The Crystal Structure of $K_{0.54}(Mn,Fe)F_3$ at Room Temperature*†

By Ephraim Banks and Shigeo Nakajima

Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201, USA

and Graheme J. B. Williams

Department of Chemistry, Brookhaven National Laboratory, Upton, LI, New York 11973, USA

Abstract

A specimen of flux-grown $K_{0.54}(Mn,Fe)F_3$ was studied at room temperature by single-crystal X-ray diffractometry. The crystal has a structure of the tetragonal tungsten-bronze type with a doubled c axis. The unit-cell parameters are $a = 12.765$ (1), $c = 8.002$ (1) Å, and the space group is $P4_2bc$. Least-squares refinement was carried out with 2395 symmetry-independent reflections collected with an automatic diffractometer (Mo $K\alpha$ radiation). The final R value $(\sum |F_o^2 - kF_c^2|/\sum |F_o^2|)$ is 0·049, with anisotropic thermal parameters. In the structure, K atoms fully occupy pentagonal (CN = 15) sites and partially occupy tetragonal (CN = 12) sites. The transition-metal ions occupy three different kinds of octahedra. The mean $M–F$ distances in each octahedron are: 2·100 Å for $M(1)–F$, 1·939 Å for $M(2)–F$, and 1·995 Å for $M(3)–F$. These distances indicate that the $M(1)$ sites are mainly occupied by bivalent ions, chiefly Mn^{2+}, the $M(2)$ sites by Fe^{3+} and the $M(3)$ sites by Mn^{2+} and Fe^{3+}.

Introduction

In recent years, considerable attention has been focused on ternary metal fluorides of the general type $A_x M_x^{II} M_{(1-x)}^{III} F_3$, where A is an alkali metal and M^{II} and M^{III} may be the same or different transition-metal ions (Babel, Pausewang & Viebahn, 1967; Babel, 1972; De Pape, 1965). Interest in these compounds has been from the viewpoint of studying the nature of magnetic ordering, and, in the case where the bivalent and tervalent ions are of the same element, the possibility of metallic conductivity by delocalization of the electrons

over the crystallographic sites. No such cases have yet been discovered.

The K compounds in these series all show a phase having the 'tetragonal-bronze' structure in the homogeneity range $0.4 \le x \le 0.6$, which has been studied, in the system $K_x FeF_3$, by De Pape (1965). The only single-crystal X-ray study yet reported was by Hardy, Hardy & Férey (1973) who proposed a structure for $K_{0.6}FeF_3$ based on an orthorhombic cell of dimensions $a = 12.750$, $b = 12.637$, $c = 3.986$ Å. This is a slightly distorted version of the tetragonal cell found in $K_x WO_3$ (Magnéli, 1950a).

In the tetragonal-bronze-type structure, K ions are distributed over sites which lie in the pentagonal and tetragonal tunnels formed by a network of corner-sharing octahedra centered on the transition-metal ions (Fig. 1). The coordination number of anions about the K ions is 15 for the pentagonal tunnel site and 12 for the site in the tetragonal tunnel, the latter environment being the same as is found in the perovskite structure for the large cations. Férey (1977) has found that the K
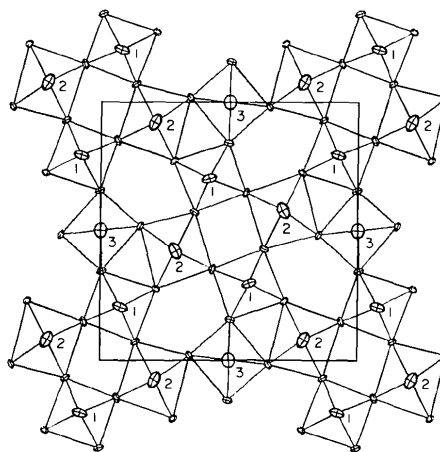

Fig. 1. One layer of connected octahedra viewed in the c direction. Transition-metal sites 1, 2 and 3 are indicated. Sites 1 and 2 alternate in successive layers, sites 3 stack above one another. Potassium ions K(1) are in the square tunnels and K(2) in the pentagonal tunnels. Probability ellipsoids are drawn at the 30% level.

