

Reinvestigation of the $\text{LuFeO}_3(\text{ZnO})_m$ Homologous Series: Insights from Charge Distribution Analysis on the Effect of the Coordination Polyhedra Shape on the Cation Distribution

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A previous report on the homologous series $\text{LuFeO}_3(\text{ZnO})_m$ ($m = 1, 4, 5, 6$) is reanalyzed in terms of the charge distribution (CD) approach, an alternative to the bond valence method, which exploits the geometry of the coordination polyhedra. It is shown that in the $m = 1$ member the octahedral site is not well balanced; besides, members $m = 4, 5, 6$ are well balanced only assuming that Fe^{3+} avoids the cation site next to Lu. The main reason for these effects is likely in the shape of the trigonal bipyramids hosting Fe and Zn. The polyhedron next to the Lu site is highly distorted, with the three basal $M\text{-O}$ distances midway between those of the two apical ones. This geometry, approaching the tetrahedral shape, is more suitable for hosting Zn than Fe; besides, the short apical $M\text{-O}$ distance results in enhancement of the intercationic (Lu–M1) repulsion. For members $m > 1$ such repulsion is likely avoided by distributing the trivalent cation into the $m-1$ trigonal bipyramids not directly bound to the octahedron. The $m = 1$ member contains only one trigonal bipyramid and cannot thus adopt the same scheme of cation distribution. As a result, Lu is probably shifted outside the center of symmetry. A new refinement of the $m = 1$ member, based on the original intensities, shows that Lu is displaced by $\pm 0.14 \text{ \AA}$ from the center of symmetry. With respect to the refinement in the central atom model, a lower R factor, a lower Fourier difference and thermal parameters have been obtained. The results of the present research suggest the Lu– Fe^{3+} repulsion, related to the asymmetry of the trigonal bipyramidal coordination of Zn/Fe, as a possible cause of the deviation from the average structure.

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INTRODUCTION

Isobe *et al.* (1) investigated the structure of the $\text{LuFeO}_3(\text{ZnO})_m$ homologous series ($m = 1, 4, 5, 6$) by single-crystal X-ray diffraction (XRD), as part of a project aimed at determining the phase diagrams of oxides with relevant electronic properties. This series of compounds belongs to the so-called *accretional 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 (2). The members of this accretional homologous series are based on the YbFe_2O_4 structure (3) and consist essentially of the close packing of O atoms, with Lu in the octahedral voids and Fe/Zn in trigonal bipyramidal coordination. From the structure refinement, the displacement parameters U_{33} of Lu and O(1) of the $m = 1$ member were abnormally high. A refinement adopting the split-atom model for Lu was attempted and gave uncertain deviations, although with a lower R factor, and the average structure was accepted (1). For $m > 1$ members, the distribution of Fe^{3+} in the trigonal bipyramidal sites could not be determined on the basis of the R factor (1).

More recently, a neutron powder diffraction study of $\text{LuFeO}_3(\text{ZnO})_4$ (4) has indicated that the split-atom model, rather than the central-atom model, better describes the structure. In this research we present the charge distribution (CD) analysis (5, 6) (a method used to calculate the bond strengths on the basis of the geometry of the coordination polyhedra) of the accretional homologous series (1) and a new refinement of the $m = 1$ member, using the original intensities collected by Isobe *et al.* (1), which confirms the displacement of Lu from the center of symmetry.

DESCRIPTION OF THE STRUCTURE OF THE $\text{LuFeO}_3(\text{ZnO})_m$ ACCRETIONAL HOMOLOGOUS SERIES

The structure of the $\text{LuFeO}_3(\text{ZnO})_m$ accretional homologous series can be rationalized by writing m as a function of two integral numbers, K and L , as

$$m = 2K + L, \quad [1]$$

where $K \geq 0$ and $L = 0$ or 1. Members with $L = 1$ belong to space group $R\bar{3}m$; those with $L = 0$ to space group

$P6_3/mmc$. Differently from the previous classification in terms of the parity of m (odd m , $R\bar{3}m$; even m , $P6_3/mmc$; (1)) Eq. [1] gives a general scheme for the coordination polyhedra. In all the members of the accretional homologous series, the Lu atom is in octahedral coordination, and the Fe/Zn atoms are in trigonal bipyramidal coordination (M sites). The number of M sites is $K + 1$, and the number of crystallographically independent oxygen atoms is $K + 2$. Lu is octahedrally coordinated by the $(K + 2)$ th oxygen, whereas the i th M site is coordinated by the oxygen atoms of types $i - 1$, i , and $i + 1$ [only O(1) and O(2) for $M1$], $M_i\text{-O}_i$ being the basal bonds (in number of three). The M site adjacent to the Lu sheet is the $(K + 1)$ th one (hereinafter labeled M_{K+1}); the octahedral site and the M_{K+1} site share the $(K + 2)$ th oxygen atom (hereinafter labeled O_{K+2}), which forms the shortest of the two apical bonds of the trigonal bipyramid.

