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Crystal structure and charge distribution of $YbFeMnO_4$

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The structure of synthetic $YbFeMnO_4$ has been refined by single-crystal X-ray diffraction. Space group $R\bar{3}m$, a = 3.4580 (1), c = 25.647 (3) Å, V = 265.59 (3) Å^3, Z = 3. Yb is in octahedral coordination, whereas Fe and Mn are disordered on a single crystallographic type of trigonal bipyramid, in which the cation is off-centred from the basal plane. Assuming perfect stoichiometry, R_1 = 0.0195, but the charge distribution (CD) analysis suggests incomplete occupation of the Yb site. Refinement of the occupancy lowers R_1 to 0.0175, resulting in s.o.f.(Yb) = 0.963 (3), with a significant improvement of the Fourier difference. The electroneutrality is likely preserved through incomplete occupancy of one of the two oxygen sites: the compound is thus non-stoichiometric, with the formula $Yb_{0.963}FeMnO_{3.945}$. Another mechanism for preserving the electroneutrality is the oxidation of a small amount of Mn^{2+} to Mn^{3+}, which is, however, less probable because of the reduction conditions in which the sample was synthesized. Both models give a satisfactorily CD result, but they cannot be definitively distinguished by X-ray data.

1. Introduction

Compounds with layer structure and high electric conductivity have been the subject of intensive research over the last 30 years. The binary R_2O_3–MO and ternary R_2O_3–A_2O_3–MO or R_2O_3–TiO_2–MO systems (R = In, Ga or a rare earth element; A = In, Ga, Fe, Al; M = Mg, Mn, Fe, Co, Cu, Zn, Cd) have been investigated to clarify the synthesis conditions, phase relations, and stabilities and magnetic properties (Kimizuka *et al.*, 1990, 1993, 1995; Siratori, 1993; Iida *et al.*, 1990; Nakamura *et al.*, 1990, 1993*a*,*b*; Yamaguchi *et al.*, 1991; Nakamura & Kimizuka, 1993; Brown *et al.*, 1999). Structural studies have considered both the local structure, through high-resolution transmission electron microscopy (HRTEM) and/or electron diffraction (Matsui *et al.*, 1979; Matsui, 1980; Cannard & Tilley, 1988; Uchida *et al.*, 1994; Hörlin *et al.*, 1998; Li *et al.*, 1997, 1998, 1999*a*,*b*; Li, Bando, Nakamura, Kurashima & Kimizuka, 1999; Wolf & Mader, 1999), and the global one, through powder (Cannard & Tilley, 1988; Nakamura & Kimizuka, 1993; Cava *et al.*, 1998; Moriga *et al.*, 1999) and single-crystal X-ray diffraction (Geller *et al.*, 1975; Kato *et al.*, 1975, 1976; Malaman *et al.*, 1975, 1976; Isobe *et al.*, 1990, 1991, 1994; Nespolo, Nakamura & Ohashi, 2000; Nespolo, Sato *et al.*, 2000).

The structural *motif* of this type of compound consists of layers of octahedrally coordinated R^{3+} cations alternated with layers of M^{2+}/M^{3+} cations in trigonal bipyramidal coordination. Barbier (1989) has pointed out that the cation close packing is much more regular than the oxygen packing. The stacking of these layers along the c direction produces accre-

Table 1
Experimental details for $YbFeMnO_4$.