Table 1. *Crystal data for* $K_{0.54}(Mn,Fe)F_3$

Space group $P4_2bc$ $Z = 20$
$a_0 = 12.765$ (1) Å $\bar{\mu}(Mo\ K\alpha) = 6.275\ mm^{-1}$
$c_0 = 8.002$ (1)

ions in $K_{0.5}FeF_3$ completely occupy the pentagonal sites and half fill the tetragonal sites.

Experimental

The crystals were grown from molten potassium chloride flux (Perez, 1972) using a powdered sample of $KMnFeF_6$ previously prepared by solid-state reaction of the simple fluorides in a sealed platinum capsule in an argon atmosphere. The flux mixture was heated to 1173 K in a Pt crucible under argon and cooled at 5 K h^{-1} to 573 K. After cooling, dark-brown, transparent crystals were recovered by washing out the flux. Powder samples of $KMnFeF_6$ and melts prepared in sealed graphite crucibles were much less deeply colored. We believe the color is due to the reduction of some Fe^{3+} to Fe^{2+} by Cl ions in the flux, thereby increasing the ratio of bivalent to tervalent ions in the melt, causing the increased value of x determined in the X-ray refinement. A suitable crystal was selected and mounted on a goniometer. Precession photographs (Mo $K\alpha$ radiation) showed these crystals to have a super-structure of the tetragonal-bronze unit cell, with the tetragonal a axis unchanged, but the c axis doubled.

A crystal of parallelepiped shape $0.11 \times 0.11 \times 0.35$ mm was mounted on an Enraf–Nonius CAD-4 automatic diffractometer. Three-dimensional intensity data for a total of 7088 reflections, using Mo $K\alpha$ radiation up to $\sin \theta/\lambda = 0.90\ Å^{-1}$ were collected from the quadrant with $h \geq 0$ and $l \geq 0$. Data were corrected for Lorentz, polarization and absorption effects and symmetry-equivalent points were merged, $R_m = 0.03$, to yield 2397 unique intensities. The unit-cell parameters and their estimated standard deviations were obtained by the least-squares method, using the 2θ values of 12 high-angle reflections. These are shown with other crystal data in Table 1.

Structure determination and refinement

From the systematic extinctions (hhl, $l \neq 2n$; $h0l$, $h \neq 2n$; $h00$, $h \neq 2n$; $00l$, $l \neq 2n$), the crystal has a space group of $P4_2bc$ or $P4_2/mbc$. Starting with the atomic coordinates determined for $K_{0.6}WO_3$ by Magnéli (1950a) least-squares refinements were carried out for both space groups, using mean values of the scattering factors for Fe and Mn (Doyle & Turner, 1968), with fixed isotropic temperature factors of $1.5\ Å^2$ for K, 0.4

$Å^2$ for Mn and Fe and $2.0\ Å^2$ for F. This calculation yielded R factors of 0.151 for $P4_2bc$ and 0.248 for $P4_2/mbc$. Parallel refinements in both groups were conducted and the eventual selection (see below) was for $P4_2bc$. The function minimized was $\sum w|F_o^2 - k^2 F_c^2|^2$, where k is a scale factor and $w^{-1} = \sigma_c^2 + (0.01F_o^2)^2 + [0.01(F_o^2 - F_o^2/A)]^2$. In this expression σ_c^2 is the counting-statistics variance corrected for Lp and absorption; A is the transmission coefficient. Using the atomic coordinates from the initial refinements, electron-density and difference electron-density syntheses were calculated to determine the K site occupancy. Finally, a full-matrix least-squares refinement was performed, varying atomic coordinates, multiplicities of K atoms, anisotropic thermal parameters for all atoms, and an extinction parameter.

