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Low-Temperature Antiferromagnetic Behavior of α-$Rb_2FeF_5 \cdot H_2O$ and α-$Cs_2FeF_5 \cdot H_2O$

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D.C. susceptibility and zero field Mössbauer spectroscopy measurements are used to characterize the low-temperature magnetism of α-$Rb_2FeF_5 \cdot H_2O$ and α-$Cs_2FeF_5 \cdot H_2O$. The compounds are rigorously isotypic quasi-1D Heisenberg magnets based on hydrogen bonded chains of $-\{FeF_5H_2O\}^{2-}-$ pseudo-octahedra with intervening Rb^+ and Cs^+ cations that enhance the low dimensionality. The 1D antiferromagnetic effects appear comparable, $T_{\chi max}$(1D) ~5 K, while their 3D ordering temperatures are quite different, $T_N(Rb^+) = 4.0$ K, $T_N(Cs^+) = 2.7$ K. The internal hyperfine fields extrapolated to $T = 0$ K are ~ 51 T suggesting zero point spin reduction (~15%) consistent with 1D behavior. High field d.c. susceptibility measurements for polycrystalline $Cs_2FeF_5 \cdot H_2O$ suggest spin–flop behavior with $H_{SF} < 1$ T. A qualitative comparison of the low-temperature magnetic properties of the F^- and Cl^- analogues for the series $M_2FeX_5 \cdot H_2O$ ($M = NH_4^+, K^+, Rb^+, Cs^+$) is given. © 1994 Academic Press, Inc.

INTRODUCTION

$Rb_2FeF_5 \cdot H_2O$ exists in two crystalline polymorphs. The first to be characterized, β-$Rb_2FeF_5 \cdot H_2O$ (1) is orthorhombic (*Cmcm*), with $a = 9.691$ Å, $b = 8.446$ Å, and $c = 7.947$ Å, consisting of infinite isolated and slightly kinked *trans*-linked chains of FeF_4F_2' octahedra with intervening "free" Rb^+ cations and H_2O molecules, and isotypic to $Rb_2AlF_5 \cdot H_2O$. Owing to the presence of true covalent (superexchange) Fe–F′–Fe bridging units and significant chain dilution by Rb^+ and H_2O, the system is highly one-dimensional ($J/k_B = -13.1$ K, $J'/J = 2.2 \times 10^{-3}$, with H_n (0 K) only 39.6 T, suggesting significant zero point spin reduction (2), a hallmark of low dimensionality. This polymorph orders three-dimensionally at 9.7 K. The single crystal structure determination of the other form, α-$Rb_2FeF_5 \cdot H_2O$, has recently been reported (3). This form also crystallizes in the space group *Cmcm* ($a = 9.73$ Å, $b = 7.905$ Å, and $c = 8.292$ Å), but with pseudo-octahedra $-\{FeF_5H_2O\}-$ units linked via hydrogen bonds to form zigzag chains articulated along c and where Fe–F and Fe–O bond vectors of the local Fe(III) coordination polyhedra are parallel to the unit cell edges. α-$Rb_2FeF_5 \cdot H_2O$ is isotypic to $Cs_2FeF_5 \cdot H_2O$ (hereafter α-$Cs_2FeF_5 \cdot H_2O$, *Cmcm*: $a = 10.361$ Å, $b = 8.266$ Å, and $c = 8.401$ Å). The latter compound was synthesized by hydrothermal methods and its structure determined by Belov *et al.* (4). They also reported aspects of the compound's magnetic behavior but gave no indication of 1D behavior. It exhibits 3D antiferromagnetic ordering at $T_N = 2.4$ K ± 0.1 as determined from single crystal vibrating sample (d.c.) magnetometry measurements which also show that the easy axis of magnetization coincides with the a cell edge direction. α-$Cs_2FeF_5 \cdot H_2O$ and the Rb^+ analog are similar to but not isomorphous with α-$(NH_4)_2FeF_5 \cdot H_2O$ (*Pbcn*, $a = 10.49$ Å, $b = 8.09$ Å, and $c = 7.997$ Å), which has recently been characterized as also having zigzag chains directed parallel to the c cell edge (5). A schematic of the chains for Rb^+ is given in Fig. 1.