Crystal data		
Cell setting		Hexagonal
Space group		$R\bar{3}_m$
a (Å)		3.4580 (1)
c (Å)		25.647 (3)
V (Å^3)		265.59 (3)
Z		3
Radiation type		Mo $K\alpha$
Wavelength (Å)		0.71073
No. of reflections for cell parameters		18
θ range (°)		40.98–45.30
Temperature (K)		293 (2)
Crystal form		Sphere
Crystal radius (mm)		0.055
Crystal colour		Black
Data collection		
Diffractometer		Enraf–Nonius CAD-4
Data collection method		ω–θ scans
Absorption correction		Sphere
$T_{\min}$		0.086
$T_{\max}$		0.166
No. of measured reflections		655
No. of independent reflections		577
No. of observed reflections		528
Criterion for observed reflections		$I > 2\sigma(I)$
$R_{\rm int}$		0.0196
$\theta_{\max}$ (°)		59.84
Range of h, k, l		$0 \rightarrow h \rightarrow 7$ $0 \rightarrow k \rightarrow 4$ $-60 \rightarrow l \rightarrow 61$
No. of standard reflections		3
Frequency of standard reflections		Every 240 min
Intensity decay (%)		−0.5
Refinement		
Refinement on	F^2	
	s.o.f. (Yb) = 1	s.o.f. (Yb) = 0.963
Chemical formula weight	347.83	341.49
D_x (Mg m^{-3})	6.524	6.405
μ (mm^{-1})	33.593	32.637
$R[F^2 > 2\sigma(F^2)]$	0.0195	0.0175
$wR(F^2)$	0.0524	0.0437
S	1.153	1.184
No. of reflections used in refinement	577	577
No. of parameters used	13	14
$(\Delta/\sigma)_{\max}$	0.000	0.001
$\Delta\rho_{\max}$ (e Å^{-3})	3.39 at 2/3,1/3,0.1059 (0.30 Å from Fe/Mn)	2.55 at 0,0,0.1109 (0.44 Å from O1)
$\Delta\rho_{\min}$ (e Å^{-3})	−6.20 at 0,0,0.0214 (0.55 Å from Yb)	−4.88 at 0,0,0.0217 (0.56 Å from Yb)
Extinction method	*SHELXL* (Sheldrick, 1997)	*SHELXL* (Sheldrick, 1997)
Extinction coefficient	0.0237	0.0290 (11)

tional homologous series, *i.e.* series in which the type(s) and the general shapes of building blocks, as well as the principles defining their mutual relationships, are preserved, but the size of these blocks increases with the number of coordination polyhedra in them (Makovicky, 1997).

Ideal trigonal bipyramids, with two identical apical bonds, have been found only in compounds where the bipyramids host a single type of cation, such as $InGaO_3$ (II) (Shannon & Prewitt, 1968). When different cations enter the bipyramids, these no longer have their two apical bonds identical and have been classified into two types. Type I has the three basal M—O bonds shorter than the two apical ones: the cation is still relatively close to the basal plane, and the bipyramid is not much distorted. Type II has the cation significantly off-centred from the basal plane, towards one of the corners: one of the apical bonds is shorter and the other is longer than the three basal ones (Nespolo, Sato *et al.*, 2000).

The above compounds can be classified into two accretional homologous series: $(R^{3+}M^{3+}O_3)_nM^{2+}O$, analogous to the $(YbFeO_3)_nFeO$ series (Kato *et al.*, 1975, 1976; Malaman *et al.*, 1975, 1976; Kimizuka *et al.*, 1976), and $R^{3+}M^{3+}O_3(M^{2+}O)_m$, analogous to the $LuFeO_3(ZnO)_m$ series (Isobe *et al.*, 1994). The latter has recently drawn attention from different research groups, because of the unusual features of higher members. In particular, for R = In or Ga, M^{3+} = Fe and M^{2+} = Zn, extra reflections in the selected-area electron diffraction pattern were reported (Li *et al.*, 1997, 1998, 1999*a*; Li, Bando, Nakamura, Kurashima & Kimizuka, 1999) and interpreted in terms of superspace group analysis (Li *et al.*, 1998). TEM observations have revealed the existence of a modulation wave involving the octahedral cation (Li *et al.*, 1997, 1998, 1999*a*; Li, Bando, Nakamura, Kurashima & Kimizuka, 1999; Hörlin *et al.*, 1998; Wolf & Mader, 1999), whose origin is at present unclear. No modulated structure has been reported so far in members with $m < 6$. The structure of this series has been recently rationalized in terms of

$$m = 2K + L, \tag{1}$$

where $K \geq 0$ and L = 0 or 1 (K and L are both integers). The ideal symmetry is $P6_3/mmc$ and $R\bar{3}m$ for L = 0 and L = 1, respectively. In higher members with a modulated structure the symmetry is actually reduced, at least locally, to orthorhombic and monoclinic, respectively (Li *et al.*, 1998).