In all but the $m = 6$ member, the trigonal bipyramid around M_{K+1} is highly distorted, having the apical $M_{K+1}\text{-O}_{K+2}$ bond shorter and the other apical $M_{K+1}\text{-O}_K$ bond longer than the three basal $M_{K+1}\text{-O}_{K+1}$ bonds (this is equivalent to saying that the cation is significantly displaced from the basal plane). The same distortion was reported in several compounds isostructural with the $m = 1$ member of the series, YbFe_2O_4 (3), LuFe_2O_4 and LuFeCoO_4 (7), InCuAlO_4 (8), $\text{Yb}_{0.5}\text{Eu}_{0.5}\text{Fe}_2\text{O}_4$ (9), and also in a recent powder neutron diffraction study of the same compound, LuFeZnO_4 (4).

CHARGE DISTRIBUTION ANALYSIS

The charge distribution (CD) method (5) is the most recent development of the classical theory of bond strength (10). The latter was introduced as an empirical method to discuss the chemical bonds around each cation in an experimentally determined structure, by assigning to each bond a “bond strength” corresponding to the ratio of the formal oxidation number to the coordination number.

The bond strength approach was further developed to treat nonionic bonds (and thus the words “cations” and “anions” have to be considered in their purely formal meanings, indicating simply the sign of the formal oxidation number, and not necessarily the presence of an ionic bond) and relatively distorted coordination polyhedra by employing the so-called R_s curves, i.e., empirical curves giving the bond strength (s) as a function of the bond lengths (R). Several kinds of R_s curves have been introduced (e.g., 11–14), all containing two or more empirical parameters obtained by fitting on a large set of well-refined structures. The bond strength computed employing the R_s curves is called *bond valence*, and the theory that aims to interpret the chemical bonds on the basis of the R_s curves is itself called *bond valence (BV) theory* (15). The empirical parameters used in the BV theory depend upon the cation–anion pair

and the experimental conditions (pressure, temperature) in which they have been derived. The “charge” (Q) of each cation and anion is *computed* as the sum of the bond valences.

On the other hand, the CD employs a single empirical parameter, which is characteristic of the anion (to date, this parameter has been refined only for the oxygen) and does not depend upon either the cation or the experimental conditions. The CD exploits the experimental bond distances to compute a noninteger coordination number (ECoN: effective coordination number) and *distributes* the formal oxidation number (q) of each atom among all its bonds as a function of ECoN. It is thus more related to the geometry of each coordination polyhedron, rather than to the true crystal chemistry, as instead is the BV. Since the Q computed according to CD is the result of the *distribution* of q , it is suitable to investigate isomorphic substitutions of cations with different q : a distribution giving $Q \neq q$ indicates the possible presence of a mistake in the assigned site occupancy (6).

All these empirical methods should be always used critically, since they try to explain in a simple way the main features of something as complex as the chemical bond. However, in contrast to the BV method, the CD method possesses an internal criterion indicating the reasonableness of the analysis performed. In the BV theory, the Q obtained as a summation of the bond valences of each chemical bond is defined and computed in exactly the same way for both the cations and the anions. A deviation from q in principle measures the deviation from the “ideal” structure, and it is commonly used to discuss the presence and the possible causes of valence unbalances. However, this analysis is acceptable only if the structure is correctly solved, and only if it does not extend beyond the limits of applicability of the BV method itself (e.g., it does not contain polyhedra that are too distorted). The evaluation of applicability should be performed through an independent route, and before any discussion based on the bond valences is proposed. On the other hand, in the CD method the Q for the anions is computed by distributing q as a function of ECoN, whereas Q for the cations is computed by distributing the q/Q of the anions, again as a function of ECoN. It follows that even when $q/Q(\text{anions})$ is significantly different from 1, $q/Q(\text{cations})$ is expected to be close to 1 for the method to be applicable. A $q/Q(\text{cations})$ ratio significantly different from 1 suggests that the structure may not be completely refined (6).

In Table 1 the results of the CD analysis are given for the four known members of the $\text{LuFeO}_3(\text{ZnO})_m$ series. The deviation of Q with respect to q is rather high for the $m = 1$ member ($\sigma = 18.6\%$), as well as for the $m = 4$ member, when a trivalent cation is located in the M_{K+1} site ($\sigma = 14\%$). For the two other members the agreement is better ($m = 5$, $\sigma = 9.3\%$; $m = 6$, $\sigma = 8.6\%$). For $m = 1$, q/Q differs from

TABLE 1
Charge Distribution (5, 6) for the Accretional Homologous Series $\text{LuFeO}_3(\text{ZnO})_m$, Computed on the Basis of the Refined Structures in (1)