We (6) have found that α-$(NH_4)_2FeF_5 \cdot H_2O$ exhibits more distinct 1D behavior: $T_{\chi/max}$(1D) = 3.6 K, $J/k_B = -0.4$ K, $R = J'/J = 0.01$, and H_n(0 K) = 41 T with $T_N = 2.2$ K via both Mössbauer spectroscopy and a.c. susceptibility characterization. We have also observed, through differential scanning calorimetry, that this material undergoes a structural transformation at ~141 K which leads to a permanent paramagnetic fraction for $T < T_N$ for both gradually and rapidly cooled samples.

Finally, since the sodium analogue has apparently never been isolated, the "α" series is completed insofar as we know with α-$K_2FeF_5 \cdot H_2O$. This material is monoclinic (*C2/c*, $a = 9.71$ Å, $b = 7.79$ Å, and $c = 7.95$ Å, $\beta = 96.5$) (7). Its magnetic susceptibility (8) and Mössbauer spectra (9–11) have been reported. In the present investigation we report and discuss details of the Mössbauer spectra and d.c. susceptibility of polycrystalline samples of α-$Rb_2FeF_5 \cdot H_2O$ and α-$Cs_2FeF_5 \cdot H_2O$, and give brief qualitative comparative

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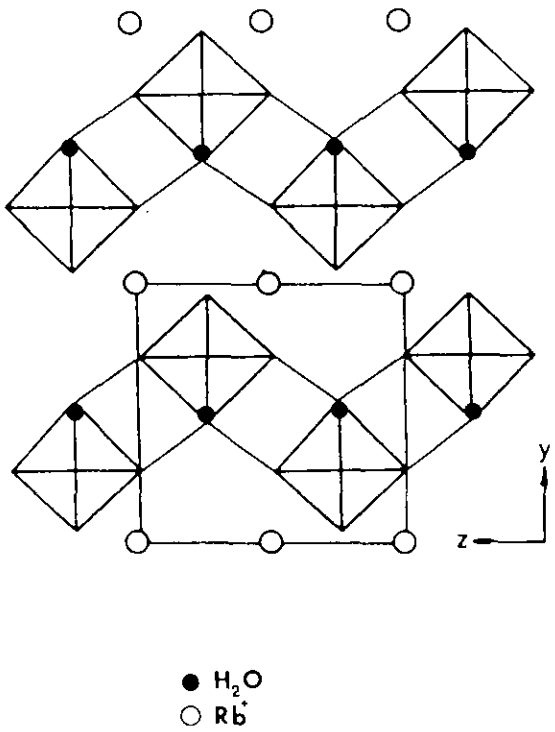

FIG. 1. $Rb_2FeF_5 \cdot H_2O$: hydrogen bonded chains of $\{FeF_5(H_2O)\}$ octahedra. Projection of the layer (Fe in $x = 0.5$) on (100) plane (Ref. (3)).

considerations of the entire fluoride and related chloride series. A review of the latter series of compounds has recently been published (12).

EXPERIMENTAL

Synthesis. The compounds were prepared by hydrothermal synthesis in HF solutions by the classical method (3). The samples investigated were polycrystalline powders.

Mössbauer spectroscopy. Mössbauer spectra were determined using a conventional constant acceleration apparatus and cryogenics described previously (10). Both neat (unground and undiluted) polycrystalline absorbers and samples finely ground and mulled with apiezon-m grease or petroleum jelly were investigated. Various rates of sample cooling were employed.