Important insights into the structural details of these compounds can be obtained by the charge distribution (CD) analysis (Hoppe *et al.*, 1989; Nespolo *et al.*, 1999). The CD method is the most recent development of the classical theory of bond strength (Pauling, 1929) and differs from the bond valence (BV) approach (Brown, 1978) in exploiting the true bond distances in a kind of self-consistent computation rather than employing empirical curves. Differently from the BV method, in the CD approach the computed 'charges' (Q) of the cations and of the anions convey different information. In short, by labelling q the formal oxidation number, the q/Q ratio for the cations indicates the correctness of the structure determination, whereas the same ratio for the anions measures the degree of over- or under-bonding. The analysis of the structural details on the basis of the strength of each bond (called 'bond valence' in the BV and 'bond weight' in the CD) is meaningful only when the structure is correctly refined and the empirical method itself is applicable. The BV method does not contain any internal criterion for such an evaluation, while the CD method has in the q/Q ratio for the cations precisely this kind of criterion (for details refer to Nespolo *et al.*, 1999).

The CD analysis of several compounds belonging to the two accretional homologous series described above has revealed that those containing type II trigonal bipyramids have a q/Q

ratio for the octahedral cation significantly different from 1, thus questioning the correctness of the structure. A re-refinement of $LuFeO_3(ZnO)$, in which Fe/Zn are in type II trigonal bipyramids, has demonstrated that the Lu atom is not at the centre of symmetry, as previously assumed, but is actually split between two half-sites along z (Nespolo, Nakamura & Ohashi, 2000), confirming a similar result obtained by neutron powder diffraction (Cava *et al.*, 1998). The same analysis also suggested that in the higher members containing type II trigonal bipyramids, the M^{3+} cation tends to avoid the bipyramid directly bound to the R^{3+} octahedron. On the contrary, structures containing only type I trigonal bipyramids have a q/Q ratio very close to 1 for all the cations and R^{3+} occupies the centre of symmetry, without splitting.

The above results call for further studies on this class of compound. The simplest (m = 1) member of the series is the most suitable candidate for investigating the geometry of the coordination polyhedra and its structural effects. In fact, it contains a single crystallographically independent trigonal bipyramid and thus the shape of this polyhedron directly influences the R^{3+} cation. For the higher members its effect is diluted among the other bipyramids, in which the cation distribution is often hardly determined by X-ray diffraction.

2. Materials and methods

Single crystals of $YbFeMnO_4$ were grown at 1723–1773 K from a mixture of the ratio Yb_2O_3:Fe_2O_3:MnO = 1:1:2 by the floating zone method, as described in Iida *et al.* (1990), but in a controlled CO_2 atmosphere to prevent as much as possible oxidation to Mn^{3+}. Layered compounds RFe_2O_4 and $RFeMnO_4$ (R = rare-earth elements or Y) are known to melt incongruently (Shindo *et al.*, 1976; Iida *et al.*, 1990), with a final composition of the solid phase that differs from that of the liquid one. The composition of the crystal is therefore determined hereafter by refinement of the occupancy factors.

One of the synthesized crystals was chosen for X-ray diffraction investigation and mounted on an Enraf–Nonius CAD-4 diffractometer. Intensity collection was performed using variable-rate ω–2θ scans, with the scan range 1.275 + 0.525tanθ° (details are given in Table 1). The Lp corrections were performed through the *XCAD*4 program (Harms, 1996) and the spherical absorption correction with the *PLATON* package (Spek, 1990). The structure refinement was performed against F^2 with *SHELX*97 (Sheldrick, 1997). Initial positional parameters and displacement factors were taken from $InGaZnO_4$ (Nespolo, Sato *et al.*, 2000).