m	Compound	Cation	q	Q	q/Q
1 ^a	LuFeZnO_4 $\sigma = 0.186$	Lu	3.00	2.83	1.06
		Zn/Fe	2.50	2.58	0.97
4 ^a	$\text{LuFeZn}_4\text{O}_7$ (1/5, 2/5, 2/5) $\sigma = 0.140$	Lu	3.00	2.88	1.04
		Zn/Fe	2.20	2.40	0.92
		Zn/Fe	2.20	2.22	0.99
	$\text{LuFeZn}_4\text{O}_7$ (1/3, 2/3, 0) $\sigma = 0.066$	Zn/Fe	2.20	2.14	1.03
		Lu	3.00	2.96	1.01
		Zn/Fe	2.33	2.40	0.97
5 ^a	$\text{LuFeZn}_5\text{O}_8$ (1/3, 1/3, 1/3) $\sigma = 0.093$	Zn/Fe	2.33	2.27	1.03
		Zn	2.00	2.05	0.98
		Zn/Fe	2.17	2.27	0.96
	$\text{LuFeZn}_5\text{O}_8$ (1/2, 1/2, 0) $\sigma = 0.054$	Zn/Fe	2.17	2.17	1.00
		Zn/Fe	2.17	2.13	1.02
		Lu	3.00	2.94	1.02
6	$\text{LuFeZn}_6\text{O}_9$ (1/7, 2/7, 2/7, 2/7) $\sigma = 0.086$	Zn/Fe	2.25	2.27	0.99
		Zn/Fe	2.25	2.21	1.02
		Zn	2.00	2.06	0.97
		Zn/Fe	2.00	2.06	0.97
		Zn/Fe	2.00	2.06	0.97
	$\text{LuFeZn}_6\text{O}_9$ (1/5, 2/5, 2/5, 0) $\sigma = 0.073$	Lu	3.00	3.05	0.98
		Zn/Fe	2.14	2.28	0.94
		Zn/Fe	2.14	2.17	0.99
		Zn/Fe	2.14	2.10	1.02
		Zn/Fe	2.14	2.07	1.04
		Lu	3.00	3.10	0.97
		Zn/Fe	2.20	2.28	0.97
Zn/Fe	2.20	2.17	1.01		
Zn/Fe	2.20	2.13	1.03		
Zn	2.00	2.01	1.00		

Note. Numbers in parenthesis below the chemical formula represent the fractional occupations of the M sites; $\sigma = [\sum_{i=1}^N (q_i - Q)^2 / N - 1]^{1/2}$ measures the deviation of the computed "charges" (Q) with respect to the formal oxidation numbers (q).

^aStructures with distorted trigonal bipyramid ($M_{K+1}-\text{O}_{K+2} < M_{K+1}-\text{O}_{K+1}$).

1 by 6% for the Lu site, but by only half that for the $M1$ (Fe/Zn) site: this suggests that some problems still remain in the structural determination of the Lu site. For the $m = 4$ member, when disordered Fe/Zn distribution is assumed, the highest deviation (8%) is for the $M1$ site, followed by Lu (4%). Assuming only Zn in the $M3$ site, a significant improvement (reduction to 3 and 1%, respectively) is obtained. For $m = 5$, assuming no Fe in the $M3$ site, a general improvement is again obtained, whereas for $m = 6$ the indications are less clear. In the $m = 1, 4$ and 5 members, the trigonal bipyramid around M_{K+1} is distorted ($M_{K+1}-\text{O}_{K+2} < M_{K+1}-\text{O}_{K+1}$) and approaches the tetrahedral shape, whereas it is more regular for the $m = 6$ member. The improved charge distribution obtained when the trivalent cation avoids the polyhedron next to the Lu

octahedron seems thus related to the existence of distorted polyhedra midway between tetrahedra and trigonal bipyramids. The Zn is known to prefer a tetrahedral coordination (16): the distorted M_{K+1} is thus likely to be preferentially occupied by Zn, leaving Fe distributed among the other M_K sites. Besides, entrance of Fe^{3+} in the distorted M_{K+1} , which shares O_{K+2} with the Lu octahedron and has $M_{K+1}-\text{O}_{K+2}$ as the shortest of the five $M-\text{O}$ distances, would likely produce a Lu-Fe repulsion, which would not occur in an undistorted bipyramid. The Lu in the octahedral site can thus tend to prevent the entrance of a trivalent cation in the neighboring M_{K+1} site.

For the $m = 1$ member, since there is only one M site, no site preference for Zn is possible, and the Lu- Fe^{3+} repulsion cannot hinder Fe^{3+} from entering there. In order to reduce the repulsion, the Lu may thus be displaced from the center of symmetry. This appears as a large U_{33} factor for Lu and high positive and negative values of the Fourier difference around the center of symmetry. This hypothesis is supported by a recent neutron study of the same compound (4), in which the structure could be correctly refined only by adopting the split-atom model for Lu.

REVISED REFINEMENT OF THE LuFeZnO_4 STRUCTURE

To test the hypotheses described in the previous section, we have re-refined the LuFeZnO_4 structure starting from the original intensities collected by Isobe *et al.* (1). For the description of synthesis and starting materials see (1, 17). The $m = 1$ member was chosen as the most significant test structure because of the sharing of the M_{K+1} site by Fe and Zn. Intensities had been collected in the $R\bar{3}m$ asymmetric unit; however, re-examination of the original file revealed that, different from what was reported by Isobe *et al.* (1), data collection was not performed in the ($0 \leq h \leq 7$; $0 \leq k \leq 7$; $0 \leq l \leq 61$) region but in the ($0 \leq h \leq 4$; $0 \leq k \leq 7$; $-61 \leq l \leq 60$) one. Isobe *et al.* (1) transformed the indices from the second to the first region, and merged reflections that were on the border of the asymmetric unit. The refinement was then performed against F . We have kept the original indexing and used the whole set of data, to check the consistency of the equivalents. Six strong reflections ($003, 006, 009, -129, -12\bar{1}\bar{2}, -24\bar{1}\bar{2}$) are actually not consistent and give an $R_{\text{int}} = 0.0272$. The LP corrections were performed through the XCAD4 program (18), and the spherical absorption correction with the PLATON package (19). The structure refinement was performed against F^2 with SHELX-97 (20) (observed and calculated F are in Table 2). A first refinement with Lu on the center of symmetry (*central-atom model*) was performed, which gave an $R1$ similar to that obtained by Isobe *et al.* (1) (Table 3). In the Fourier difference, the highest peak was lower than that reported by Isobe *et al.* (1), but the deepest hole was higher. However, the locations of both the peak

