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# Preparation, Magnetic Properties and Mossbauer Study of the Modified Pyrochlores $M^{II}M^{III}F_6A$*

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The preparation, lattice parameters, densities, and results of magnetic susceptibility and Mossbauer effect studies of some cubic modified pyrochlores $M^{II}M^{III}F_6A$, where A = Rb, Cs, Tl and M is a 3*d* transition metal, are reported. Evidence of magnetic ordering at temperatures below 26 K has been found for several of the materials. The room temperature Mossbauer data are consistent with the results of Babel's X-ray study from which he deduced that the transition metal ions are randomly distributed on a site of distorted octahedral symmetry. The relative magnitudes of the $\theta$ values and the large values of $-\theta/T$ measured are discussed in terms of the crystal structure of the modified pyrochlores and the nature of the exchange interactions.

## Introduction

A number of preparative and structural studies of the fluorides $M^{II}M^{III}F_6A$ (A = Rb, Cs, Tl; M = first row transition metal) have been reported. The studies of Jacoboni et al. (*1*) and de Pape et al. (*2*) demonstrated that an appreciable range of homogeneity can be expected for these materials. From X-ray powder diffraction data, Babel (*3*) determined that a large number of these fluorides have a cubic structure related to the pyrochlore structure of the mineral $NaCaNb_2O_6F$ (*Fd*3*m*).

Several descriptions of the pyrochlore structure can be found in the literature (*4–6*). If one writes the generalized formula as $B_2M_2X_6A$, then the B ions occupy the sites 16*d* (1/2, 1/2, 1/2), the M ions occupy the sites 16*c*, the X ions are on the sites 48*f*, and the A ions occupy the sites 8*b* in the unit cell. The modified structure is represented by the formula $M_2X_6A$ (e.g., $Fe^{II}Cr^{III}F_6Rb$). The monovalent cations, which are too large for the sites 16*d* (*4*), fill the more open sites 8*b* (*3*). Both modifications of the pyrochlore structure are characterized by the same $M_2X_6$ network of corner sharing octahedra.

We have extended the investigation of a number of the fluorides $M^{II}M^{III}F_6A$ in order to study their properties by magnetic susceptibility and Mossbauer effect measurements. It will be seen that the $M_2X_6$ network characteristic of both modifications of the pyrochlore structure is not favorable for cooperative magnetic ordering of the transition metal ions. The results of Molecular Field Theory (*7*) and the predictions of Goodenough's superexchange rules (*8*) are used to rationalize the results of the magnetic susceptibility measurements.

## Experimental

### *Preparation of Materials*

All materials were prepared by firing stoichiometric mixtures of the appropriate binary fluorides in sealed platinum tubes. The materials AF (A = Rb, Cs, Tl) were transferred directly

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from a drying oven to tarred plastic capsules in order to avoid moisture contamination. The other reactants were added to the capsule and mixed by an automatic shaking device before being sealed in the reaction tube, these operations being performed under dry argon. The reaction mixture was prefired overnight at 500°C followed by grinding under dry argon. The Rb and Cs materials were refired for three days at 800°C. The thallium preparations were refired at 600°C.

The starting materials RbF, CsF, TlF, and $MgF_2$ were obtained commercially. The transition metal fluorides were prepared in this laboratory. The materials $CrF_3$, $FeF_3$, and $NiF_2$ were prepared by heating the anhydrous chlorides in a flow of HF. The anhydrous chlorides were obtained by treating the hydrated salts with thionyl chloride as described by Pray (*9*).

Samples of $MnF_2$ and $VF_3$ were prepared by thermally decomposing, under an HF flow, the product obtained by adding the appropriate reagent ($MnCO_3$ or $V_2O_3$) to an excess of molten ammonium bifluoride.

The material $FeF_2$ was obtained by reducing a sample of $FeF_3$ at 890°C in an atmosphere of argon, HF, and hydrogen corresponding to flow rates of 0.3, 0.6, and 0.75 SCFH, respectively.

