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Lower Valence Fluorides of Vanadium, Chromium, and Iron $A_X MF_3$ (A = K, Rb, or Cs: M = V. Cr, or Fe; and x=0 To 1).

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LOWER VALENCE FLUORIDES OF VANADIUM, CHROMIUM, AND IRON A_xMF_3 (A = K, Rb, or Cs; M = V, Cr, or Fe; AND x = 0 TO 1).

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Abstract Some of the more interesting aspects of the A_xMF_3 compounds are their tendencies to display small lattice distortions, superlattice structures, and composition-dependent properties. All of these phenomena are a result of ionic ordering, of which there are three kinds (1) ordering of partially filled A^+ sites, (2) M^{2+}-M^{3+} electronic ordering, and (3) cooperative Jahn-Teller ordering. Hexagonal tungsten bronze-like phases (A = K, Rb, or Cs and x ~ 0.2-0.3), and modified pyrochlore phases (A = Rb or Cs, and x ~ 0.4-0.6) crystallize for M = V, Cr, and Fe. Tetragonal tungsten bronze-like phases form in K_xVF_3 (x = 0.45-0.56) and K_xFeF_3 (x = 0.40-0.60), but a new hexagonal phase forms in K_xCrF_3. In an octahedral crystal field V^{3+} and Cr^{2+} are Jahn-Teller ions, and their presence has a profound effect on the lattice that is formed. Comparisons are made between the A_xVF_3, A_xCrF_3, and A_xFeF_3 systems.

INTRODUCTION

The phase systems A_xMF_3 (A = K, Rb, or Cs and M = V,[1,2] Cr,[3] or Fe[4,5]) were reported several years ago. In each system, the hexagonal bronze structure spans the composition x ~ 0.2 to 0.3, and the modified pyrochlore structure forms for A = Rb or Cs at x ~ 0.4 to 0.6. The tetragonal bronze structure exists for K_xVF_3 (x = 0.45 to

0.56) and K_xFeF_3 (x = 0.40 to 0.60), but a yet undetermined hexagonal structure forms for K_xCrF_3 (x ~ 0.4 to 0.6).

We have recently completed a more detailed characterization of the A_xVF_3 systems,[6,7,8] and have begun examining the A_xCrF_3 systems.[9] Comparisons of work done on the V, Cr, and Fe systems reveal certain common characteristic for the A_xMF_3 compounds. These include: small crystal distortions, superlattice structures, and composition-dependent properties. Furthermore, these mixed divalent-trivalent compounds are interesting as a group because of the unique electronic structures of the paramagnetic ions (Table I). In the octahedral crystal field provided by fluoride ions, V^{3+} and Cr^{2+} become Jahn-Teller ions, but neither of the Fe ions is a Jahn-Teller ion. These features are reflected in the structures and in many of the physical properties of the A_xMF_3 compounds.

TABLE I. Electronic Configurations in Octahedral Coordination

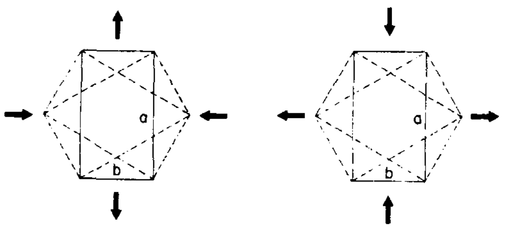
V^{2+}	$(t_{2g})^3$	
V^{3+}	$(t_{2g})^2$	(weak Jahn-Teller ion)
Cr^{2+}	$(t_{2g})^3(e_g)$	(strong Jahn-Teller ion)
Cr^{3+}	$(t_{2g})^3$	
Fe^{2+}	$(t_{2g})^4(e_g)^2$	
Fe^{3+}	$(t_{2g})^3(e_g)^2$	

THE HEXAGONAL BRONZE-LIKE FLUORIDES

In the hexagonal bronze fluorides, observable superlattice X-ray reflections are associated with ordering of A^+ ions in half-filled, two-thirds filled, and three-fourths filled sites. These correspond to stoichiometric compounds with formulas AM_6F_{18}, $A_2M_9F_{27}$, and AM_4F_{12}, respectively, and are optimum near compositions $x = 0.167$, 0.222, and 0.250, respectively. In some cases, several sets of superlattice X-ray reflections are present for a single sample. The cell dimensions of the AM_6F_{18} superstructure are the same as those of the parent MF_3 unit cell (which is sometimes distorted from hexagonal to orthorhombic), but AM_6F_{18} is body-centered, whereas, the parent lattice is primitive. The *a* and *b* dimensions of $A_2M_9F_{27}$ are the same as the parent lattice but the *c* dimension is increased from two layers to three layers, and the structure is base-centered. AM_4F_{12} is primitive, but its dimensions are much larger than the others with *a* doubled, *b* tripled, and *c* doubled. The approximate dimensions of the parent lattice and the three modulated structures are shown in Table II.

