/k_B values. An analogous relation between T_c and R given by Villain and Loveluck[16] yields $R = 0.10$. For a given T_c, Oguchi's approach tends to give lower values for the R ratio than the approach followed by Villain and Loveluck. These values must be considered as an indication of the order of magnitude of R owing to the simplifications used in these models. A high-temperature series expansion model, extrapolated with Padé approximants for a lattice dimensionality crossover from a linear-chain to an anisotropic simple cubic lattice,[17] suggests a ratio $R = |J'/J|$ smaller than 0.05 by considering T_c, J/k_B, $T\chi_{max}$ and χ_{max} values obtained for $(NH_4)_2FeF_5 \cdot H_2O$. This result is consistant with the quality of the fit of the experimental data to a linear-chain model (see Figure 2).

The dc Magnetic Susceptibility. The preceding Curie–Weiss parameters are typical of high spin ferric ions and consistent with those ($C = 4.51$ emu K mol^{-1} and $\Theta = -5.8$ K) determined from the temperature dependence dc susceptibility for applied fields, H_o, ranging from 0.5 to 1.9 T (Figure 4). These data suggest low field spin–flop behavior in a polycrystalline sample, i.e. χ becoming more or less constant below T_c. A similar dc susceptibility vs temperature study for the related $Cs_2FeF_5 \cdot H_2O$ compound with $0.15 \text{ T} < H_o < 1.9 \text{ T}$, $T_c = 2.4$ K, also suggests low field spin–flop behavior, while $Rb_2FeF_5 \cdot H_2O$, $T_c = 4.1$ K, does not exhibit this effect in this applied field range.[8] The latter is consistent with the larger T_c and exchange field (H_E) for the rubidium analogue and the molecular field result, $H_{SF} \propto (H_E)^{1/2}$.

Mössbauer Spectroscopy. Ambient temperature and 77 K Mössbauer spectra indicate that the samples studied herein have isomer shift, quadrupole splitting, and line width parameters essentially identical to those found in the initial investigation of this material.[5] The Mössbauer spectra in the general vicinity of the phase transition (160,140, and 120 K) do not give evidence of temperature dependent behavior. However in the temperature range below 2.2 K, it is clear that an unordered, i.e. rapidely relaxing, phase coexists with a hyperfine split 3-d ordered component. This effect is seen in Figure 5 wherein the onset of hyperfine splitting occurs at 2.2 K, in reasonable agreement with the value of T_c determined from the inflection point of the zero field susceptibility data (vide supra). For an essentialy instantaneus quench of the sample from ambient temperature to 77 K followed by a rapid decrease in sample temperature from 77 to 4.2 K (<5 min), there is 53 ± 5% persistent rapidly relaxing fraction. When the sample is cooled slowly (~20 min) through the range 300–77 K, the limiting low temperature Mössbauer spectrum corresponds to 63 ± 5% persistent rapidly relaxing fraction. Thus, it appears that the Mössbauer spectra in the 3-d ordered temperature regime demonstrate the existence of an unordered rapidly relaxing phase whose intensity, within the experimental error, does not seem to be a sensitive function of sample cooling rate. **In view of the susceptibility data, the rapidly relaxing fraction must exhibit at least pairwise antiferromagnetic exchange interactions, since otherwise** χ_m vs T would diverge at very low temperatures.

The limiting value of the internal hyperfine field, $H_n(0 \text{ K})$, obtained from extrapolation of H_n vs T to $T = 0$ K (Figure 6) is near 45 T. This is greatly reduced from that normally expected (~60 T) of typical 3-d ordered ionic fluorides of high spin Fe^{3+}, e.g. $H_n(\text{saturation}) = 61.81$ T for FeF_3.[18] This corresponds to significant zero point spin-reduction (~25%) characteristic of 1-d magnetic behavior.[19] These observations are consistent with the analysis of the ac susceptibility data vs temperature using a Heisenberg 1-d antiferromagnetic model.

