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IONIC AND MAGNETIC ORDERING IN FIRST ROW TRANSITION METAL FLUORIDES

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Abstract Divalent fluorides of first row transition metals, MF_2(rutile) and KMF_3(perovskite) have provided the means for studying 90, 135, and 180° magnetic superexchange interactions. Their limitation has been that interactions are between identical ions and, consequently, are usually antiferromagnetic. Recently, M^{2+}-M^{3+} ionic ordering has been established in $LiM^{II}M^{III}F_6$(trirutile) and $KM^{II}M^{III}F_6$(tetragonal bronze). These structures are rutile like and perovskite like respectively and their ionic order makes them interesting candidates for studying superexchange interactions between dissimilar ions. These interactions are often ferromagnetic.

INTRODUCTION

Divalent fluorides of first-row transition metals MF_2[1] and KMF_3[2,3,4] (M = V, Mn, Fe, Co, Ni, Zn) crystallize in the rutile and perovskite lattices, respectively. For M = Cr and Cu, the rutile lattice is distorted from tetragonal to monoclinic,[5,6] and the perovskite lattice from cubic to tetragonal.[7] In both structures, M^{2+} ions are subjected to an octahedral crystal field; hence, 3d energy states are separated into two levels: a lower level which is threefold degenerate (t_{2g}), and an upper level which is twofold degenerate (e_g). In the rutile compounds, small crystal distortions remove some of the degeneracy. The important M-F-M magnetic interactions in rutile are

approximately 90° (J_1) and 135° (J_2); and in perovskite, they are 180°. One shortcoming of the above systems is that all M-F-M superexchange interactions are between like ions; consequently, the important interactions are almost without exception antiferromagnetic.

According to qualitative rules proposed by Goodenough[8] and Kanamori,[9] 90, 135, and 180° M-X-M' interactions (where M and M' may be different transition-metal ions and X is a closed-shell anion) can be predicted to be antiferromagnetic (ferrimagnetic) or ferromagnetic, depending upon electronic configurations and crystal field symmetry. In an octahedral field, for example, the 180° interactions [1/2 filled e_g-empty e_g] and [1/2 filled t_{2g}-empty t_{2g}] are both predicted to be ferromagnetic. What has long been needed are ionically ordered fluoride structures in which first-row transition metal ions (M,M') can be substituted systematically so that antiferromagnetic, ferrimagnetic, or ferromagnetic ordering are clearly and quantitatively demonstrated. The fluoride analogs of trirutile[10,11] and tetragonal tungsten bronze bronze[12-16] are structures which fulfill these criteria.

THE TRIRUTILE COMPOUNDS

The mineral tapiolite ($FeNb_{0.2}Ta_{1.8}O_6$) and numerous synthetic oxides of the general formula $M^{II}M^{V}_2O_6$, which crystallize in a trirutile lattice, were found to belong to space group $P4_2/mnm$ (D^{14}_{4h}).[17] The trirutile fluorides ($LiM^{II}M^{III}F_6$) have also been reported to belong to space group $P4_2/mnm$ (D^{14}_{4h}).[18-21] This implies that Li^+ ions occupy (2a) lattice sites and that M^{2+} and M^{3+} ions randomly occupy (4e) sites. The crystal structures of the

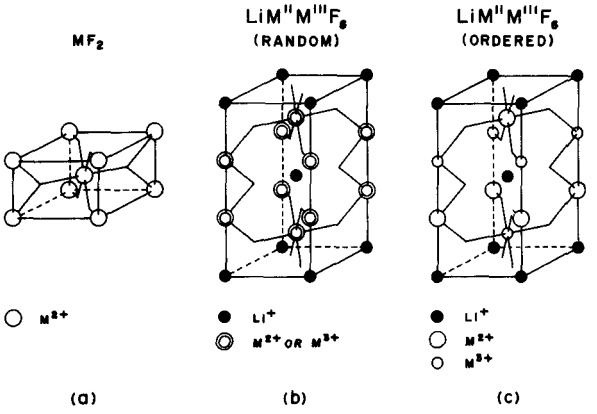

FIGURE 1. (a) rutile structure (b) random trirutile structure (c) ordered trirutile structure

alloy $Li_{0.75}Zn_{0.25}(Zn_{1.25}Cr_{0.75})F_6$[21] and LiV_2F_6[10] have both been reported to belong to this space group; however, neither of these materials is representative of $LiM^{II}M^{III}F_6$ compounds in general.