Table II. Orthorhombic Unit Cell Dimensions of the Parent Lattice and the of Modulated Structures Which Form in the Hexagonal Bronze-like A_xMF_3 Compounds

Parent Lattice	Primitive Ortho, 2 layers deep	*a* ~ 12.9 Å *b* ~ 7.4 Å *c* ~ 7.4 Å
AM_6F_{18}	A^+ Sites 1/2 Filled, Body Centered Ortho, 2 Layers Deep	*a* ~ 12.9 Å *a* ~ 7.4 Å *c* ~ 7.4 Å
$A_2M_9F_{27}$	A^+ Sites 2/3 Filled, Base Centered Ortho, 3 Layers Deep	*a* ~ 12.9 Å *b* ~ 7.4 Å *c* ~ 11.3 Å
AM_4F_{12}	A^+ Sites 3/4 Filled, Primitive Ortho, 4 Layers Deep	*a* ~ 25.8 Å *b* ~ 22.2 Å *c* ~ 15.0 Å



I FIRST KIND

$\frac{|a|}{\sqrt{3}\,|b|} > 1$

II SECOND KIND

$\frac{|a|}{\sqrt{3}\,|b|} < 1$

FIGURE 1. Two Possible kinds of distortion to the ortho-hexagonal unit cell.

Jahn-Teller distortions generate novel effects in the A_xVF_3 and A_xCrF_3 compounds, but there are several significant differences between the two Jahn-Teller ions in the hexagonal bronze-like fluorides. First, V^{3+} is a weak Jahn-Teller ion and Cr^{2+} is strong; second, one is a +3 ion the other a +2 ion; and third, the fraction of V ions which are V^{3+} is ~0.8 to 0.7, where the fraction of Cr ions which are Cr^{2+} is ~0.2 to 0.3.

Cooperative Jahn-Teller ordering can distort the ortho-hexagonal unit cell to orthorhombic in two ways as illustrated in Figure 1. The dimensions of the undistorted ortho-hexagonal unit cell are related to the hexagonal unit cell as follows: $|\underline{a}(\text{ortho})| = 3^{1/2}|\underline{a}(\text{hex})|$, b(ortho) = $\underline{b}$(hex), and $\underline{c}$(ortho) = $\underline{c}$(hex). It is possible to describe quantitatively the distortion present in a structure by defining a distortion ratio. We have defined this ratio for the ortho-hexagonal unit cell as $|\underline{a}|/3^{1/2}|\underline{b}|$. For a distortion of the first kind, the ratio is greater than unity, and if the distortion is of the second kind, the ratio is less than unity.

The distortion ratios for the three modulated structures observed in the V and Cr systems are shown in Table III. Some additional comments should be made. Both kinds of distortion are present in the V systems. In the Cs_xVF_3 system (at all compositions) and in the K_xVF_3 (for larger values of x) no modulated structures were formed; however, distortions of these compounds were always of the second kind. In the Cr systems the only kind of distortion observed is of the second kind. Although no modulated structures form for the K_xCrF_3 system, the Jahn-Teller effect distorts the lattice to monoclinic. In the Rb_xCrF_3 and Cs_xCrF_3 systems, it is possible by controlled synthesis to induce ordering of A^+ ions in partially filled sites (modulated structures), in which case the

TABLE III. Modulated Structures and their Distortion Ratios Observed in the A_xVF_3 and A_xCrF_3 Systems.

	AM_6F_{18}	$A_2M_9F_{27}$	AM_4F_{12}
K_xVF_3 (a)	1.007	1.006	-----
Rb_xVF_3 (a)	1.005	1.004	0.991
Cs_xVF_3 (a)	-----	-----	-----
$KxCrF_3$ (b)	-----	-----	-----
Rb_xCrF_3 (b)	1.000	0.978	0.980
Cs_xCrF_3 (b)	1.000	0.997	0.993

(a) Data from Reference 7; (b) Data from Reference 9 lattice is distorted to orthorhomibc (second kind), or to eliminate A^+ ordering in which case the lattice remains undistorted (hexagonal).