The limiting value of the quadrupole splitting (ΔE) for the paramagnetic phase is 0.42 mm/s. This value and the quadrupole shift (ϵ) perturbation of the Zeeman split spectrum allows one to calculate a value of $\theta = 72.5°$ using the relation $\epsilon = \Delta E/8\ (3 \cos^2 \theta\text{- } 1)$ where θ is the angle between the principal axis of the electric field gradient tensor (V_{zz}) and the internal hyperfine field (easy axis of magnetization). Here it is assumed that V_{zz} is positive[1] and that the EFG tensor is axially symmetric, i.e. $\eta = 0$. These assumptions are perfectly reasonable in view of the types of ligation involved (ionic $Fe^{3+} \cdots F$ and $Fe^{3+} \cdots O$) and the available room temperature crystallographic data for the local coordination environment. That is, using a point charge model with local C_{4v} symmetry for the trans-$[FeF_4F'O]$ coordination chromophore one predicts V_{zz} *positive*. The value of $\theta = 72.5°$ implies that the easy axis of $(NH_4)_2FeF_5 \cdot H_2O$ is not in the *ac* plane as in $K_2FeF_5 \cdot H_2O$ for which $\theta = 90°$ by both single crystal susceptibility and Mössbauer data.[1,2] With this statement, we are assuming the principal axis (V_{zz}) is parallel

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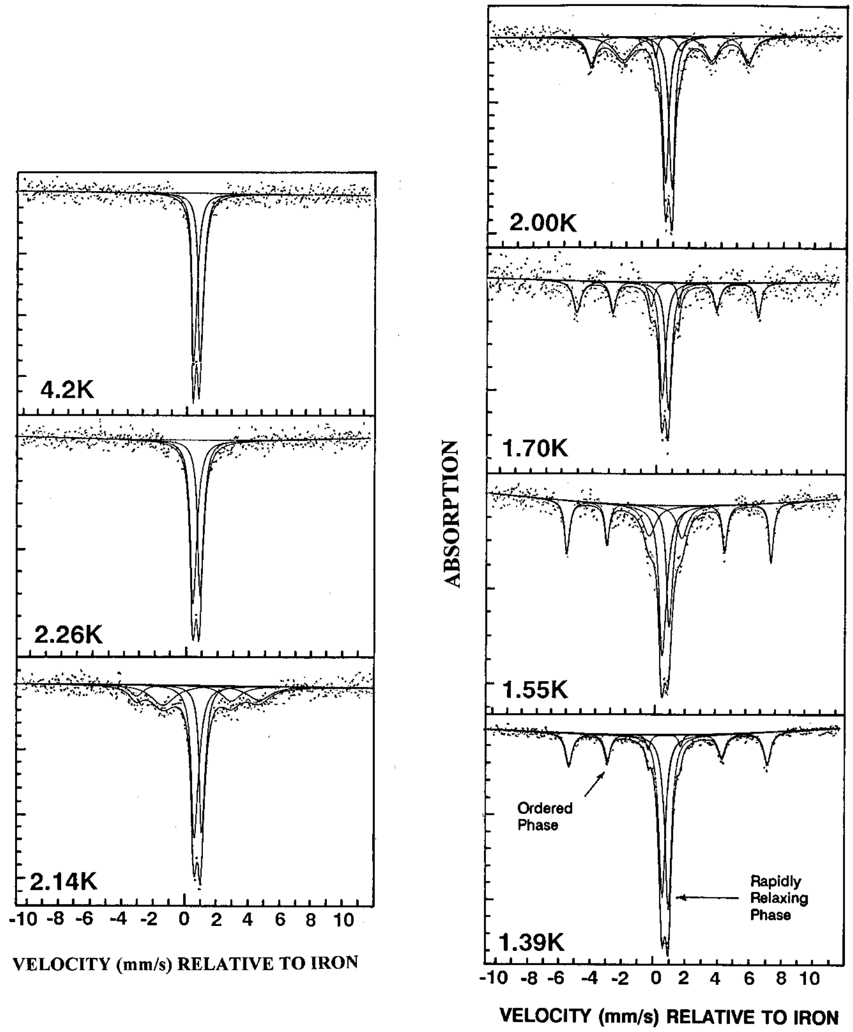

Figure 5. Temperature dependence of the Mössbauer spectra for $(NH_4)_2FeF_5{\cdot}H_2O$ below 4.2 K.