RESULTS

Mössbauer Spectra

The temperature dependence of the Mössbauer spectra of α-$Rb_2FeF_5 \cdot H_2O$ and α-$Cs_2FeF_5 \cdot H_2O$ is given in Figs. 2 and 3. The Mössbauer spectra in the paramagnetic temperature regime confirm sample purity. The quadrupole splitting and the isomer shift values (with respect to iron metal) at 4.2 K are $\Delta E = 0.55$ mm/sec, $\delta = 0.52$ mm/sec for Cs^+ and $\Delta E = 0.48$ mm/sec, $\delta = 0.48$ mm/sec for Rb^+. These are typical of high spin Fe^{3+} in a relatively undistorted local coordination environment (13). The very low temperature behavior indicates cooperative 3D order, with $T_N(Rb^+) = 4.0$ K and $T_N(Cs^+) = 2.7$ K. The latter is in reasonable agreement with the value (2.4 ±0.1 K) determined by Belov *et al.* (4) using vibrating sample magnetometry, while the rubidium system has not been previously investigated. The limiting low-temperature spectra of the present compounds (~1.4 K) give no evidence of an accompanying rapidly relaxing paramagnetic phase. Such a phase is observed in our (6) study of α-$(NH_4)_2FeF_5 \cdot H_2O$ for both gradual and rapid cooling from ambient temperature. The effect likely arises on cooling the sample through its structural phase transition at 141 K. The transition (also observed using differential scanning calorimetry and ESR spectra) is thought to involve quenching the rotational motion of the NH_4^+ cations in the lattice as preferred NH_4^+–H_2O conformations and strong hydrogen bonds are achieved at low T. Such hydrogen bonding related behavior is less apt to occur for the present Rb^+ and Cs^+ cations. The limiting value of the internal hyperfine fields $H_n(0\ K)$ for both of these systems is 51 T. This indicates appreciable zero point spin reduction (~15%), assuming a saturation value for H_n for ionic fluorides of high spin Fe III to be 60 T (14). These observations are consistent with significant 1D chain antiferromagnetic interactions.

Magnetic Susceptibility

1D behavior. The 1D chain magnetic behavior is revealed via the very broad maximum in χ_m vs. T (d.c. susceptibility data obtained using a standard Faraday balance) and particularly in the high density data sets at low applied fields where $T_{\chi/max}(1D) = 5.0$ K for Rb^+ and 4.5 K for Cs^+ (Fig. 4). Similar broad maxima in χ_m were observed in previous zero field a.c. studies of the related $K_2FeF_5 \cdot H_2O$ ($T_{\chi/max}(1D) = 3.4$ K) (8) and $(NH_4)_2FeF_5 \cdot H_2O$ ($T_{\chi max}(1D) = 3.4$ K) (6) and for which fits to an isotropic Heisenberg 1D chain model gave $J/k_B \sim -0.4$ to -0.5 K and $R = J'/J$; the ratio of the inter- to intra-chain exchange parameters was $\sim 1.5 \times 10^{-2}$.

3D magnetism. The dashed vertical lines on the χ vs T plots correspond to T_N as determined via Mössbauer spectroscopy (2.7 K (Cs^+) and 4.0 K (Rb^+)). These are close to what appear to be the inflection points of the χ vs T curves. The latter are usually taken as T_N from susceptibility data of 1D chain systems such as those studied herein. They are very difficult to estimate precisely from the broad maxima exhibited by these materials. In any event, the internal consistency of the present