### *Lattice Parameters and Densities*

Samples for X-ray analysis were mixed with a germanium powder internal standard and the diffraction pattern ($CuK\bar{\alpha}$) recorded with a Norelco powder diffractometer equipped with an AMR graphite crystal monochromator. The lattice constant of the standard had been determined from the high angle Debye-Scherrer data by the usual extrapolation procedure.

The densities of the powder samples were determined pycnometrically with carbon tetrachloride as the measuring fluid. In Table I are listed the materials prepared together with the measured densities, the lattice constants, and the densities calculated on the basis of the unit cell composition of the cubic modified pyrochlore structure.

### *Magnetic Susceptibility Data*

The magnetic susceptibilities of all samples were measured over the range 4.2–300 K with a Foner type vibrating sample magnetometer as described in a previous paper (*10*). The susceptibility values were corrected for diamagnetic contributions as listed by Figgis and Lewis (*11*). The values of the molar Curie constant, $C_M$, and the Weiss constant, $\theta$, were obtained for each sample by least-squares fitting the corrected $1/\chi$ vs $T$ data to a straight line for data points with $T > 150$ K. In Table II are given the values of $C_M$ (experimental), $C_M$ (spin-only) and $\theta$ for each sample. For those samples that gave evidence of a magnetic ordering transition, approximate values of the ordering temperature, $T_0$, and $-\theta/T_0$ are also listed.

### *Mossbauer Data*

Mossbauer effect measurements utilizing a $^{57}Co$ in palladium source were made on all iron-containing samples. A model NS-1 (Nuclear

TABLE I

LATTICE PARAMETERS AND DENSITIES

| Material | $a_0$ (±0.005 Å) | $D_{X\text{-ray}}$ (g/cm$^3$) | $D_m$ (g/cm$^3$) |
|---|---|---|---|
| $MnCrF_6Rb$ | 10.260 | 3.768 | 3.76 |
| $NiFeF_6Rb$ | 10.266 | 3.855 | 3.88 |
| $FeCrF_6Rb$ | 10.274 | 3.763 | 3.75 |
| $FeCrF_6Tl$ | 10.300 | 5.179 | 5.20 |
| $MgFeF_6Tl$ | 10.306 | 4.834 | 4.90 |
| $FeVF_6Rb$ | 10.321 | 3.700 | 3.73 |
| $MnCrF_6Tl$ | 10.334 | 5.119 | 5.03 |
| $MgFeF_6Cs$ | 10.341 | 3.927 | 3.96 |
| $NiFeF_6Cs$ | 10.361 | 4.315 | 4.30 |
| $FeCrF_6Cs$ | 10.407 | 4.179 | 4.16 |
| $FeVF_6Cs$ | 10.476 | 4.085 | 4.07 |
| $MnCrF_6Cs$ | 10.478 | 4.086 | 4.08 |
| $MnFeF_6Cs$ | 10.522 | 4.077 | 4.05 |

TABLE II

MAGNETIC PARAMETERS

| Material | $C_M$ (spin-only) | $C_M$ (exptl) | $-\theta$ (K) | $T_0$ (K) | $-\theta/T_0$ |
|---|---|---|---|---|---|
| $MnCrF_6Rb$ | 6.26 | 6.38 | 74 | — | — |
| $MnCrF_6Tl$ | 6.26 | 6.28 | 55 | — | — |
| $MnCrF_6Cs$ | 6.26 | 6.27 | 67 | — | — |
| $FeCrF_6Rb$ | 4.88 | 5.48 | 91 | 5 | 18 |
| $FeCrF_6Tl$ | 4.88 | 6.19 | 123 | 5 | 25 |
| $FeCrF_6Cs$ | 4.88 | 5.73 | 98 | 5 | 20 |
| $NiFeF_6Rb$ | 5.38 | 5.39 | 235 | 6 | 39 |
| $NiFeF_6Cs$ | 5.38 | 5.37 | 258 | 7 | 37 |
| $MgFeF_6Tl$ | 4.38 | 4.33 | 190 | — | — |
| $MgFeF_6Cs$ | 4.38 | 4.35 | 157 | — | — |
| $FeVF_6Rb$ | 4.00 | 4.59 | 88 | 5 | 18 |
| $FeVF_6Cs$ | 4.00 | 4.82 | 106 | 5 | 21 |
| $MnFeF_6Cs$ | 8.76 | 8.79 | 287 | 26 | 11 |