Although they are usually interdependent, there are three distinct types of ionic ordering possible in the hexagonal bronze-like A_xMF_3 compounds: (1) ordering of partially filled A^+ sites, (2) M^{2+}-M^{3+} electronic ordering, and (3) cooperative Jahn-Teller ordering. It has already been established that A^+ ordering is unique to each of the three modulated structures (Table II). It follows that since the M^{2+}/M^{3+} ratio is different for each of the three, M^{2+}-M^{3+} electronic ordering (if it is present) must also be unique in each case. From Table III we see that the distortion ratios for $RbCr_6F_{18}$ and $Rb_2Cr_9F_{27}$ are significantly different. Since cooperative Jahn-Teller ordering in the A_xCrF_3 compounds must be dependent on M^{2+}-M^{3+} electronic order, (because the Cr^{2+} ion is dilute) we conclude that electronic ordering is different in AM_6F_{18} and $A_2M_9F_{27}$. Similar arguments apply to $Rb_2V_9F_{27}$ and RbV_4F_{12}, in which case the distortion is of the first and second kind, respectively. We, therefore, have experimental evidence that M^{2+}-M^{3+} electronic ordering in AM_6F_{18}, $A_2M_9F_{27}$, and AM_4F_{12} is unique in each case. While the A^+ ordering and M^{2+}-M^{3+} electronic ordering should be the same in any given modulated structure, the Jahn-Teller distortion may be quite different for V and Cr. From Table III, the distortion in ACr_6F_{18} differs from that in AV_6F_{18}, and the distortion in $A_2Cr_9F_{27}$ is quite different from that in $A_2V_9F_{27}$.

From Table III, one can conclude that all three types of ionic ordering are present in AV_6F_{18}, $A_2V_9F_{27}$, AV_4F_{12}, $A_2Cr_9F_{27}$, and ACr_4F_{12}. ACr_6F_{18} displays only ordering of partially filled A^+ sites, but must also have some form of Cr^{2+}-Cr^{3+} electronic ordering. Although it is not shown in Table III, some combinations of ionic ordering are present even if the modulated structures are absent. These include K_xCrF_3 in which both Cr^2-Cr^{3+} electronic ordering and cooperative Jahn-Teller ordering are present at all compositions; and Cs_xVF_3 (at all compositions) and K_xVF_3 (for larger x), in which only cooperative Jahn-Teller ordering is present.

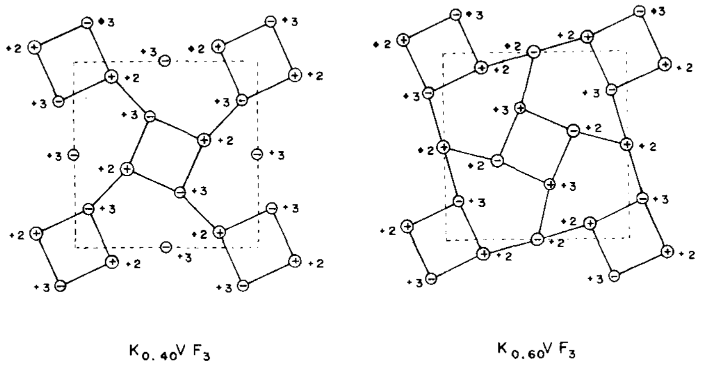
More subtle evidence of M^{2+}-M^{3+} electronic ordering in the hexagonal bronze-like fluorides is evident from the low temperature magnetic data. In the A_xVF_3 systems, for example, a sizeable induced magnetic moment is found in $A_2V_9F_{27}$.[7] In samples of the Rb_xCrF_3 system, consisting primarily of $RbCr_6F_{18}$ or $Rb_2Cr_9F_{27}$, magnetic coupling occurs in steps.[9] Each Cr^{2+} ion first couples with one of its nearest neighboring Cr^{3+} ions forming a ferromagnetic dimer, followed at lower temperatures by three-dimensional long-range (antiferro) magnetic ordering. Both of these effects reflect the fact that M^{2+} and M^{3+} ions occupy specific lattice sites in these structures.