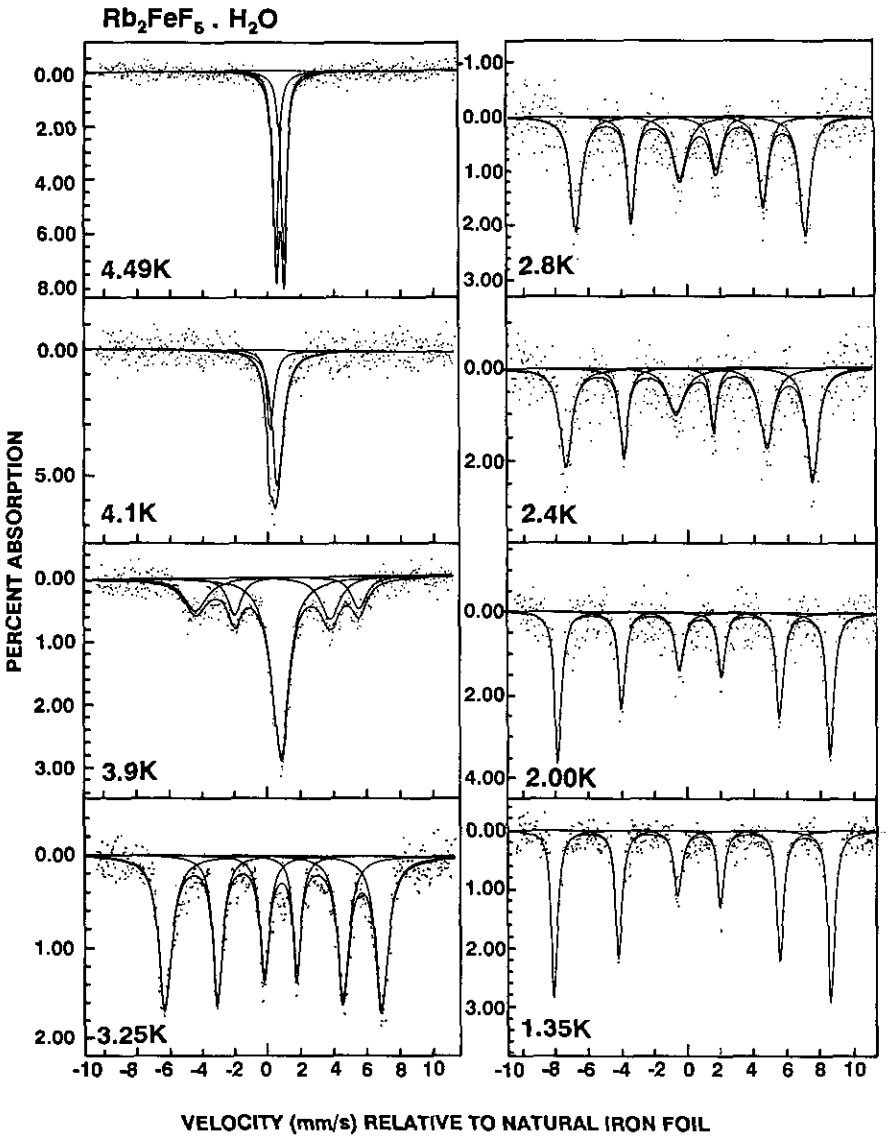

FIG. 2. Temperature dependence of the Mössbauer spectra for $Rb_2FeF_5 \cdot H_2O$.

results is reasonable, considering that the data corresponds to nonzero field (d.c.) susceptibility measurements on polycrystalline powders. The high-temperature data fit a Curie–Weiss law (Fig. 5) for $Rb_2FeF_5 \cdot H_2O$ with $\vartheta_p = -8.58$ K, C = 4.52 emu K/mole and for $Cs_2FeF_5 \cdot H_2O$ $\vartheta_p = -3.62$ K, C = 4.46 emu K/mole. The parameters are typical of weakly interacting high spin iron III systems.

It is clear that a more complete understanding of the magnetism of the present systems awaits single crystal a.c. susceptibility, and Mössbauer spectroscopy studies and the latter are planned. However, at present it is useful to further consider the higher field d.c. susceptibility data of $Cs_2FeF_5 \cdot H_2O$ (Fig. 6). Here, it is seen that for $H >$ 0.5 T and $T < T_N$, χ vs T levels off and becomes more or less constant. The behavior is that expected of a single crystal for which the applied field, H_0, is perpendicular to the preferred or so-called easy axis of magnetization of the material. The implication is that applied fields of ~0.5 T have driven essentially all of the antiferromagnetic domains of the sample polycrystals of $Cs_2FeF_5 \cdot H_2O$ to the spin–flop state, resulting in the classic $\chi(\perp)$ constant susceptibility in the 3D ordered state, i.e., $H_{SF} < 0.5$ T. Although first order in nature, such spin–flop transition will necessarily be broadened and smeared out for an initially random orientation, as in polycrystalline powder samples. The overall result of the present study is consistent with a low value of spin–flop field. A similar situation