The refinement (in $P4_2bc$) converged to a final R value $(\sum |F_o^2 - F_c^2|/\sum |F_o|^2) = 0.049$ for 2395 reflections (002 and 004 reflections showed exceptionally poor agreement, which could not be accommodated by refining an isotropic extinction term and they were therefore excluded). The final weighted R factor $R_w = (\sum w|F_o^2 - k^2 F_c^2|^2/\sum w|F_o^2|^2)^{1/2}$ was 0.054.

Trial least-squares refinements in space group $P4_2/mbc$ were conducted, resulting in values of $R = 0.065$ and $R_w = 0.098$. According to a standard significance test (Hamilton, 1965) the non-centrosymmetric group ($P4_2bc$) is the most probable at the 0.995 acceptance level.

Final atomic coordinates are listed in Table 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33951 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates for* $K_{0.54}(Mn,Fe)F_3$

Estimated standard deviations given in parentheses refer to the last significant digit.

	Position	x	y	z
K(1)*	4(a)	0.0000	0.0000	0.2503 (8)
K(2)	8(c)	0.1695 (2)	0.6728 (2)	0.2501 (7)
M(1)	8(c)	0.0758 (0)	0.2144 (0)	−0.0004 (4)
M(2)	8(c)	0.2901 (0)	0.4244 (0)	0.0000 (4)
M(3)	4(b)	0.0000	0.5000	0.0000
F(1)	4(b)	0.0000	0.5000	0.2509 (15)
F(2)	8(c)	0.0783 (4)	0.2099 (5)	0.2620 (13)
F(3)	8(c)	0.9221 (5)	0.7949 (4)	0.7416 (13)
F(4)	8(c)	0.9827 (2)	0.3462 (2)	0.0074 (12)
F(5)	8(c)	0.3430 (2)	0.9962 (2)	0.0066 (14)
F(6)	8(c)	0.1483 (2)	0.0650 (2)	0.0059 (13)
F(7)	8(c)	0.0704 (2)	0.8650 (1)	0.0075 (12)
F(8)	8(c)	0.2732 (1)	0.7842 (1)	−0.0007 (10)

* Occupies 0.7 of 4(a) sites. All other sites fully occupied.

Results and discussion

Fig. 1 is a projection along the c axis of half the unit cell, having the familar 'tetragonal-bronze' structure. The Mn and Fe atoms are in octahedral sites surrounded by F ions. There are three different octahedral sites, designated $M(1)$, $M(2)$ and $M(3)$ (see Table 4). The latter sites are stacked above each other along the c axis, while the $M(1)$ and $M(2)$ sites alternate along that axis, giving rise to the observed doubling of the c axis (Fig. 2). The K atoms occupy two kinds of sites (Table 3); K(1) atoms are in tetragonal holes in an environment like that in the perovskite structure (CN 12) while K(2) atoms are in pentagonal holes (CN 15) (Fig. 3). The occupancy factor for the K(1) sites was 0·70 in the refinement and in the K(2) sites it was 1·0. On the basis of these occupancy numbers, the chemical composition is suggested to be $K_{0.54}(Mn,Fe)F_3$. The observed preferential filling of the pentagonal sites has previously been found in $PbNb_2O_6$ (Labbé, Frey & Allais, 1973) where the Pb atoms were found to occupy all the pentagonal sites and half the tetragonal sites. It would appear

that it is necessary to fill the pentagonal sites in order to stabilize this structure type; this may account·for the lower limit of $x = 0·4$ which is found for the homogeneity range of this phase in systems as diverse as the potassium–tungsten bronzes and the mixed potassium–transition-metal fluorides of the type under discussion at present. One apparent exception to this rule is the homogeneity range ($0·28 \leq x \leq 0·38$) found for this structure in Na_xWO_3 (Ribnick, Post & Banks, 1963; Magnéli, 1950b). Equilibrium preparations of Na_xWO_3 have a cubic-perovskite structure above $x \simeq 0·4$. Crystals have been prepared electrolytically which retain the tetragonal structure at higher Na content. With such crystals, Takusagawa & Jacobson (1976) studied the structures of $Na_{0.33}WO_3$ and $Na_{0.48}WO_3$, reporting that Na atoms preferentially occupy the pentagonal sites, which are completely filled at $x = 0·48$, the remaining atoms partially occupying the