Ionic ordering in the hexagonal bronze-like fluorides must depend to a large extent on how the materials are prepared. It is likely that under the proper conditions A^+ ordering and Fe^{2+}-Fe^{3+} electronic ordering could be induced in the A_xFeF_3 compounds. In the Rb_xCrF_3 compounds reported, approximately 90% of each sample was ionically ordered (90% orthorhombic) and 10% remained hexagonal; in the Cs_xCrF_3 compounds, the samples prepared were approximately 50% orthorhombic and 50% hexagonal. Ordering could be optimized if annealing temperatures were known, and in some instances, ordering could be selectively eliminated---that is, limited to one or two of the three types by using quenching techniques.

THE TETRAGONAL BRONZE-LIKE FLUORIDES

We believe that K_xVF_3 ($x = 0.45$ to 0.56) is the only candidate sofar that may crystallize in a tetragonal bronze structure with concomitant ionic ordering. The tetragonal bronze structure most probably does not form for K_xCrF_3 because Cr^{2+} is a strong Jahn-Teller ion. None of the three types of ionic ordering described in the previous section has been verified for the tetragonal bronze fluorides of Fe.[4,5] No evidence of ordering of partially filled K^+ sites was found in the tetragonal bronze fluorides of vanadium, although it is likely that the preference for pentagonal-shaped sites over square-shaped sites reported by Magneli[10] for K_xWO_3 is applicable to the fluorides as well. There are also no Jahn-Teller distortions in the tetragonal K_xVF_3 phase.

Banks, Nakajima, and Williams[11] reported that tetragonal $K_{0.54}Mn_{0.54}Fe_{0.46}F_3$ belongs to space group $P4_2bc$ (C_{4v}^8) and the two transition metal cations occupy three distinct octahedral sites. In this compound, one set of 8(c) Wyckoff positions are occupied solely by Mn^{2+} ions, a second set of 8(c) positions by Fe^{3+} ions, and 4(b) positions are occupied by either Mn^{2+} or Fe^{3+}. The ionic ordering is such that each Mn^{2+} ion located on the first set of 8(c) sites has five nearest neighboring Fe^{3+}



$K_{0.40}VF_3$ $K_{0.60}VF_3$

FIGURE 2. Two mechanisms for magnetic ordering in tetragonal K_xVF_3 at theoretical compositions $x = 0.4$ and 0.6

ions which are located on the second set of 8(c) sites, and vice versa, the sixth nearest neighbor is located on a 4(b) site and may be either Mn^{2+} or Fe^{3+}.

The magnetic properties[6] of K_xVF_3 can be explained on the basis of this ionic order. In fact, there is supporting evidence[6] that $P4_2bc$ (C^8_{4v}) is the correct space group over its entire composition span. One additional conclusion which is important at composition $x = 0.50$ is: ions on 4(b) sites which are random within the ab plane are ordered along the c direction.

The general conditions which appear to be met if the above V^{2+}-V^{3+} electronic ordering trends are true are: the number of V^{2+}-V^{3+} nearest neighbors are maximized, and the number of V^{2+}-V^{2+} and V^{3+}-V^{3+} nearest neighbors are minimized. Assuming perfect ordering at ideal compositions $x = 0.4$, 0.5, and 0.6, the relative number of

V^{2+}-V^{2+}, V^{3+}-V^{3+}, and V^{2+}-V^{3+} near neighbors are 0:3:12, 1:1:13, and 3:0:12, respectively.

From the rules of Goodenough[12] and Kanamori,[13] one would predict that the superexchange interactions for V^{2+}-V^{2+}, V^{3+}-V^{3+}, and V^{2+}-V^{3+} should all be antiferromagnetic. The magnetic susceptibility data are consistent with these predictions with Θ values ranging from −55 to −96 K and T_N values nearly constant at 45 to 50 K.[6] If we make a simple assumption that for magnetic interactions within the ab plane V^{2+}-V^{2+} > V^{2+}-V^{3+} > V^{3+}-V^{3+}, we can justify two magnetic ordering mechanisms for the ideal compositions $x = 0.4$ and $x = 0.6$. These two mechanisms are illustrated in Figure 2 and the justification of each depends on the assumption that V^{2+}-V^{3+} electronic ordering on 8(c) sites is independent of composition. In each of the two mechanisms the magnetically ordered structure consists of square columns of ferrimagnetically ordered V^{2+}-V^{3+} ions on 8(c) sites. At $x = 0.4$, coupling between square columns is such that their moments are additive; at $x = 0.6$, coupling between square columns is such that the ferrimagnetic moments of nearest neighboring squares columns are antiparallel. At some critical composition there should be a change from the first mechanism to the second. The magnetic measurements revealed that in a field of 10 kG a magnetic moment of magnitude x μ_B was observed in samples of composition $x = 0.45$, 0.4625, and 0.4750.[6] Above $x = 0.4875$, the magnetic moment is approximately zero. The experimental magnetic data, therefore, supports the assumption that V^{2+}-V^{3+} electronic ordering exists in the tetragonal bronze-like phase K_xVF_3.