Figure 1a shows the location of cations in rutile (MF_2); Figure 1b illustrates trirutile ($LiM^{II}M^{III}F_6$) in which M^{2+} and M^{3+} ions are random; and Figure 1c illustrates the most likely ordered arrangement of M^{2+} and M^{3+} ions within the trirutile lattice. In these structures, the F^- ions are located between neighboring cations such that ~90° M-F-M interactions occur between nearest neighbors, and ~135° M-F-M interacions occur between second nearest neighbors. In MF_2 (Figure 1a), each M^{2+} ion has two nearest neighbors and eight second nearest neighbors. In $LiM^{II}M^{III}F_6$ (Figure 1b), if M^{2+} and M^{3+} are paramagnetic ions, then each paramagnetic ion has only one nearest neighbor and four second nearest

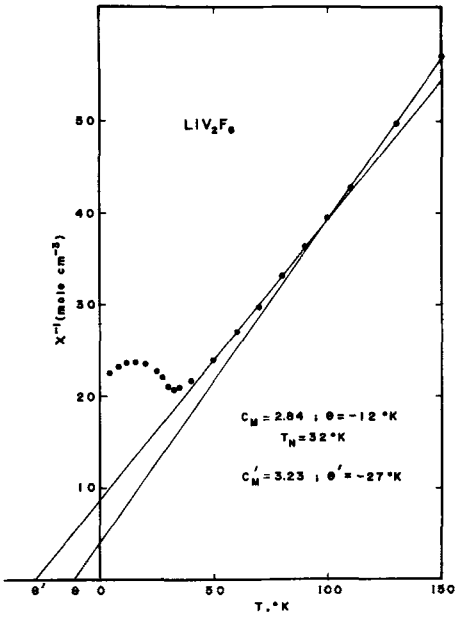

FIGURE 2. Inverse magnetic susceptibility versus temperature for LiV_2F_6. Data from reference 10.

neighbors which are also paramagnetic. If M^{2+} and M^{3+} are ionically ordered as illustrated in Figure 1c, the nearest neighbor and four second nearest neighbors to an M^{2+} ion are M^{3+} ions, and vice versa. This ordered structure was also proposed for $LiFe_2F_6$ by Greenwood, Howe, and Menil[22] based on Mossbauer studies. If this ionic ordering is true for the $LiM^{II}M^{III}F_6$ compounds in general, it should then be possible to study many 90° and 135° M^{2+}-F^--M^{3+} interactions.

The inverse magnetic susceptibility versus temperature of LiV_2F_6, is shown in Figure 2. This plot displays two linear regions. The high-temperature paramagnetic region extends down to ~100 K and the linear

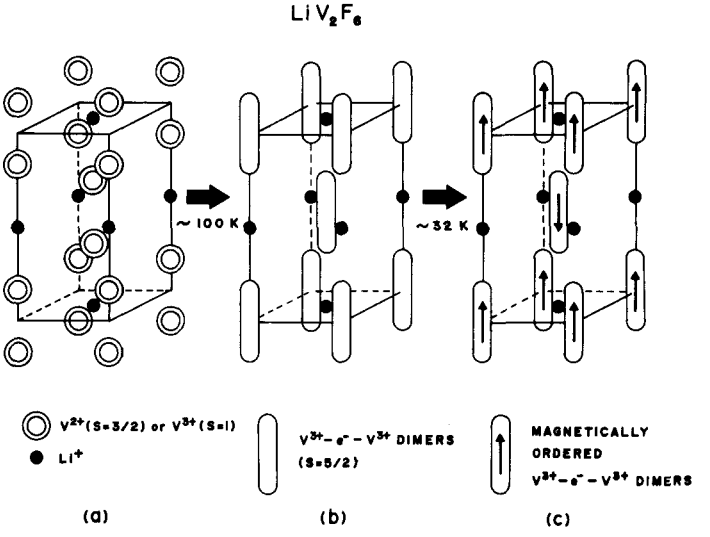

FIGURE 3. Magnetic ordering mechanism for LiV_2F_6.

region between ~100 and 50 K can be explained as a second paramagnetic region if $|J_1| >> |J_2|$. Under these conditions magnetic coupling between nearest neighbors occurs first, forming dimers. The magnitude of C_M' is greater than C_M, supporting the conclusion that J_1 is positive (ferromagnetic). Three-dimensional long-range ordering sets in at a lower temperature where the strength of J_2 is sufficient to overcome kT. From the value of θ (which is negative) we conclude that second nearest neighbor interactions are antiferromagnetic (J_2 is negative). The suceptibility passes through a maximum at 32 K, and no spontaneous magnetic moment was observed below this temperature, further supporting the above conclusions. The two-step ordering mechanism for LiV_2F_6 is dramatized in Figure 3.