TABLE 2
Observed and Calculated (Split-Atom Model) Structure Factors for LuFeZnO_4

h	k	l	$10F_o$	$10F_c$	$10s$	h	k	l	$10F_o$	$10F_c$	$10s$	h	k	l	$10F_o$	$10F_c$	$10s$	h	k	l	$10F_o$	$10F_c$	$10s$
-1	2	0	3175	3133	6	-5	6	7	314	323	5	-6	7	14	561	554	4	-2	6	22	265	265	6
0	3	0	2071	2035	8	-2	6	7	338	346	5	-3	7	14	619	630	4	-4	7	22	227	222	6
-2	4	0	1763	1752	8	-7	7	7	230	230	5	0	7	14	484	491	3	-1	7	22	194	200	6
-1	5	0	1257	1244	6	-4	7	7	295	285	5	-5	8	14	484	491	3	0	1	23	1347	1336	6
-3	6	0	1042	1039	5	-1	7	7	255	254	5	0	0	15	1264	1308	4	-2	2	23	1142	1137	5
0	6	0	836	825	4	-3	8	7	227	230	5	-1	2	15	1058	1080	8	-1	3	23	1009	992	5
-2	7	0	774	769	4	-0	1	8	1535	1506	5	-3	3	15	819	822	4	-3	4	23	794	791	3
-4	8	0	638	634	3	-2	2	8	1216	1212	5	0	3	15	807	822	3	0	4	23	722	718	4
-1	1	1	2259	2287	5	-1	3	8	1047	1036	5	-2	4	15	725	737	2	-5	5	23	571	558	4
0	2	1	1789	1759	6	-3	4	8	813	819	4	-4	5	15	561	559	4	-2	5	23	665	656	4
-2	3	1	1453	1463	7	0	4	8	735	742	3	-1	5	15	557	559	4	-4	6	23	530	518	4
-4	4	1	996	1004	4	-5	5	8	594	575	4	-6	6	15	392	392	5	-1	6	23	480	483	4
-1	4	1	1118	1119	5	-2	5	8	680	678	3	-3	6	15	465	479	3	-6	7	23	379	373	4
-3	5	1	891	910	4	-4	6	8	557	533	4	0	6	15	394	392	4	-3	7	23	418	422	4
0	5	1	769	764	4	-1	6	8	493	496	4	-5	7	15	369	368	4	0	0	24	1075	1085	11
-5	6	1	658	655	4	-6	7	8	388	386	4	-2	7	15	369	368	4	-1	2	24	904	917	3
-2	6	1	701	705	4	-3	7	8	435	435	4	-4	8	15	308	312	3	-3	3	24	696	708	3
-7	7	1	453	449	4	0	7	8	342	346	4	-1	1	16	192	216	3	0	3	24	719	708	3
-4	7	1	571	570	4	-5	8	8	352	346	4	0	2	16	199	227	4	-2	4	24	631	635	2
-1	7	1	509	504	4	0	0	9	2765	2863	45	-2	3	16	218	231	4	-4	5	24	486	483	4
-3	8	1	447	449	4	-1	2	9	2239	2208	44	-4	4	16	214	214	5	-1	5	24	488	483	4
0	1	2	221	262	2	-3	3	9	1603	1558	7	-1	4	16	234	223	5	-6	6	24	336	335	5
-2	2	2	377	378	2	0	3	9	1611	1558	7	-3	5	16	200	203	6	-3	6	24	410	413	6
-1	3	2	377	407	3	-2	4	9	1370	1365	10	0	5	16	192	182	7	0	6	24	340	335	5
-3	4	2	386	400	3	-4	5	9	1012	996	5	-5	6	16	174	164	8	-5	7	24	320	314	4
0	4	2	374	384	4	-1	5	9	1006	996	5	-2	6	16	175	172	8	-2	7	24	314	314	5
-5	5	2	309	327	5	-6	6	9	691	677	4	4	7	16	156	149	8	-1	1	25	53	36	17
-2	5	2	355	366	4	-3	6	9	832	841	2	-1	7	16	151	137	8	0	2	25	43	30	43