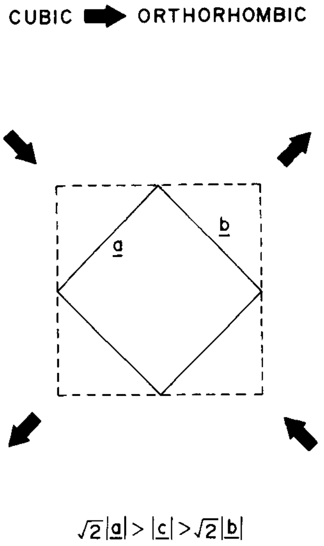


FIGURE 3. Distortion of the cubic modified pyrochlore structure to orthorhombic symmetry

THE MODIFIED PYROCHLORES

It has frequently been observed[14] that, although the cubic modified pyrochlore structure forms for many combinations of M^{2+}, M^{3+} ions, only when M^{2+} and M^{3+} are different oxidation states of the same element does the structure distort to lower symmetry. Since the distortion occurs in the Fe systems as well as V and Cr, we conclude that in Fe it is a consequence of simple M^{2+}-M^{3+} electronic ordering. It is easy to propose a model for this kind of ionic ordering since in this structure rows of M^{2+}, M^{3+} ions lie along the six <110> directions. In any proposed model for M^{2+}-M^{3+} electronic ordering, we should maximize the number of M^{2+}-M^{3+} nearest neighbors and minimize the number of M^{2+}-M^{2+} and M^{3+}-M^{3+} nearest neighbors. If at the composition x = 0.50 we arrange the ions in four of the six ⟨110⟩ directions so they are alternately M^{2+}-M^{3+}, then the ions in the two remaining ⟨110⟩ directions will consist of rows of M^{2+} ions along one direction and rows of M^{3+} ions along the other. For example, if we alternate the two ions along the [101], [$\bar{1}$01], [011], and [0$\bar{1}$1] directions, then we will have created rows of M^{2+} ions long the [110] direction and rows of M^{3+} along the [$\bar{1}$10] direction. In this ordered arrangement, the relative number of M^{2+}-M^{2+}: M^{3+}-M^{3+}: M^{2+}-M^{3+} nearest neighbors is 1:1:4, respectively. The rows of M^{2+} ions and M^{3+} ions will ultimately distort the cubic unit cell to orthorhombic symmetry, as illustrated in Figure 3. In this figure, the dashed lines represent the cubic unit cell and the solid lines marked a and b represent the new unit cell before distortion to orthorhombic symmetry. Since the rows of M^{2+} ions and M^{3+} ions lie along the cubic [110] and [$\bar{1}$10] directions, respectively, to a first approximation, the distortion should be only within the ab plane as indicated by the four arrows. From this figure, one concludes the dimensions of the orthorhombic unit cell resulting from the distortion would be $2^{1/2}|\underline{a}| > |\underline{c}| > 2^{1/2}|\underline{b}|$. In other words, the length of a increases by approximately the same amount that b decreases, and c is essentially unchanged. Again, it is convenient to define distortion ratios, but in this case, it is necessary to define a distortion ratio for each of the three orthorhombic dimensions. If there were no distortions, $2^{1/2}|\underline{a}| = |\underline{c}| = 2^{1/2}|\underline{b}| = (2V)^{1/3}$. The

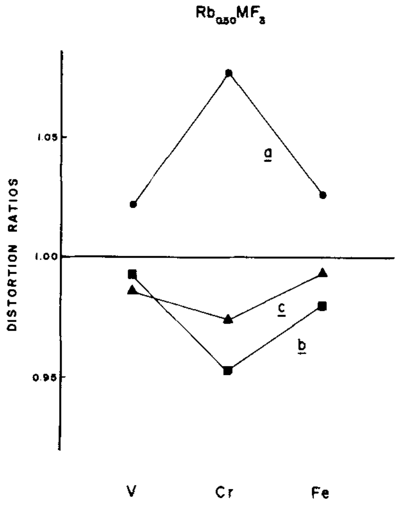


FIGURE 4. Distortion ratios of the $Rb_{0.50}MF_3$ compounds. Data from references 3,4, and 8.