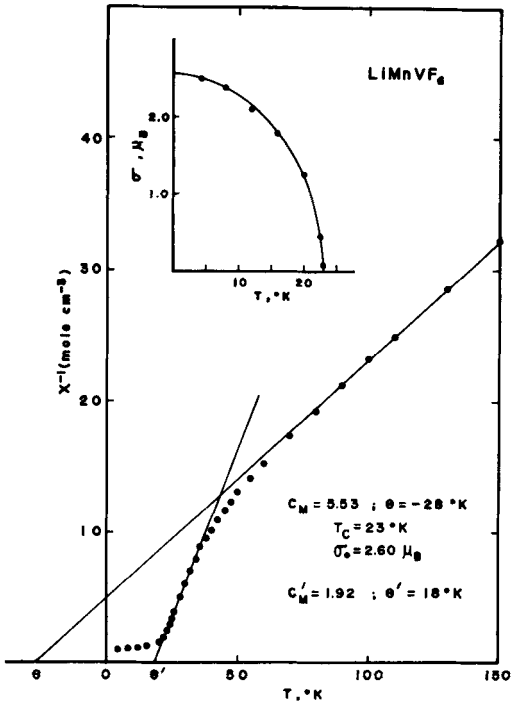

FIGURE 4. Inverse magnetic susceptibility versus temperature for $LiMnVF_6$. Data from reference 11.

The inverse susceptibility versus temperature of $LiMnVF_6$ is shown in Figure 4. The high temperature region (70–300 K) is paramagnetic, with $C_M(exp) = 5.53$. This value corresponds favorably with a spin-only value C_M (calc) = 5.38. We assume, therefore, as we did for LiV_2F_6,[10] that the orbital moment of V^{3+} is quenched, and the $LiMnVF_6$ is a spin-only system. Figure 4 shows that $LiMnVF_6$ also has a second paramagnetic region between 20 and 40 K with $C'_M(exp) = 1.92$. Again, this value corresponds favorably

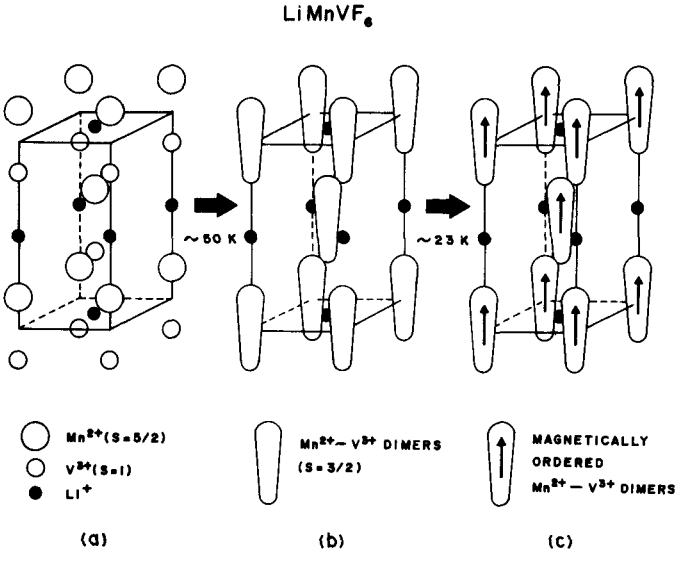

FIGURE 5. Magnetic ordering mechanism for $LiMnVF_6$.

with a paramagnetic substance of S = 3/2 for which C'_M (calc) = 1.88. Therefore, we conclude that magnetic coupling between nearest neighboring Mn^{2+}-V^{3+} pairs commences near 50 K forming dimers with a ground state that is antiferromagnetic (ferrimagnetic), and J_1 is negative. From the sign of θ' we see that J_2 is positive, and second nearest neighbor interactions are ferromagnetic. In its magnetically ordered state, one would predict that $LiMnVF_6$ could have a spontaneous moment as large as 3 μ_B. The measured moment, extrapolated to zero field and 0 K has a value of 2.6 μ_B. It is a resonable assumption, therefore, that $LiMnVF_6$ is ionically ordered, and its space group is most likely $P4_2nm$ (C^4_{4v}). The two-