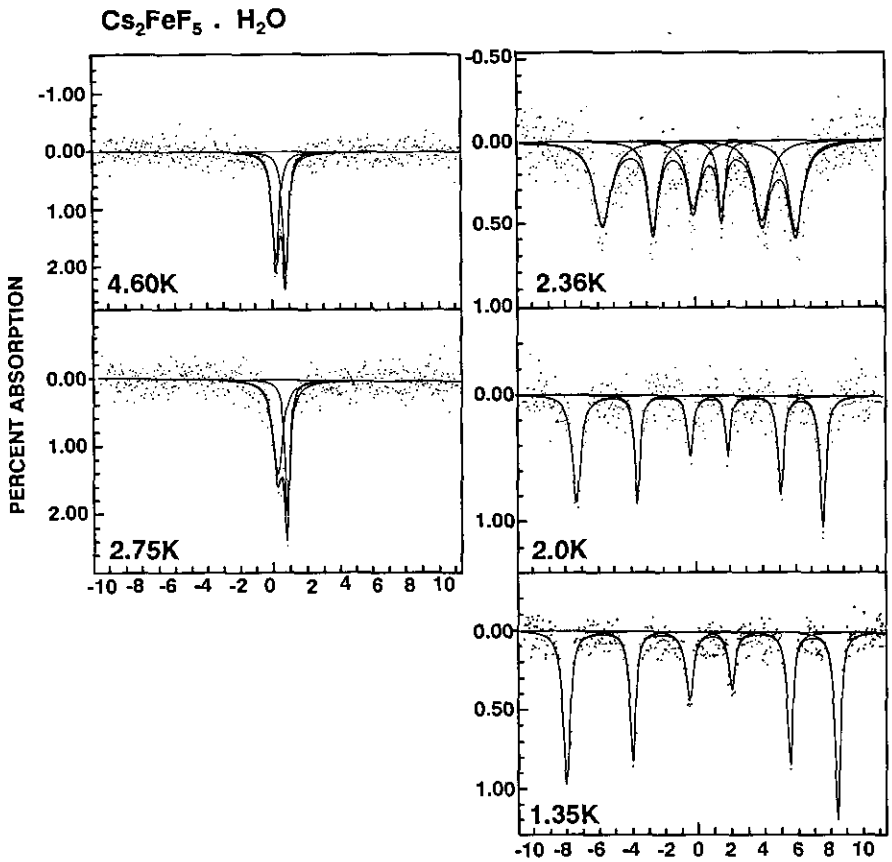

FIG. 3. Temperature dependence of the Mössbauer spectra for $Cs_2FeF_5 \cdot H_2O$.

is indicated from the applied field Mössbauer study of polycrystalline $K_2FeF_5 \cdot H_2O$ (T_N = 0.8 K) wherein initial flopping is evident for H_0 of only 0.2 T with the transition essentially complete at $H_0 \sim 1.2$ T (11) in the powder. Since $H_{SF} = (2H_EH_A - H_A^2)^{1/2}$, where H_A and H_E are the anisotropy and exchange fields, respectively, and since T_N is proportional to H_E, one expects a higher value of H_{SF} for $Rb_2FeF_5 \cdot H_2O$ for which T_N = 4.0 K. This is consistent with the *incipient* leveling effect in χ vs T as a function of H_0 for the rubidium analog relative to the cesium compound. Single crystal Mössbauer study of $Cs_2FeCl_5 \cdot H_2O$ (T_N = 6.75 K) shows $H_{SF} \rightarrow$ Para $\sim$ 10 T while H_{SF} = 1.3 T (14). Assuming that $H_A(Cs_2FeF_5 \cdot H_2O) \sim H_A(Cs_2FeCl_5 \cdot H_2O)$ and that T_N scales roughly as H_E, one estimates $H_{SF} \sim 0.5$ to 0.6 T in accord with the present d.c. powder susceptibility results. The data also suggest that it should clearly be easier to observe the field induced paramagnetic phase, i.e., the SF $\rightarrow$ P transition, for $Cs_2FeF_5 \cdot H_2O$ than $Cs_2FeCl_5 \cdot H_2O$ since $H_{SF \rightarrow P}$ is likely $\sim$5 T for the latter. In this light, very high applied field Mössbauer spectroscopy studies of powder and single crystal samples of $Rb_2FeF_5 \cdot H_2O$ and $Cs_2FeF_5 \cdot H_2O$ are planned for the near future.