Fe and Mn can hardly be distinguished by X-ray diffraction and the determination of their ratio, oxidation state and possible ordering scheme requires different techniques. Owing to the premature disappearance of one of the authors, it was not possible to locate the original sample. However, the high temperature at which it was synthesized is in favour of a model in which Fe and Mn are disordered on the single bipyramid. Besides, the previous reports of analogous structures [Zn/Fe (Isobe *et al.*, 1994; Cava *et al.*, 1998); Co/Fe (Isobe *et al.*, 1990); Zn/Ga (Nespolo, Sato *et al.*, 2000); Cu/Al (Gérardin *et al.*, 1980)] support a model with disordered distribution for the M^{2+}/M^{3+} cations in the trigonal bipyramids. Barbier (1989) has shown that in $In_{1.2}Ga_{0.8}MgO_4$, analogous to $YbFeMnO_4$, the excess In is accommodated in the trigonal bipyramids and 0.2In + 0.8Ga + Mg are completely disordered. Finally, the Mössbauer investigation of $YFe^{2+}Fe^{3+}O_4$ revealed that Fe^{2+} and Fe^{3+} are disordered at room temperature, and only at low temperature two different antiferromagnetic sublattices arise due, however, to electron diffusion between Fe^{2+} and Fe^{3+}. Disorder of Fe/Mn is therefore assumed hereafter.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $YbFeMnO_4$ refined to s.o.f.(Yb) = 0964 (3).

U_{eq} is defined as one third of the trace of the orthogonalized U^C tensor.

	Wyckoff	$x = y$	z	U_{eq}
Yb	3(*a*)	0	0	0.01184 (5)
Fe/Mn	6(*c*)	0	0.215706 (14)	0.00728 (7)
O(1)	6(*c*)	0	0.12826 (13)	0.0208 (5)
O(2)	6(*c*)	0	0.29345 (8)	0.0098 (2)

3. Results

Results of the structure refinement are given in Tables 1–3[1] and the structure is shown in Fig. 1. At first, refinement was performed assuming perfect stoichiometry, with a final R_1 of 0.0195. The CD analysis (Table 4) shows, however, that the computed charge for Yb is not satisfactory: Q is in fact only 2.87, against an expected value (q) of 3.0, leading to a q/Q ratio of 1.04_5, *i.e.* more than 4% deviation from the ideal ratio. Moreover, the Fourier difference has a deep hole close to Yb (Table 1).

In the case of $LuFeZnO_4$ the same type of anomaly led to re-refining the structure adopting the split atom model for the Lu^{3+} cation, which was found disordered at ± z around the inversion centre. In the present case, however, splitting of Yb either brings Yb again on the inversion centre or produces an unstable refinement. The low formal charge obtained by the CD analysis may have its cause in a lack of stoichiometry, in particular in the incomplete occupation of the octahedral site, a hypothesis that is also supported by the incongruent melt of these compounds when synthesized by the floating-zone method. The structure was thus further refined, including the s.o.f.(Yb) in the least-squares parameters: it refined to 0.963 (3), with a final R_1 of 0.0175 and a significant reduction of both the highest peak and the deepest hole in the Fourier difference (Table 1). To check whether the above improvements are statistically meaningful or rather an apparent effect of the different number of parameters (14 *versus* 13), the Hamilton test (Hamilton, 1965), employing the ratio of wR_2 for the two models, was performed. Interpolating the tabulated values for a significance level of 0.005 results in a 4% vacancy of Yb being correct with a significance level of 99.5%.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0104). Services for accessing these data are described at the back of the journal.

Table 3
Selected bond lengths (Å) and angles (°) for $YbFeMnO_4$.