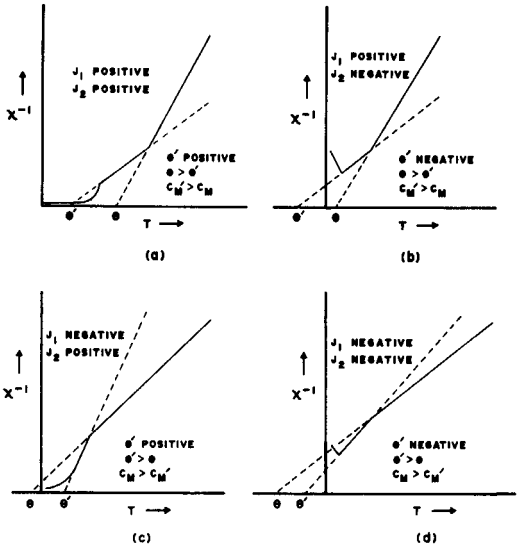

FIGURE 6. The four possibilities for two paramagnetic regions in trirutile.

step magnetic ordering mechanism for $LiMnVF_6$ is illustrated in Figure 5.

If the condition $|J_1| >> |J_2|$ exists in $LiM^{II}M^{III}F_6$, there should be two paramagnetic regions, and the resulting χ^{-1} versus T plots possible for the four combinations of signs are illustrated in Figure 6.

In Figure 6a, both J_1 and J_2 are positive. Here, θ' must be positive and θ more positive. Obviously $C_M' > C_M$. In the magnetically ordered state, all atomic moments should be parallel, and there should be a large spontaneous magnetic moment.

In Figure 6b, J_1 is positive and J_2 is negative, as was found to be the case for LiV_2F_6 (Figure 2). In Figure 6c, J_2 is negative and J_1 is positive, which is the case for $LiMnVF_6$ (Figure 5).

Finally, Figure 6d illustrates the case where both J_1 and J_2 are negative. Here Θ' should be negative and Θ more negative; $C_M > C'_M$; and there should be no spontaneous moment in the magnetically ordered state.

Most combinations of divalent and trivalent first-row transition metal fluorides (which are thermodynamically compatible) will combine with LiF to form the trirutile lattice with composition $LiM^{II}M^{III}F_6$.[10,11,18-26] Noted exceptions are $LiMnCrF_6$ and $LiMnFeF_6$, which form hexagonal lattices of a Na_2SiF_6 type;[23] the $LiCuM^{III}F_6$ phases, which form solid solutions in rutile lattices;[19] and the $LiCrM^{III}F_6$ phases, which form a structure yet to be determined.[27]

TABLE I. Spin-Only Ions in the Trirutile Lattice

	V^{2+}	Mn^{2+}	Ni^{2+}
V^{3+}	d^2-d^3	d^2-d^5	d^2-d^8
Cr^{3+}	d^3-d^3	does not form trirutile	d^3-d^8
Fe^{3+}	not thermodynamically compatible	does not form trirutile	d^5-d^8

The question then arises: what combinations of M^{2+} and M^{3+} ions which are chemically compatible, spin only, and form the trirutile lattice might also fulfill the condition $|J_1| >> |J_2|$? Table I lists the possible combinations of spin-only ions and their electronic configurations.

It has been established that the above criteria are met in LiV_2F_6 and $LiMnVF_6$. Recently, we prepared a

trirutile phase by combining VF_2, CrF_3, and LiF ($LiVCrF_6$). Although this material has not been characterized, we predict that J_1 will be greater in magnitude than J_2, as in VF_2 ($J_1 \sim -11$ k, $J_2 \sim -1$ k).[28] The three compounds $LiNiVF_6$, $LiNiCrF_6$, and $LiNiFeF_6$ have been reported to crystallize in the trirutile lattice,[19,23,24] and the magnetic susceptibilities of $LiNiCrF_6$ and $LiNiFeF_6$ have been measured from 90 to 400 K.[19] No long-range ordering temperature was observed for $LiNiFeF_6$ above 90 K, but a plot of χ^{-1} versus T clearly suggests the existence of two paramagnetic regions. This implies $|J_1| \gg |J_2|$, and the projected Θ and Θ' values indicate that J_1 is negative and J_2 is positive (Figure 6c). The plot of χ^{-1} versus T reported for $LiNiCrF_6$ is linear from 400 down to 90 K, with no apparent magnetic ordering in this range. A Θ value of ~ -40 K, however, indicates some relatively strong antiferromagnetic interactions in this compound. No magnetic data are available for $LiNiVF_6$. These three trirutile compounds are also presently under investigation in our laboratory.