Science and Engineering) spectrometer was used in the constant acceleration mode in conjunction with a Nuclear Data 2200 analyzer. The spectrometer was calibrated with an $\alpha$-iron foil.[1] In Table III are given the values of the isomer shifts, quadrupole splittings, and half widths obtained from a computer analysis[2] of the room temperature spectra. In addition, preliminary measure-

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[1] National Bureau of Standards, Iron Foil Mossbauer Standard No. 1541.

[2] Parabola-Lorentzian Least Squares Analysis of Mossbauer Data Program by E. Rhodes, A. Polinger, J. J. Spijkerman, and B. W. Christ, National Bureau of Standards, Washington, D.C.

TABLE III

ROOM TEMPERATURE MOSSBAUER PARAMETERS[a]

| $M^{II}M^{III}F_6A$ | Isomer[b] shift | Quadrupole splitting | Line halfwidths[c] |
|---|---|---|---|
| $FeCrF_6Rb$ | 1.220 (±0.012) | 2.647 (±0.011) | 0.346 (±0.015)<br>0.326 (±0.014) |
| $FeCrF_6Cs$ | 1.209 (±0.014) | 2.412 (±0.014) | 0.460 (±0.018)<br>0.421 (±0.018) |
| $FeCrF_6Tl$ | 1.225 (±0.016) | 2.570 (±0.016) | 0.367 (±0.020)<br>0.348 (±0.020) |
| $FeVF_6Rb$ | 1.225 (±0.012) | 2.556 (±0.012) | 0.371 (±0.016)<br>0.321 (±0.016) |
| $FeVF_6Cs$ | 1.234 (±0.015) | 2.319 (±0.015) | 0.482 (±0.020)<br>0.438 (±0.020) |
| $MgFeF_6Cs$ | 0.295 (±0.009) | 0.538 (±0.009) | 0.424 (±0.012)<br>0.413 (±0.012) |
| $MgFeF_6Tl$ | 0.295 (±0.011) | 0.488 (±0.011) | 0.438 (±0.015)<br>0.440 (±0.015) |
| $NiFeF_6Rb$ | 0.274 (±0.008) | 0.541 (±0.008) | 0.370 (±0.011)<br>0.351 (±0.010) |
| $NiFeF_6Cs$ | 0.279 (±0.009) | 0.519 (±0.009) | 0.395 (±0.012)<br>0.386 (±0.012) |
| $MnFeF_6Cs$ | 0.285 (±0.010) | 0.583 (±0.010) | 0.415 (±0.013)<br>0.412 (±0.013) |

[a] All values in mm-sec$^{-1}$.

[b] Relative to $^{57}Co$ in Pd.

[c] Lower velocity member listed first.

ments have been made at low temperatures for those materials in which the onset of magnetic ordering is indicated by the susceptibility data.

## Discussion

Babel (*3*) deduced from his study that the cubic materials $M^{II}M^{III}F_6A$ are well described as having a modified pyrochlore structure in which the transition-metal ions are randomly distributed over the sites 16*c*. Such a distribution is consistent with the large half widths observed in the Mossbauer spectra of the materials listed in Table III. Babel also determined that the fluoride ions about each transition metal ion do not form regular octahedra. Rather, the octahedra are compressed along a trigonal axis that is parallel to the [111] direction of the unit cell.

From the isomer shift data in Table III and the values of $C_M$ in Table II it can be seen that $Fe^{III}$ exists in the high-spin state, as might be expected. Since for high-spin $Fe^{III}$ quadrupole effects can arise only from distortions of the site symmetry from cubic, with the most important contribution arising from the symmetry of the ligands immediately associated with the $Fe^{III}$ ion, then it can be seen that the quadrupole splitting observed for the $Fe^{III}$ compounds reflects the distortion deduced by Babel from his X-ray data. This correlation is further evident in the observation that the $\Delta E_Q$ values given in Table III for $NiFeF_6Cs$ and $MnFeF_6Cs$ reflect the increased distortion found by Babel for $MnFeF_6Cs$ ($x = 0.318$) as compared to $NiFeF_6Cs$ ($x = 0.314$).