-4	6	2	317	309	5	0	6	9	679	677	4	0	1	17	747	732	3	-2	3	25	77	37	13
-1	6	2	290	293	5	-5	7	9	646	635	4	-2	2	17	684	621	3	-4	4	25	38	48	38
-6	7	2	234	242	6	-2	7	9	635	635	4	-1	3	17	624	551	3	-1	4	25	114	46	9
-3	7	2	258	264	6	-4	8	9	523	530	2	-3	4	17	461	454	3	-3	5	25	48	48	40
0	7	2	226	224	5	-1	1	10	2208	2274	6	0	4	17	445	417	4	0	5	25	81	48	16
-5	8	2	214	224	6	0	2	10	1856	1796	7	-5	5	17	344	330	5	-5	6	25	36	47	36
0	0	3	1003	1039	16	-2	3	10	1510	1504	7	-2	5	17	409	384	8	-2	6	25	56	48	56
-1	2	3	883	874	8	-4	4	10	1033	1033	5	4	6	17	311	307	5	-4	7	25	77	47	16
-3	3	3	691	706	8	-4	4	10	1164	1152	5	-1	6	17	305	287	5	-1	7	25	0	46	1
0	3	3	689	706	3	-3	5	10	930	936	4	-6	7	17	239	226	5	0	1	26	155	152	5
-2	4	3	689	648	4	0	5	10	796	786	4	-3	7	17	265	253	5	-2	2	26	119	106	7
-4	5	3	506	514	4	-5	6	10	684	674	4	0	0	18	1592	1563	10	-1	3	26	80	76	13
-1	5	3	512	514	4	-2	6	10	727	726	4	-1	2	18	1327	1304	4	-3	4	26	32	46	32
-6	6	3	365	369	5	-7	7	10	451	461	4	-3	3	18	1005	988	5	0	4	26	23	38	22
-3	6	3	441	446	6	-4	7	10	588	587	4	0	3	18	1020	988	5	-5	5	26	0	27	1
0	6	3	370	369	5	-1	7	10	535	518	4	-2	4	18	894	882	3	-2	5	26	58	32	57
-5	7	3	349	348	5	-3	8	10	460	461	4	-4	5	18	679	666	4	-4	6	26	49	25	49
-2	7	3	338	348	5	0	1	11	434	456	2	-1	5	18	1664	666	4	-1	6	26	0	24	1
-4	8	3	302	299	4	-2	2	11	451	463	2	-6	6	18	468	466	4	3	7	26	0	24	1
-1	1	4	2419	2479	5	-1	3	11	438	450	3	-3	6	18	572	571	3	0	0	27	715	693	10
0	2	4	2016	1969	6	-3	4	11	394	408	3	0	6	18	451	466	4	-1	2	27	608	606	2
-2	3	4	1652	1651	7	0	4	11	377	385	4	-5	7	18	440	439	4	-3	2	27	494	485	4
-4	4	4	1148	1132	5	-5	5	11	336	319	5	-2	7	18	443	439	4	0	3	27	486	485	4
-1	4	4	1316	1263	6	-2	5	11	351	362	4	-1	1	19	1262	1257	6	-2	4	27	443	441	3
-3	5	4	1017	1025	5	-4	6	11	295	301	5	0	2	19	1117	1087	5	-4	5	27	344	345	5
0	5	4	858	861	4	-1	6	11	286	284	5	-2	3	19	969	956	4	-1	5	27	349	345	5
-5	6	4	737	739	4	-6	7	11	221	233	6	-4	4	19	705	700	3	-6	6	27	253	248	5
-2	6	4	786	796	4	-3	7	11	259	255	6	-1	4	19	782	769	3	-3	6	27	297	300	4
-7	7	4	511	509	3	0	7	11	227	214	5	-3	5	19	643	642	4	0	6	27	236	248	6
-4	7	4	634	645	4	-5	8	11	208	214	5	0	5	19	558	550	4	-5	7	27	236	234	5
-1	7	4	565	570	4	0	0	12	229	186	4	-5	6	19	484	481	4	-2	7	27	234	234	5