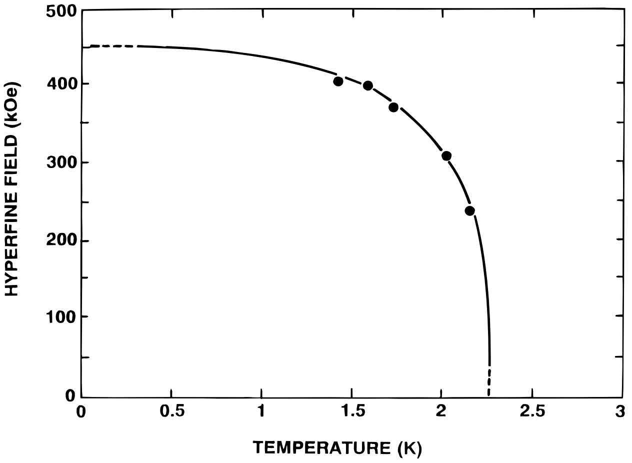

Figure 6. Variation of the internal hyperfine field with temperature for $(NH_4)_2FeF_5{\cdot}H_2O$.

to b. This may not be the case for the room temperature structure. Single-crystal Mössbauer spectroscopy study is needed to determine this with certainty. In view of the demonstrated phase transformation, the structure is likely different at lower temperatures, and thus even less can be said with certainty vis à vis magnetostructural correlations and the value of θ. For the present, all that one can say is that the somewhat different value of θ is likely related to differences in their structure details although these compounds are grossly similar in structure with the chain direction along c.

Discussion

A schematic of the 1-d character of the structure of $(NH_4)_2FeF_5{\cdot}H_2O$ is shown in Figure 3. The superexchange pathways within the chains involve hydrogen bonds of O−H···F type. The susceptibility data of $K_2FeF_5{\cdot}H_2O$ and $(NH_4)_2FeF_5{\cdot}H_2O$ exhibit essentially identical 1−d effects, $T\chi_{max}(K) = 3.4$ K, $T\chi_{max}(NH_4) = 3.5$ K, $J/k_B(K) = -0.40$ K, $J/k_B(NH_4) = -0.40$ K, as perhaps expected from the very similar chain structures.[2,5] Interestingly enough the ordering temperatures are not similar, 0.80 and 1.61 K, respectively, for the K and NH_4 derivatives. A comparison between the $R = |J'/J|$ values obtained by applying the Oguchi approach gives $R = 1.4 \times 10^{-2}$ for $K_2FeF_5{\cdot}H_2O$[2] and $R = 5.0 \times 10^{-2}$ for $(NH_4)_2FeF_5{\cdot}H_2O$ and indicates less one-dimensional character for the latter compound. Fourquet et al.[5] report that, for $(NH_4)_2FeF_5{\cdot}H_2O$, each NH_4^+ ion is surrounded by and hydrogen bonded to four $[FeF_5H_2O]^{2-}$ octahedra from adjacent zigzag chains (Figure 3). Magnetic interactions between chains are thus likely enhanced by hydrogen bonding through the NH_4^+ ions, i.e., $T_c(NH_4^+) \approx 2T_c(K^+)$.

Some further qualitative considerations seem worthwhile. The related Na_3FeF_6 and $(NH_4)_3FeF_6$ are unordered rapidly relaxing paramagnets to as low as 0.33 K as shown by Mössbauer spectroscopy.[20] Thus the replacement of Na^+ entirely by NH_4^+, with its hydrogen-bonding capabilities, apparently has little effect on the exchange interactions in the

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FeF_6^{3-} systems. These materials contain *no structural aspect* that can be construed as "chainlike". At low temperature they are distorted variants of the idealized high temperature face centered cubic (*Fm*3*m*) form of Na_3AlF_6, i.e. cryolite. The significant effect clearly occurs when definite structural chains of complex paramagnetic ions ($[FeF_5H_2O]$ in this case) are formed via replacement of one F^- by one H_2O unit as in $A_2FeF_5\cdot H_2O$ and the corresponding chloride series. The magnetic interaction is then enhanced by the establishment of O−H···F hydrogen bonds. Even so, the overall strength of 3-dimensional exchange in these systems must be viewed as weak since T_c is <2 K.

The structural phase transition clearly indicated by DSC measurements is an important aspect in the complete understanding of the magnetic properties of this compound at low temperature. Additional evidence for the phase transition considered herein comes from the X-band ESR study of $(NH_4)_2FeF_5\cdot H_2O$ by Lück et al.[21] On cooling from ambient to 77 K, they found (for an undiluted sample) a large increase in line width Γ for the intense signal at $g \sim 2$. It changed from 335 to 440 G, i.e. $\Delta\Gamma\Delta/\Gamma_{RT} \times 100 \sim 31\%$. Our study of the X-band ESR spectrum of $K_2FeF_5\cdot H_2O$ shows no similar effect.