Table 3. The K—F distances (Å)

(a) K(1)—F distances, in the tetragonal site

K(1)—F(7)	2·748 (6) 2×	K(1)—F(2)	2·861 (5) 2×
K(1)—F(7')	2·830 (7) 2×	K(1)—F(3)	2·801 (4) 2×
K(1)—F(6)	2·845 (6) 2×	K(1)—F(Mean)	2·832
K(1)—F(6')	2·908 (7) 2×		

(b) K(2)—F distances, in the pentagonal site

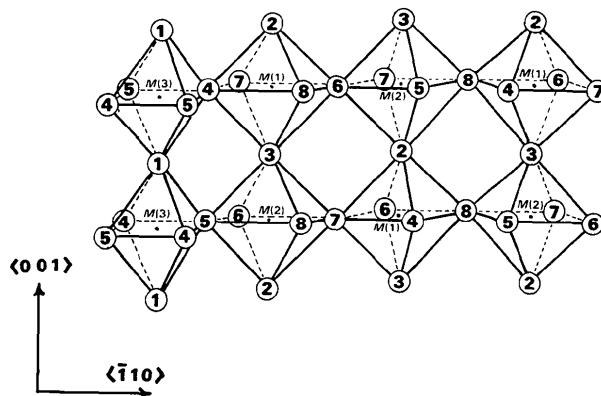|			
K(2)—F(4)	2·867 (5)	K(2)—F(6)	3·335 (6)
K(2)—F(4')	2·758 (5)	K(2)—F(6')	3·344 (6)
K(2)—F(5)	2·984 (6)	K(2)—F(7)	3·375 (5)
K(2)—F(5')	3·025 (7)	K(2)—F(7')	3·490 (5)
K(2)—F(8)	2·792 (6)	K(2)—F(2)	3·256 (7)
K(2)—F(8')	2·786 (7)	K(2)—F(2')	3·501 (8)
K(2)—F(1)	3·090 (4)	K(2)—F(3)	3·215 (6)
K(2)—F(Mean)	2·900	K(2)—F(3')	3·579 (8)
		K(2)—F(Mean)	3·387

Fig. 2. An illustration of two chains of connected octahedra viewed along a $\langle 110 \rangle$ direction. The fluorine atoms are numbered.

Table 4. The M—F distances (Å) in octahedral sites

$M(1)$ octahedra

$M(1)$—F(2)	2·101 (8)	$M(1)$—F(7)	2·125 (2)
$M(1)$—F(3)	2·068 (8)	$M(1)$—F(8)	2·124 (2)
$M(1)$—F(4)	2·061 (2)	$M(1)$—F(Mean)	2·100
$M(1)$—F(6)	2·120 (2)		

$M(2)$ octahedra

$M(2)$—F(2)	1·905 (8)	$M(2)$—F(7)	1·937 (2)
$M(2)$—F(3)	1·934 (7)	$M(2)$—F(8)	1·964 (2)
$M(2)$—F(5)	1·931 (2)	$M(2)$—F(Mean)	1·939
$M(2)$—F(6)	1·960 (2)		