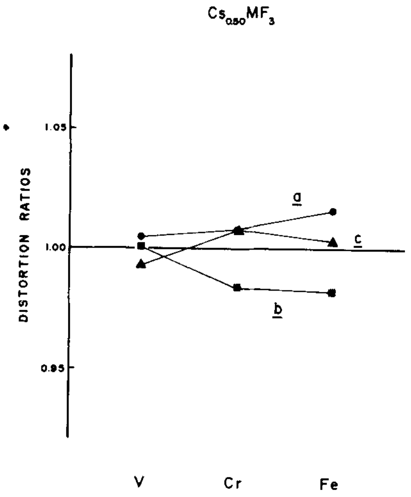


FIGURE 5. Distortion ratios for the $Cs_{0.50}MF_3$ compounds. Data from references 3,4, and 8.

distortion ratios are, therefore, defined as $\delta_a = 2^{1/2}|\underline{a}|/(2V)^{1/3}$, $\delta_b = 2^{1/2}|\underline{b}|/(2V)^{1/3}$, and $\delta_c = |\underline{c}|/(2V)^{1/3}$, respectively. The distortion ratios for $Rb_{0.50}MF_3$ (M = V, Cr, or Fe) are plotted on Figure 4, and the ratios for $Cs_{0.50}MF_3$ are shown on Figure 5. We see from these figures that for $Rb_{0.50}FeF_3$ and $Cs_{0.50}FeF_3$, $\delta_a > \delta_c > \delta_b$, $\delta_a \approx 1/\delta_b$, and δ_c is approximately unity as predicted by our model (i.e. only M^{2+}-M^{3+} electronic ordering is present). The distortion ratios for V and Cr do not fit this simple model and we conclude, therefore, that in addition to M^{2+}-M^{3+} electronic ordering, cooperative Jahn-Teller effects are present as well in these systems. It is obvious that for $Rb_{0.50}CrF_3$ the Jahn-Teller distortion is large. It should be pointed out that in the case of $Rb_{0.50}FeF_3$ and $Cs_{0.50}FeF_3$, the orthorhombic $\underline{a}$ and $\underline{b}$ directions correspond to the directions of rows of Fe^{2+} and rows of Fe^{3+} ions, respectively. In the case of the V and Cr modified pyrochlores, $|\underline{a}|$ may be defined as being larger than $|\underline{b}|$ but we cannot be sure which is the direction of the rows of M^{2+} ions and which is the direction of the rows of M^{3+} ions. V^{3+} and Cr^{2+} have different charges and different electronic configurations, and one would again expect the Jahn-Teller distortion associated with each to be different. Both M^{2+}-M^{3+} electronic ordering and cooperative Jahn-Teller ordering contribute to the crystal distortion of the modified pyrochlore structure, and it is uncertain as to whether the two effects are additive or opposed.

CONCLUSIONS

Ionic ordering superimposed on the parent lattice of a crystal will almost always lower the symmetry of the crystal. The hexagonal bronze fluorides and modified pyrochlore crystal systems are lowered from hexagonal to orthorhombic and from cubic to orthorhombic, respectively. In the tetragonal bronze fluorides of V, ionic ordering does not change the crystal system, but it changes the space group to one of lower symmetry.

Three kinds of ionic ordering are characteristic of the A_xVF_3 and A_xCrF_3 compounds. Although only M^{2+}-M^{3+} electronic ordering was observed for the modified pyrochlore fluorides of Fe, ordering of partially filled A^+ sites is also a possibility in some of the A_xFeF_3 compounds. The types of ionic ordering found thus far in the A_xMF_3 compounds are summarized in Table IV.

TABLE IV. Ionic Ordering in A_xMF_3 Compounds

(1) Partially Filled A^+ Sites
(2) M^{2+}-M^{3+} (Electronic Order)
(3) Cooperative Jahn-Teller Order

	V	Cr	Fe
Hexagonal Bronze	(1),(2),(3)	(1),(2),(3)	?
Tetragonal Bronze	(2)	---	?
Modified Pyrochlore	(2),(3)	(2),(3)	(2)

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