COMPARISONS

Comparisons of the low-temperature magnetic behaviors of the chloride and fluoride series are tempting but difficult. There are superficial similarities among the systems that at first suggest that such comparisons are credible. For example, all of these systems are orthorhombic or "nearly so." Unfortunately, all of the existing structural data correspond to ambient temperature X-ray studies. This is problematical in that several of the systems ($(NH_4)_2FeCl_5 \cdot H_2O$, $(NH_4)_2FeF_5 \cdot H_2O$, and $Cs_2FeCl_5 \cdot H_2O$) have already been demonstrated to undergo solid state structural phase transitions at temperatures well above $T_{N\acute{e}el}$. For example, a crystallographic phase transition is observed at $\sim$151 K for $Cs_2FeCl_5 \cdot H_2O$ (15) at which temperature its Mössbauer spectrum changes from a singlet to a quadrupole doublet.

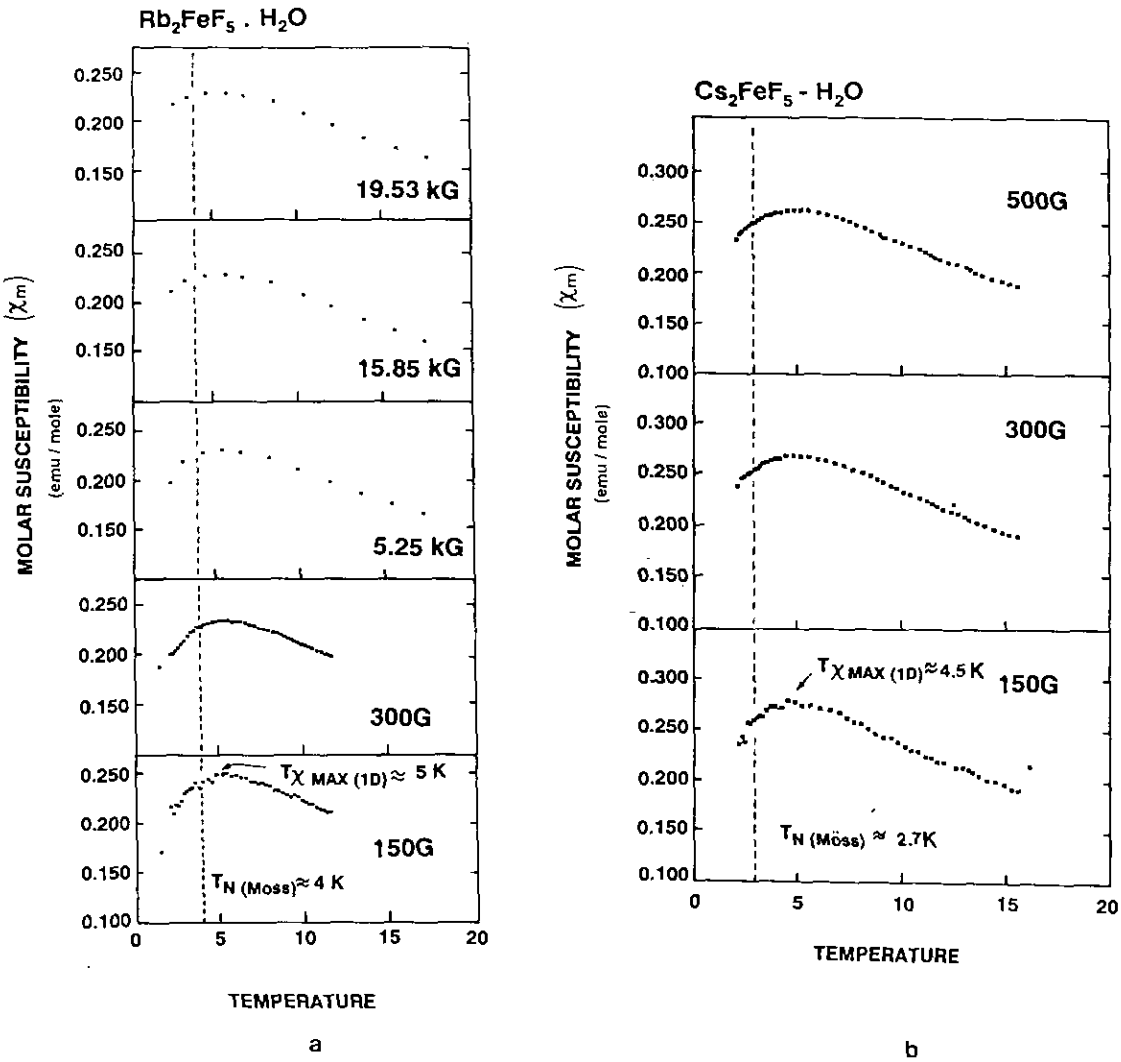

FIG. 4. d.c. magnetic susceptibilities for $Rb_2FeF_5 \cdot H_2O$ (a) and $Cs_2FeF_5 \cdot H_2O$ (b) at low applied fields in the vicinity of T_N.

It appears that detailed comparisons within and between these series may in fact be meaningless until definitive low-temperature (preferably neutron diffraction) crystallographic and magnetic structural data are available. In particular, for the fluorides, the interplay of