THE TETRAGONAL TUNGSTEN BRONZE PHASES

The fluoride perovskites, KMF_3, also have a structural counterpart in which ~180° M^{2+}–F^-–M^{3+} magnetic interactions may be studied. This is the fluoride analog of tetragonal tungsten bronze with composition $KM^{II}M^{III}F_6$. Recently, Banks, Nakajima and Williams[12] determined the crystal structure of $K_{0.54}Mn_{0.54}Fe_{0.46}F_3$, which belongs to space group $P4_2bc$ (C_4^8). In this structure, the transition metal ions occupy three distinct lattice sites, as illustrated in Figure 7. There are three kinds of ~180°

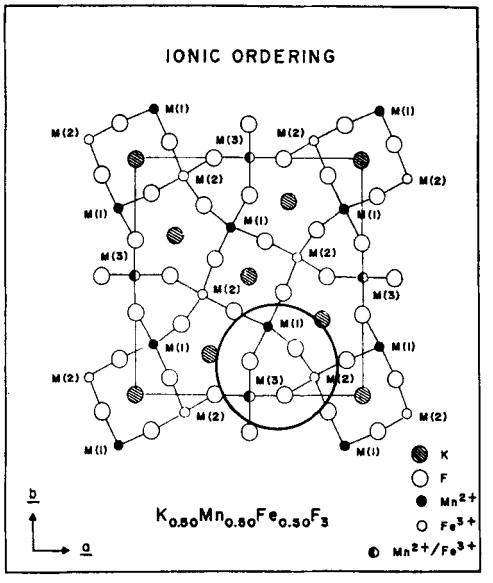

FIGURE 7. Ionic ordering in $K_{0.50}Mn_{0.50}Fe_{0.50}F_3$. From reference 12.

magnetic interactions in $KM^{II}M^{III}F_6$: M^{2+}-F^--M^{2+}, M^{3+}-F^--M^{3+}, and M^{2+}-F^--M^{3+}; for a perfectly ordered crystal, the relative number of these interactions is 1:1:13, respectively. Each M^{2+} ion located on an M(3) site has two M^{2+} nearest neighbors on M(1) sites, two M^{3+} nearest neighbors on M(2) sites, and two M^{3+} nearest neighbors on M(3)sites. Since an analogous conditions hold true for each M^{3+} ion located on M(3) sites, the structure consists largely of linear trimers of M^{2+} ions and trimers of M^{3+} ions which lie in the ab plane. One feature of the $KM^{II}M^{III}F_6$ compounds not present in KMF_3 is constraints to magnetic ordering. One of these constraints is indicated

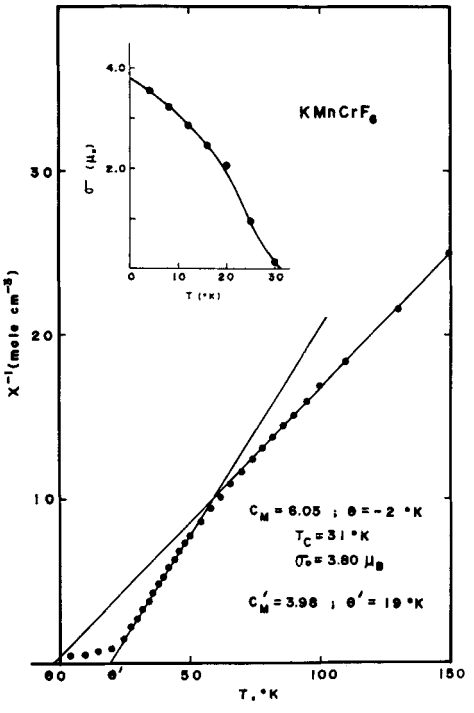

FIGURE 8. Inverse magnetic susceptibility versus temperature for $KMnCrF_6$. Data from reference 16.

by the circle in Figure 7. Although single crystal X-ray structure determinations have not yet been possible for most of the $KM^{II}M^{III}F_6$ compounds studied, magnetic properties in some cases clearly reflect ionic ordering (and magnetic ordering) trends.