As would be expected for the 3*d* transition metal ions involved (*12*), spin only magnetic behavior was observed (>150 K) for the materials $MnCrF_6A$ (A = Rb, Cs, Tl), $NiFeF_6A$ (A = Rb, Cs), $MgFeF_6A$ (A = Cs, Tl), and $MnFeF_6Cs$. The $C_M$ values measured for the samples $FeCrF_6A$ (A = Rb, Cs, Tl), and $FeVF_6A$ (A = Rb, Cs) deviate significantly from the spin-only values and may reflect the effects of spin-orbit coupling associated with the $Fe^{II}$ and $V^{III}$ ions (*12*).

It has been shown (*10*) that the structure of the modified pyrochlores is such that the sign and magnitude of the Weiss constant is determined by first neighbor exchange interactions. It was also shown that the large values of $-\theta/T_0$ observed are a consequence of a transition metal ion lattice with face centered cubic symmetry in which exchange forces other than first-neighbor interactions are very weak.

Starting with the knowledge that the sign and magnitude of $\theta$ is determined by first-neighbor interactions, one can rationalize the relative magnitudes of the $\theta$ values in Table II by assuming that Goodenough's superexchange rules (*8*) for 180° cation–anion–cation interactions apply also to the ~137° interactions found in the network of corner sharing octahedra in the modified pyrochlore structure. Because of the random distribution of magnetic ions on the sites 16*c* in the materials $M^{II}M^{III}F_6A$, there will be interactions involving the cation pairs ($M^{II}$–$M^{III}$), ($M^{II}$–$M^{II}$), and ($M^{III}$–$M^{III}$). For the materials in Table II that contain the ion pairs ($Mn^{II}$, $Cr^{III}$), ($Fe^{II}$, $Cr^{III}$), and ($Fe^{II}$, $V^{III}$), Goodenough's rules predict a moderate ferromagnetic term for the interaction ($M^{II}$–F–$M^{III}$), a weak antiferromagnetic term for the interaction ($M^{III}$–F–$M^{III}$), and a strong antiferromagnetic term for the interaction ($M^{II}$–F–$M^{II}$). For the remaining materials of Table II strong antiferromagnetic terms are predicted for all first-neighbor exchange interactions between magnetic ions. It can be seen from Table II that the $\theta$ values of those materials

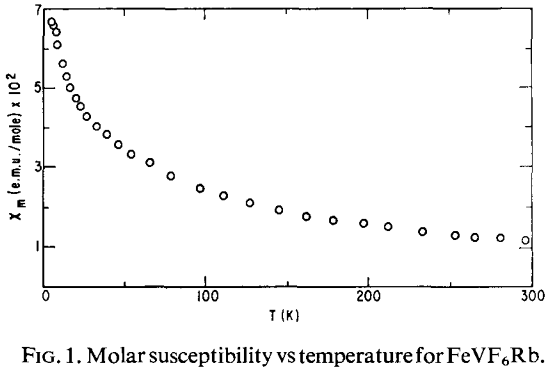

FIG. 1. Molar susceptibility vs temperature for $FeVF_6Rb$.

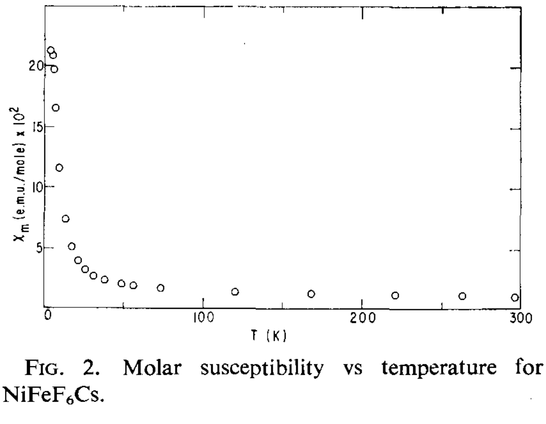

FIG. 2. Molar susceptibility vs temperature for $NiFeF_6Cs$.