very strong hydrogen bonding effects and slight but nevertheless magnetically significant structure differences is simply imponderable in the absence of detailed low-temperature structure data. From data of Table 1, it is clear that the fluorides as a class exhibit significantly weaker 3D exchange interactions. This observation is consistent with the general view that such interactions importantly involve close contacts of centers of delocalized metal electron spin density. The latter delocalization is in turn more or less a direct function of the halogen polarizability, where, of course, chloride anions are more polarizable than fluoride. In summary, the definitive magnetic interpretation of the "homologous" series such as those considered herein must await polarized neutron diffraction investigation, where the pattern and magnitude of spin delocalization is in principle measurable in addition to the detailed magnetic structure.

TABLE 1
Néel Temperatures (K) for M_2 Fe^{III} $X_5 \cdot H_2O$ Compounds

	K^+	NH_4^+	Rb^+	Cs^+
F^-: by susceptibility	0.80[a]	2.2[b]	4.0[c]	2.4[d]
by Mössbauer spectroscopy	(0.85)[e]	(2.2)[b]	(4.0)[c]	(2.7)[c]
Cl^-: by heat capacity	14.06[f]	7.25[f]	10.0[f]	6.54[f]

[a] Single crystal (Ref. 8).
[b] Reference (6).
[c] This work.
[d] Single crystal (Ref. 4).
[e] Reference (10).
[f] Reference (12).