The inverse magnetic susceptibility of $KMnCrF_6$ versus temperature over the range 0 to 150 K is illustrated in Figure 8. Of interest in this figure are the two linear regions. The upper region is the usual high-temperature paramagnetic region. The second linear region is also a paramagnetic region, which is possible because of the special condition $|J_{2+,2+}| \sim |J_{3+,3+}| \gg |J_{2+,3+}|$. Each

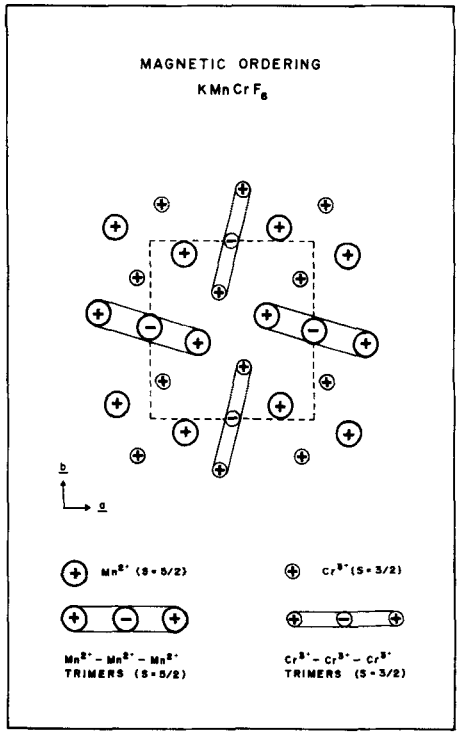

FIGURE 9. Magnetic ordering in $KMnCrF_6$. From reference 16.

Mn^{2+} ion on M(3) sites forms magnetically ordered trimers with its two nearest neighboring Mn^{2+} ions on M(1) sites. These interactions are antiferromagnetic, hence, the three Mn^{2+} ions, each with a spin of 5/2, form a trimer with a resultant spin of 5/2. The same occurs for each Cr^{3+} ion on an M(3) site, which forms a magnetically ordered trimer with its two nearest neighboring Cr^{3+} ions on M(2) sites, but with a resultant spin of 3/2. With the formation of

magnetically ordered trimers, the number of paramagnetic species with S = 5/2 is reduced from ten to six; likewise, the number with S = 3/2 is also reduced from ten to six. This feature is reflected in the Curie constants such that $C'_M = 0.6\ C_M$. All of the experimental values for $KMnCrF_6$ correspond reasonably well with calculated values. The magnetically ordered structure of $KMnCrF_6$ is dramatized on Figure 9. The calculated spontaneous magnetic moment for this arrangement is 4.8 μ_B and the observed moment was 3.8 μ_B.

The tetragonal bronze lattice forms for most thermodynamically compatible combinations of divalent and trivalent first-row transition metal fluorides when reacted 1:1:1 with KF. Exceptions are the $KNiM^{III}F_6$ phases,[29] which form the modified pyrochlore structure ($KNiFeF_6$ may form the bronze structure), and the $KCrM^{III}F_6$ phases,[27] which form a hexagonal lattice. As in trirutile, the orbital moment of $V^{3+}(d^2)$ is totally quenched. Table II lists the possible combinations of spin-only ions that form the tetragonal bronze structure and their electronic configurations.

TABLE II. Spin-Only Ions Which Form the Tetragonal Bronze Lattice.

	V^{2+}	Mn^{2+}	Ni^{2+}
V^{3+}	d^2-d^3	d^2-d^5	does not form tetragonal bronze structure
Cr^{3+}	d^3-d^3	d^3-d^5	does not form tetragonal bronze structure
Fe^{3+}	not thermodynamically compatible	d^5-d^5	d^5-d^8

CONCLUSIONS

Concomitant ionic ordering makes $LiM^{II}M^{III}F_6$ and $KM^{II}M^{III}F_6$ interesting candidates for studying magnetic superexchange interactions between dissimilar paramagnetic ions. Other features that make these compounds attractive for quantitative studies include: (1) magnetic ordering occurs between 4.2 and 300 K in all of these materials, (2) different magnetic interactions can often be separated thermally, and (3) many of the compounds of interest are spin-only.

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