TABLE 2—Continued

<i>h</i>	<i>k</i>	<i>l</i>	10 <i>F</i> _o	10 <i>F</i> _c	10 <i>s</i>	<i>h</i>	<i>k</i>	<i>l</i>	10 <i>F</i> _o	10 <i>F</i> _c	10 <i>s</i>	<i>h</i>	<i>k</i>	<i>l</i>	10 <i>F</i> _o	10 <i>F</i> _c	10 <i>s</i>	<i>h</i>	<i>k</i>	<i>l</i>	10 <i>F</i> _o	10 <i>F</i> _c	10 <i>s</i>
-3	8	4	501	509	3	-1	2	12	362	106	109	-2	6	19	505	513	4	-1	1	28	927	880	4
0	1	5	2476	2386	5	-3	3	12	263	205	4	-4	7	19	421	425	4	0	2	28	766	771	3
-2	2	5	1955	1965	6	0	3	12	281	205	3	-1	7	19	381	380	4	-2	3	28	686	686	3
-1	3	5	1718	1669	7	-2	4	12	249	218	35	0	1	20	444	454	2	-4	4	28	527	514	4
3	4	5	1272	1285	6	-4	5	12	213	212	6	-2	2	20	402	417	3	-1	4	28	556	561	4
0	4	5	1135	1153	5	-1	5	12	217	212	5	-1	3	20	376	385	3	-3	5	28	477	474	4
-5	5	5	882	878	4	-6	6	12	177	177	8	-3	4	20	320	331	4	0	5	28	407	409	4
-2	5	5	1015	1045	5	-3	6	12	207	197	4	0	4	20	305	307	5	-5	6	28	356	357	5
-4	6	5	807	813	4	0	6	12	171	177	8	-5	5	20	273	251	5	-2	6	28	380	381	5
-1	6	5	742	755	4	-5	7	12	179	171	7	-2	5	20	285	286	5	-4	7	28	311	315	4
-6	7	5	583	586	4	-2	7	12	162	171	8	-4	6	20	231	235	7	0	1	29	215	226	5
-3	7	5	642	661	4	-4	8	12	154	158	6	-1	6	20	220	222	6	-2	2	29	200	210	5
0	7	5	515	524	3	-1	1	13	1566	1579	6	-6	7	20	185	181	6	-1	3	29	201	195	5
-5	8	5	517	524	3	0	2	13	1322	1306	6	-3	7	20	217	199	6	-3	4	29	193	169	6
0	0	6	1440	1535	24	-2	3	13	1134	1123	5	0	0	21	53	39	52	0	4	29	160	158	8
-1	2	6	1181	1205	14	-4	4	13	815	801	4	-1	2	21	66	60	10	-5	5	29	138	133	9
-3	3	6	888	903	4	-1	4	13	880	885	4	-3	3	21	87	90	11	-2	5	29	157	149	8
0	3	6	891	903	4	-3	5	13	733	730	3	0	3	21	136	90	7	-4	6	29	131	126	10
-2	4	6	780	811	8	0	5	13	614	619	4	-2	4	21	73	94	15	-1	6	29	133	120	9
-4	5	6	605	619	4	-5	6	13	543	535	4	-4	5	21	123	91	10	-3	7	29	114	110	10
-1	5	6	627	619	3	-2	6	13	562	574	4	-1	5	21	96	91	13	0	0	30	188	168	7
-6	6	6	432	433	4	-7	7	13	374	373	4	-6	6	21	101	77	12	-1	2	30	157	135	4
-3	6	6	516	530	6	-4	7	13	460	470	4	-3	6	21	97	85	24	-3	3	30	110	95	10
0	6	6	435	433	4	-1	7	13	420	417	4	0	6	21	78	77	17	0	3	30	53	95	52
-5	7	6	413	407	4	-3	8	13	368	373	4	-5	7	21	93	75	13	-2	4	30	103	83	8
-2	7	6	401	407	4	0	1	14	2467	2431	6	-2	7	21	73	75	18	-4	5	30	78	60	18
-4	8	6	341	345	3	-2	2	14	1911	1941	7	-1	1	22	567	567	2	-1	5	30	0	60	1
-1	1	7	842	903	4	-1	3	14	1647	1630	7	0	2	22	500	507	3	-6	6	30	0	38	1
0	2	7	658	694	3	-3	4	14	1242	1247	6	-2	3	22	453	458	3	-3	6	30	0	50	1
-2	3	7	569	600	2	0	4	14	1104	1117	5	-4	4	22	381	352	4	0	6	30	65	38	64
-4	4	7	456	465	3	-5	5	14	855	847	4	-1	4	22	378	382	4	-5	7	30	46	34	46
-1	4	7	457	502	3	-2	5	14	1005	1011	5	-3	5	22	332	325	5	-2	7	30	45	34	35
-3	5	7	413	431	4	-4	6	14	783	782	4	0	5	22	284	282	5	-1	1	31	196	179	5
0	5	7	368	372	4	-1	6	14	716	725	4	-5	6	22	257	249	6	0	2	31	142	162	7
-5	5	41	115	125	10	-2	2	44	210	211	6	0	1	47	157	149	8	-1	3	50	31	12	30
-2	5	41	125	144	10	-1	3	44	199	195	7	-2	2	47	162	137	8	-3	4	50	66	9	66
-4	6	41	98	116	11	-3	4	44	157	168	9	-1	3	47	131	126	10	0	4	50	0	8	1
0	0	42	268	274	4	0	4	44	124	157	11	-3	4	47	133	108	9	0	0	51	192	191	5
-1	2	42	248	250	7	-5	5	44	116	128	9	0	4	47	115	101	10	-1	2	51	184	176	13
-3	3	42	208	213	7	-2	5	44	125	146	10	-2	5	47	111	94	10	-3	3	51	157	151	8
0	3	42	201	213	7	0	0	45	96	44	29	0	0	48	117	107	24	0	3	51	166	151	7
-2	4	42	189	198	5	-1	2	45	41	41	40	-1	2	48	84	100	16	-2	4	51	136	140	42
-4	5	42	165	162	7	-3	3	45	0	37	1	-3	3	48	87	88	15	-1	1	52	52	25	52
-1	5	42	138	162	9	0	3	45	0	37	1	0	3	48	0	88	1	0	2	52	36	23	35
-3	6	42	135	142	5	-2	4	45	28	35	28	-2	4	48	65	83	14	-2	3	52	53	21	31
-1	1	43	0	80	1	-4	5	45	0	30	1	-1	1	49	257	229	6	-1	4	52	61	17	60
0	2	43	51	71	51	-1	5	45	54	30	53	0	2	49	239	212	6	0	1	53	186	206	7
-2	3	43	61	64	60	-1	1	46	172	177	8	-2	3	49	208	196	7	-2	2	53	160	191	8
-4	4	43	0	47	1	0	2	46	166	163	8	-4	4	49	161	158	7	-1	3	53	146	178	8
-1	4	43	0	52	1	-2	3	46	159	151	8	-1	4	49	183	170	7	-3	4	53	130	154	8
-3	5	43	0	42	1	-4	4	46	139	123	8	-3	5	49	162	147	6	0	0	54	125	119	14
0	5	43	26	35	25	-1	4	46	141	131	9	0	1	50	67	16	22	-1	2	54	110	111	8
0	1	44	218	230	6	-3	5	46	45	115	44	-2	2	50	35	14	35	-3	3	54	41	98	41