Yb—O(2)	2.243 (1) (×6)	O(2)—Yb—O(2)	100.8 (1) (×6) 79.2 (1) (×6)
*M*1—O(2)	1.994 (2)	O(1)—*M*1—O(1)	118.2 (1) (×3) 82.2 (1) (×3)
*M*1—O(1)	2.015 (1) (×3)	O(2)—*M*1—O(1)	97.8 (1) (×3)
*M*1—O(1)	2.243 (3)		

Table 4
Charge distribution for $YbFeMnO_4$ in the hypotheses of perfect stoichiometry and within two different models to compensate the 4% vacancy of Yb.

σ measures the deviation of Q with respect to q and is defined as $\sigma = [\Sigma_i(q_i - Q_i)^2/(N-1)]^{1/2}$. For O atoms (as well as in the case of cations all with the same formal oxidation number) σ reduces to the classical standard uncertainty.

Formula	Atom	s.o.f.	*q*	*Q*	*q*/*Q*
$YbFe^{3+}Mn^{2+}O_4$	Yb	1.0	3.00	2.87	1.04_5
	M^{2+}/M^{3+}	1.0:1.0	2.50	2.56_5	0.97_5
				$\sigma = 0.14_5$	
	O1	1.0	−2.00	−1.91	1.05
	O2	1.0	−2.00	−2.09	0.96
				$\sigma = 0.13$	
$Yb_{0.963}Fe^{3+}Mn^{2+}O_{3.945}$	Yb	0.96	2.89	2.84	1.02
	M^{2+}/M^{3+}	1.0:1.0	2.50	2.53	0.99
				$\sigma = 0.060$	
	O1	0.97	−1.95	−1.91	0.98
	O2	1.0	−2.00	−2.04	1.02
				$\sigma = 0.053$	
$Yb_{0.963}Fe^{3+}Mn^{2+}_{0.88}$-$Mn^{3+}_{0.12}O_4$	Yb	0.96	2.89	2.82	1.02_5
	M^{2+}/M^{3+}	0.88:1.12	2.56	2.59	0.99
				$\sigma = 0.079$	
	O1	1.0	−2.00	−1.95	1.03
	O2	1.0	−2.00	−2.05	0.97_5
				$\sigma = 0.071$	

The overall neutrality can be maintained in two ways. An oxygen vacancy, which leads to the formula $Yb_{0.963}Fe^{3+}Mn^{2+}O_{3.945}$, is highly probable, also because the related compound YFe_2O_4 was found to be non-stoichiometric and more precisely with an oxygen vacancy (Sugihara *et al.*, 1978; Akimitsu *et al.*, 1979), while only with special care can a pure stoichiometric compound be obtained (Nakagawa *et al.*, 1979). The role of oxygen vacancies in the electronic properties of this type of compound is also known (*e.g.* Palmer *et al.*, 1997). Refinement of the occupancy of O atoms in the presence of heavy metals is hardly reliable: by including the occupancies of both O1 and O2 in the least-squares parameters, they refined to 0.926 (21) and 0.979 (16), respectively, while s.o.f.(Yb) remained practically unchanged at 0.961 (3). The *R* factor did not change, in spite of an increase in the number of parameters (16 *versus* 14), but the U_{eq} of O1 decreased slightly from 0.0208 (5) to 0.0197 (7). Besides, the overall s.o.f.(O) was too low to preserve the electroneutrality. We conclude that there are indications of oxygen deficiency at the O1 site, which is also in agreement with the high displacement parameter, but the actual occupation of O atoms cannot be reliably refined. The large displacement parameter of O1 can also be related to the presence of a long cation–oxygen bond along *z*, as pointed out by Barbier (1989), who used a numeration of O atoms inverted with respect to ours.