It is well-known that structural phase transitions are often exhibited by compounds containing the NH_4^+ ion. Thus, $(NH_4)_3FeF_6$ and the cubic elpasolite $(NH_4)_2NaFeF_6$ undergo cubic (*Fm*3*m*) to pseudotetragonal distortions at 263 and 159.5 K, respectively.[22] The transitions involve cooperative rotations of *both cations and anions* leading to structural ground states with ionic conformations that maximize hydrogen bonding. The subject is far too complex to discuss in detail here except to say that Hirokawa et al.[23] have recently reviewed it in some detail as part of an NMR study of $(NH_4)_{3-x}K_xAlF_6$. Suffice it to say for now that the transition we observe probably primarily involves the NH_4^+ cations, as the anions are certainly more rigid in their hydrogen-bonded chains when compared to the cryolite or elpasolite structures which have no H_2O.

Conclusion

Considering the persistent rapidly relaxing phase detected by Mössbauer spectroscopy experiments for $(NH_4)_2FeF_5\cdot H_2O$ below the ordering temperature, a highly probable explanation is the destruction of the magnetic equivalence between the Fe^{3+} sites at low temperature as a consequence of the reported structural phase transition. This hypothesis is strongly supported by previous Mössbauer measurements performed on related compounds, β-$(NH_4)_2FeF_5$[10,24] and $(NH_4)_2FeCl_5.H_2O$.[11,12] These experiments indicate the presence of two different Fe^{3+} magnetic contributions, two corresponding hyperfine fields, and two magnetic critical temperatures. In passing, we note that none of the related complexes, $K_2FeF_5\cdot H_2O$, $Cs_2FeF_5\cdot H_2O$, and $Rb_2FeF_5\cdot H_2O$, exhibits a persistent rapidly relaxing phase below T_N in the zero field Mössbauer spectra.[1,8] It is clear that more information concerning the structural phase transition and the low temperature structure is necessary in order to achieve complete understanding of the magnetic properties of $(NH_4)_2FeF_5\cdot H_2O$ at low temperatures. In this light, more detailed Mössbauer spectroscopy line width studies near T_s are planned. Neutron diffraction experiments will also be useful in determining both the crystal and magnetic structures of this compound **at low temperature**. Finally, it seems clear that the common practice of interpretation of very low temperature magnetic behavior, largely on the basis of the ambient temperature structure determinations in the absence of calorimetry measurements, should be viewed and pursued with caution if not outright skepticism.

Experimental Section

Synthesis. The samples investigated were polycrystalline powders as obtained by the method of Fourquet et al.[5] No impurities were found when the samples were analyzed with conventional X-ray powder diffraction techniques.

Differential Scanning Calorimetry. DSC measurements were performed in the temperature range 110−200 K at varied cooling and heating rates by using a commercial Perkin-Elmer DSC-7 instrument.

The ac Magnetic Susceptibility. The ac magnetic susceptibility measurements were made using a commercial (Quantum Design) magnetometer with SQUID detection. The range of temperature covered was 1.8−300 K; the amplitude of the exciting field was 4.5 G and the frequency 10 Hz. Two different sample cooling rates were used. High resolution ac susceptibility measurements were also made at Northeastern University over the range 1.3−80 K at 125 Hz with $H(\mathrm{ac}) = 1$ Oe using a Lakeshore Cryotronics Model 7000 susceptometer.

The dc Magnetic Susceptibility. The dc susceptibility measurements were made using a standard Faraday balance.

Mössbauer Spectroscopy. Mössbauer spectra were determined using a conventional constant acceleration apparatus and cryogenics described previously.[20] Both neat (unground and undiluted) polycrystalline absorbers and samples finely mulled with Apiezon-m grease or petroleum jelly were investigated. Various rates of sample cooling were employed.

Acknowledgment. The authors gratefully acknowledge Prof. J. L. Fourquet and Mrs. H. Duroy for the preparation of samples, Dr. A. Gibaud for X-ray powder diffraction experiments, J. Campo, R. M. García−Casanova, and E. Martínez for support in ac and DSC measurements and Prof. F. Palacio for useful discussions. We also thank the North Atlantic Treaty Organization for travel monies to W.M.R. and Y.C. under a Nato Collaborative Research Grant, No. 920936; Grants MAT94-43/MAT92-896/MAT91-681 from CICYT (Spain) are also acknowledged. Finally, the authors thank the staff (particularly Mr. Scott Mc Clean) at E. I. Dupont de Nemours Inc. Central Research and Development, Wilmington, DE, for (dc) Faraday susceptometry and X-band ESR measurements. Y.C. dedicates this work to the memory of his friend G. Lecoze, while W.M.R. makes a similar dedication to the memory of the recently deceased W. E. Hatfield.

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