$M(3)$ octahedra

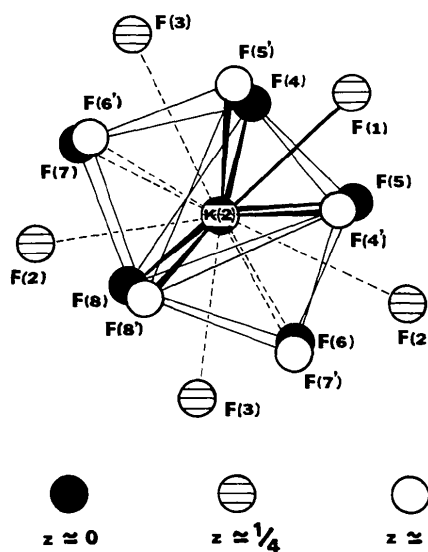|			
$M(3)$—F(1)	2·007 (10)	$M(3)$—F(4)	1·977 (2) 2×
$M(3)$—F(1)	1·994 (10)	$M(3)$—F(5)	2·006 (2) 2×
		$M(3)$—F(Mean)	1·995

Fig. 3. A view along c of the first and second neighboring fluorine ions for a K(2) ion.

tetragonal (perovskite-like) sites. As noted in the *Introduction*, Férey (1977) has found a similar situation in $K_{0.5}FeF_3$. The only exception known to the authors to preferential occupancy of the pentagonal sites in this structure is the report by Brusset, Gillier-Pandraud & Mahé (1970) on the structure of $Pb_{0.7}Ba_{0.3}Nb_2O_6$, where the tetragonal sites are preferentially occupied.

The K—F distances in the 'tetragonal' K(1) sites (Table 3) average to 2·832 Å, which compares reasonably to the sum of ionic radii (Shannon & Prewitt, 1969) for 12-coordinate K and four-coordinate F (each F atom in this structure has two transition-metal and two K neighbors). In the pentagonal positions, involving K(2), there are seven K—F distances less than 3·10 Å, as shown in Fig. 2. The distances from K(2) to F(2), F(3), F(6) and F(7) range from 3·215 to 3·579 Å, much larger than the maximum sum of ionic radii, even with allowance for 15-coordination. The coordination polyhedron about K(2) is therefore a trigonal prism with one rectangular face capped. This was also found in $K_{0.6}FeF_3$ by Hardy *et al.* (1973).

The distances in the three octahedral sites permit some conclusions about the distribution of bivalent and tervalent transition-metal ions in the structure. The mean M—F distances are 2·100 Å for the M(1) site, 1·939 Å for the M(2) site, and 1·995 Å for the M(3) site. Radius sums for six-coordinate high-spin Mn^{2+} and Fe^{3+} with two-coordinate F^- give values of 2·105 and 1·930 Å, respectively, and the mean radius of Mn^{2+} and Fe^{3+} gives a value of 2·018 Å. These agree remarkably well with the observed distances and we therefore postulate that the M(1) site is primarily occupied by bivalent ions, M(2) by tervalent ions (Fe^{3+}) and the M(3) site is occupied by a mixture of bivalent and tervalent ions. A recent Mössbauer study of site preferences of Mn^{2+} and Fe^{2+} in a series of tetragonal-bronze-type fluorides (Banks, Torre & De Luca, 1977) showed that Fe^{2+} strongly preferred the 2(c) site [in $P4/mbm$, corresponding to the present M(3) site] in competition with Mn^{2+}, in $K_{0.5}Fe^{2+}_{0.2}Mn^{2+}_{0.3}Fe^{3+}_{0.5}F_3$. If this site preference is present here, the presence of Fe^{2+} on these sites in preference to Mn^{2+} may explain the shorter M(3)—F distance and the longer M(2)—F distance, relative to the distances calculated using Mn^{2+} and Fe^{3+} radii.

The z parameters of the atoms in Table 2 indicate that the substance is probably ferroelectric. With the M(3) atom fixed at $z = 0$, the other metal atoms show negligible displacements from that value, whereas five F atoms show average displacements of about 0·008 Å in the positive z direction, two [F(1) and F(8)] show no significant displacement and only one [F(3)] has a significant negative displacement. The resulting net charge displacement should produce spontaneous polarization. We have not yet been able to test for ferroelectricity, and the strong light absorption of the material makes it impossible to test for second-harmonic generation.

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