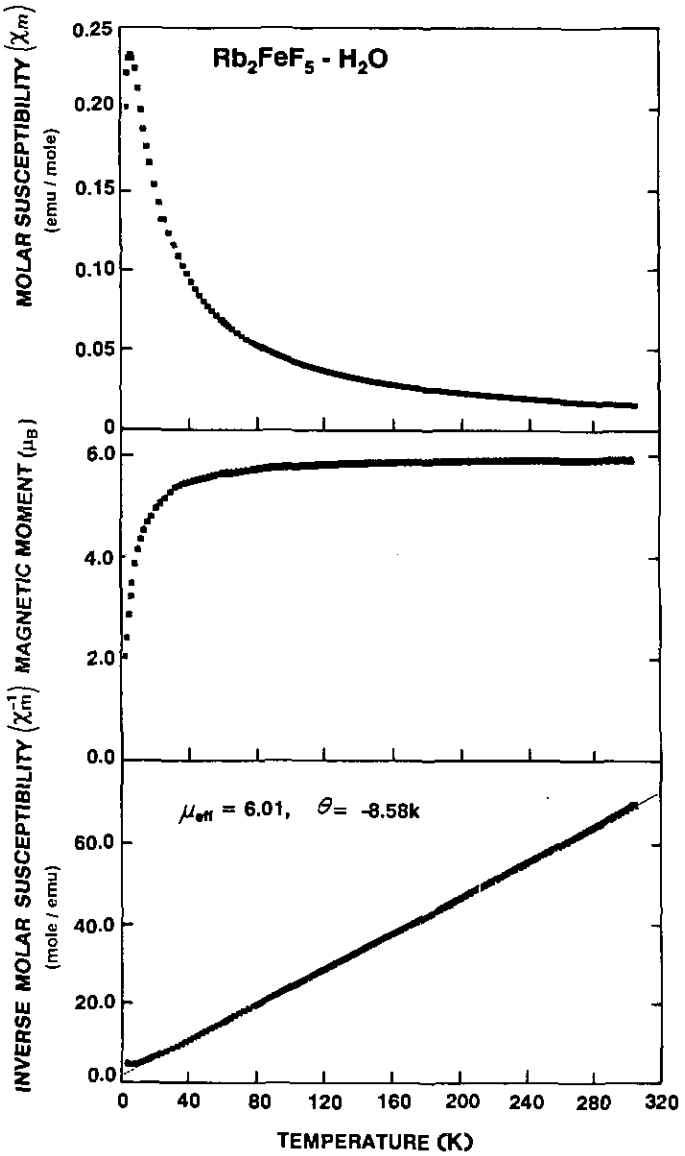

FIG. 5. High-temperature magnetic data vs T for $Rb_2FeF_5 \cdot H_2O$.

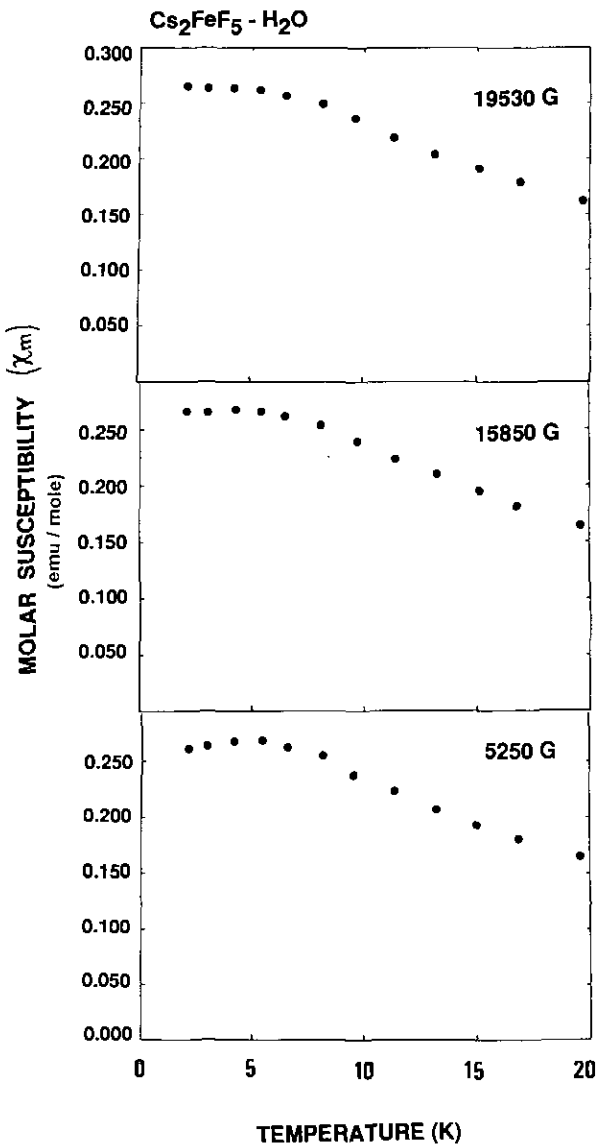

FIG. 6. High applied field d.c. susceptibility data for $Cs_2FeF_5 \cdot H_2O$.

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