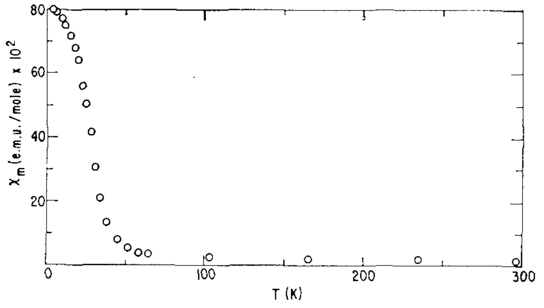

FIG. 3. Molar susceptibility vs temperature for $MnFeF_6Cs$.

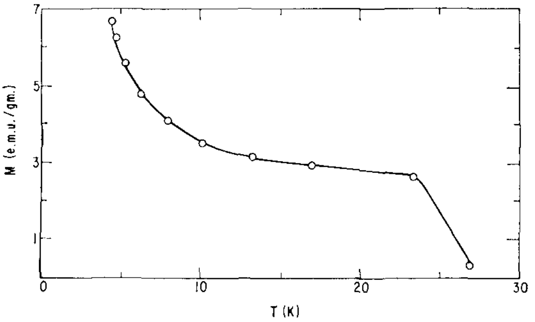

FIG. 4. Remanent field magnetization vs temperature for $MnFeF_6Cs$.

predicted to have both antiferromagnetic and ferromagnetic first-neighbor interactions are ~1/3 to 1/2 the magnitude of the $\theta$ values determined for materials predicted to have only strong antiferromagnetic interactions. That is, since $\theta$ represents the sum of the first-neighbor interactions in the modified pyrochlores, the combination of positive and negative exchange terms of comparable magnitude results in a lower magnitude of $\theta$ for the materials $Fe^{II}Cr^{III}F_6A$, $Fe^{II}V^{III}V_6A$, and $Mn^{II}Cr^{III}F_6A$ relative to the $\theta$ values of the remaining materials for which the sum consists of negative terms only.

The general features of the magnetic behavior of some of the materials in Table II are worth noting. The shape of the $\chi$ vs $T$ curves for the samples $FeCrF_6A$ and $FeVF_6A$ suggests an antiferromagnetic transition at low temperatures (~5 K). The curve for $FeVF_6Rb$ is typical and is shown in Fig. 1. The presence of a transition in $FeCrF_6Rb$ and $FeVF_6Rb$ has been confirmed by the appearance of a broad unresolved magnetic hyperfine pattern in the Mossbauer spectra obtained at the transition temperatures estimated from the $\chi$ vs $T$ plots.

A weak magnetization was found at low temperatures for the materials $NiFeF_6A$. The $\chi$ vs $T$ curve for $NiFeF_6Cs$ shown in Fig. 2 is typical, and the estimated transition temperature of 7 K corresponds to the temperature at which a magnetic hyperfine pattern was observed in the Mossbauer spectra. A weak magnetization was also observed in $MnFeF_6Cs$ for which was measured (4.2 K) a saturation moment of 19.7 emu/g (0.63 unpaired electrons per magnetic ion). The $\chi$ vs $T$ curve and remanent field magnetization curve are reproduced in Figs. 3 and 4. The transition temperature of 26 K was also observed in the low-temperature Mossbauer spectra. Since the exchange interactions in the materials $NiFeF_6A$ and $MnFeF_6Cs$ are expected to be antiferromagnetic, the low-temperature data suggest the possibility that these materials may have canted antiferromagnetic structures below their transition temperatures.

Additional studies are certainly required to characterize the nature of the ordered state in the above materials, and we are continuing our investigation of these materials to that end.

## Acknowledgment

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