(exactly above Lu) and the hole (at 0.60 Å from Lu along *z*) suggested that Lu was probably not on the center of symmetry. Therefore, a second refinement was performed, adopting the *split-atom model* for Lu. As shown in Table 3,

the *R* factor, the *U*_{eq} displacement, and especially the Fourier difference improved significantly (anisotropic displacement parameters are in Table 4). The displacement of Lu from the center of symmetry is about ±0.14 Å. The

TABLE 3

Results of the Structure Refinement of LuFeZnO₄ in the Central-Atom Model (CAM) and in the Split-Atom Model (SAM)

	Isobe <i>et al.</i> (1)
M_r	360.19
Calculated density	6.96 Mg/m ³
Radiation	MoK α ($\lambda = 0.71073$ Å)
Number of reflections for cell parameters	25
T	295 K
Crystal shape, size, color	sphere, 0.0525 mm (radius), brown
Diffractionmeter	Enraf-Nonius CAD 4
Scan	$\omega/2\theta$
Standard reflections and frequency of measurements	3, 240 min
Intensity variation	– 0.2%
Absorption coefficient	39.70 mm ^{–1}
ϑ_{max}	60°
Range for cell parameters	39° $\leq \vartheta \leq$ 48°
Limiting indices	0 $\leq h \leq$ 4, 0 $\leq k \leq$ 7, –61 $\leq l \leq$ 60
Space group	$R\bar{3}m$ (D_{3d}^5) (No. 166)
Z	3
Collected reflections	558 (actually 635)
Unique reflections	558
Reflections with $I > 1.5\sigma(I)$	484
$R1$	0.036
w $R1$	0.036
Goof (S) parameters	2.3
$\Delta\rho_{max}$	7.9 eÅ ^{–3}
$\Delta\rho_{min}$	–11.9 eÅ ^{–3}
Extinction coefficient	7.0 $\times 10^{-6}$

	Wyckoff position	$x = y$	z	U_{eq}
Lu:	3a	0	0	0.0184(1)
M1	6c	0	0.21564(3)	0.0084(1)
O(1)	6c	0	0.1287(3)	0.022(1)
O(2)	6c	0	0.2923(2)	0.013(1)
Lu–O(2)		2.233(2) ($\times 6$)		
M1–O(2)		1.952(5)		
M1–O(1)		1.993(1) ($\times 3$)		
M1–O(1)		2.215(8)		
O(2)–Lu–O(2)		99.9(1) ($\times 6$)		
O(2)–Lu–O(2)		80.1(1) ($\times 6$)		
O(2)–Fe–O(1)		98.1(2) ($\times 3$)		
O(1)–Fe–O(1)		118.1(1) ($\times 3$)		
O(2)–Fe–O(1)		81.9(2) ($\times 3$)		

	Present study
M_r	360.19
Volume	257.70(3) Å ³
Calculated density	6.963 Mg/m ³
Absorption coefficient	39.442 mm ^{–1}
Range for data collection	2.40 $\leq \vartheta \leq$ 59.63°
Limiting indices	0 $\leq h \leq$ 4, 0 $\leq k \leq$ 7, –61 $\leq l \leq$ 60
Space group	$R\bar{3}m$ (D_{3d}^5) (No. 166)
Z	3
Completeness to $\vartheta = 59.63$	100.0%
Collected reflections	635
Unique reflections	558
Reflections with $I > 2\sigma(I)$	484
$R(\text{int})$	0.0272

TABLE 3—Continued

	Central-atom model (Lu at 0,0,0)	Split-atom model (Lu at 0, 0, z)			
$R1[I > 2\sigma(I)]$	0.0360	0.0262			
$R1$ (all data)	0.0452	0.0368			
w $R2[I > 2\sigma(I)]$	0.0843	0.0672			
w $R2$ (all data)	0.0872	0.0700			
Goof (S)	1.219	1.211			
No. of parameters	13	14			
$\Delta\rho_{max}$	6.131 eÅ ^{–3}	5.388 eÅ ^{–3}			
	(0, 0, 0)	(2/3, 1/3, 0.1022)			
	0.0 Å	0.39 Å from M1			
	from Lu				
$\Delta\rho_{min}$	– 13.928 eÅ ^{–3}	– 3.774 eÅ ^{–3}			
	(0, 0, 0.0236)	(0, 0, 0.0272)			
	0.60 Å from Lu	0.55 Å from Lu			
$F(000)$	477	477			
Extinction coefficient	0.0110(9)	0.0008(6)			
	Wyckoff pos.	$x = y$	z	U_{eq}	
Lu:	3a	0	0	0.019(1)	
M1	6c	0	0.2156(1)	0.009(1)	
O(1)	6c	0	0.1288(4)	0.021(1)	
O(2)	6c	0	0.2926(2)	0.013(1)	
	Wyckoff pos.	Occupancy	$x = y$	z	U_{eq}
Lu:	6c	0.5	0	0.0056(1)	0.010(1)
M1	6c	1.0	0	0.2156(1)	0.008(1)
O(1)	6c	1.0	0	0.1292(3)	0.019(1)
O(2)	6c	1.0	0	0.2924(2)	0.012(1)
Lu–O(2)		2.230(2) ($\times 6$)		2.1700(15) ($\times 3$)	2.3020(19) ($\times 3$)
M1–O(2)		1.959(5)		1.954(4)	
M1–O(1)		1.9938(13) ($\times 3$)		1.9951(9) ($\times 3$)	
M1–O(1)		2.210(9)		2.202(6)	
O(2)–Lu–O(2)		100.08(15) ($\times 6$)		103.94(10) ($\times 3$)	
O(2)–Lu–O(2)				95.89(11) ($\times 3$)	
O(2)–Lu–O(2)		79.92(15) ($\times 6$)		79.87(10) ($\times 3$)	
O(2)–Lu–O(2)				173.58(4) ($\times 3$)	
O(2)–Fe–O(1)		98.2(3) ($\times 3$)		98.40(19) ($\times 3$)	
O(1)–Fe–O(1)		118.02(13) ($\times 3$)		117.90(9) ($\times 3$)	
O(2)–Fe–O(1)		81.8(3) ($\times 3$)		81.59(17) ($\times 3$)	