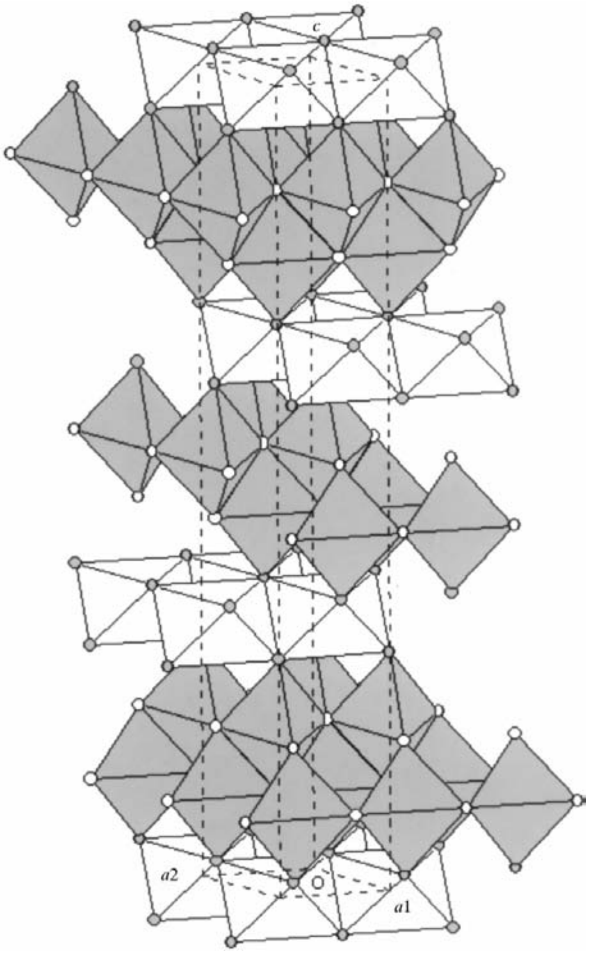

Figure 1
The structure of $YbFeMnO_4$. Octahedra (white) host Yb, and trigonal bipyramids (grey) host Fe and Mn. White and grey small circles represent O1 and O2, respectively.

Another way of maintaining the electroneutrality is through the oxidation of a limited (12%) amount of Mn^{2+} to Mn^{3+}. Although the synthesis was performed in a reducing atmosphere, partial oxidation to Mn^{3+} cannot be excluded and the oxidation state of Mn cannot be determined by a normal structure refinement. We, however, consider $Mn^{2+} \rightarrow Mn^{3+}$ to be less probable than the oxygen vacancy.

In Table 4 the CD calculation is presented for the three models: stoichiometry, Yb and O1 deficiency, and Yb deficiency plus 12% $Mn^{2+} \rightarrow Mn^{3+}$ oxidation. For both the latter two models the overall structure has a significantly better balance than under the hypothesis of stoichiometry. It is however much more difficult to discriminate between the two non-stoichiometric models. In the case of partial oxidation to Mn^{3+} the Jahn–Teller effect should appear. The peak in the difference Fourier close to O1 but directed opposite Fe/Mn and towards Yb (Table 1) may be in favour of this model. On the contrary, the U_{eq} of O1, large and comparable to the corresponding parameters of other analogous compounds containing type II trigonal bipyramids, may be in favour of vacancies at this site. Both these indications are however not conclusive.

It should be noted that in case of $LuFeZnO_4$ the splitting of the Lu position into two half-sites along $\pm z$ reduced not only R_1, but also U_{eq} of Lu. In the case of $YbFeMnO_4$ the refinement does not indicate splitting into two half-sites. However, a more complex pattern of splitting cannot be excluded, for instance with half of the Yb at the inversion centre and the remaining half distributed in the two sites $\pm z$. A further refinement adopting this partially disordered model for Yb gave an R_1 value close to, but slightly higher than, 0.0176 and reduced U_{eq} of Yb, and further reduced the highest peak and the deepest hole in the Fourier difference. Owing to the larger number of parameters in spite of no improvement of R_1, this further refinement was not accepted. The possibility of a certain degree of disorder of Yb around the centre of symmetry, less marked than in the case of $LuFeZnO_4$, cannot be excluded and should be taken into account for further studies of related compounds.

As a general conclusion it has to be emphasized that compounds containing type II trigonal bipyramids were refined in the past assuming perfect stoichiometry and the cation in the octahedral site was kept fixed at the centre of symmetry. It is now clear that deviations from the perfect mean structure should be considered and these compounds need to be studied in more detail.

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