Note. Here, $R1$ is computed in terms of F , and $wR2$ is computed in terms of F^2 and is thus more than twice $wR1$. Cell dimensions in hexagonal axes $a = b = 3.4185(1)$ Å, $c = 25.463(3)$ Å, cell volume $V = 257.71(3)$ Å³ (after (1)).

U_{eq} displacement factor of Lu, although significantly lower than the value for the average structure reported in Isobe *et al.* (1), is still relatively high. The cause can be likely found in the statistical distribution of Lu between the two half-sites. The U_{eq} displacement factor of O(1) is not significantly influenced by the model adopted, as could be foreseen from the fact that O(1) is not bound to the octahedral site. A relatively large value of the displacement parameter U_{33} of O(1) has been repeatedly reported for the compounds isostructural with LuFeO₃(ZnO) (e.g., (1, 3, 7)).

TABLE 4
Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for LuFeZnO_4

	Central-atom model (Lu at 0, 0, 0)						Split-atom model (Lu at 0, 0, z)					
	U11	U22	U33	U23	U13	U12	U11	U22	U33	U23	U13	U12
Lu	4(1)	4(1)	49(1)	0	0	2(1)	4(1)	4(1)	23(1)	0	0	2(1)
Fe/Zn	7(1)	7(1)	11(1)	0	0	4(1)	7(1)	7(1)	10(1)	0	0	4(1)
O(1)	14(1)	14(1)	35(3)	0	0	7(1)	15(1)	14(1)	28(2)	0	0	7(1)
O(2)	13(1)	13(1)	13(2)	0	0	6(1)	12(1)	12(1)	12(1)	0	0	6(1)

Note. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12}]$.

DISCUSSION

In the accretional homologous series under consideration, the shape of the trigonal bipyramid of the first K M sites ($K \geq 0$; the total number of M sites is $K + 1$) is more regular, with the three basal M_i - O_i bonds shorter than the M_i - O_{i+1} and M_i - O_{i-1} apical bonds. The shape of the M_{K+1} trigonal bipyramid is, however, distorted, with the M_{K+1} - O_{K+2} apical bond shorter than the three basal bonds M_{K+1} - O_{K+1} , and approaches an irregular tetrahedron. This asymmetric coordination results in an anomalous CD for the cations. A few examples have been reported in which the trigonal bipyramid around the $(K + 1)$ th site is more regular, with the three basal M_{K+1} - O_{K+1} bonds shorter than the apical M_{K+1} - O_{K+2} bond ($\text{InFe}_{0.5}^3\text{Fe}_{1.25}^2\text{Si}_{0.25}\text{O}_4$ (8); $\text{LuFeO}_3(\text{ZnO})_6$ (1); InGaZnO_4 (21)). Those structures do not show any significant anomaly in the cationic CD (21).

The unsatisfactory $q/Q(\text{cation})$ for the $m = 1$ member suggests a displacement of the octahedral cation from the center of symmetry. This displacement has been reported for another sample with the same composition (4) and confirmed in the present study by a re-refinement adopting the split-atom model. When $m > 1$ the effect of the geometrical distortion of the trigonal bipyramid around the M_{K+1} site likely results in a site preference of Zn and in the distribution of the trivalent cation in the other M sites, without necessity of displacing Lu from the center of symmetry. In fact, the structure refinement of the $m = 4, 5, 6$ members did not reveal the same high displacement parameters for Lu that have been found for the $m = 1$ member. The cation distribution could not be determined by structure refinement (1). The indications of the CD analysis for the higher members thus require confirmation from further experimental study.

From the YbFe_2O_4 structure (3) two different accretional homologous series can be derived, $\text{YbFeO}_3(\text{FeO})_m$, isostructural with the $\text{LuFeO}_3(\text{ZnO})_m$ series, and $(\text{YbFeO}_3)_m\text{FeO}$, of which members corresponding to $n = 1$ (3), $n = 2$ (22, 23), $n = 3$, and 4 (24) have been reported. Also

in this second series, the Yb is in octahedral coordination, and the Fe is in trigonal bipyramidal coordination. Only for the first two members, however, has single-crystal structure refinement been reported. The structure of two different samples of the $n = 2$ member are available (22, 23). Within the limits of the quality of the structure refinements (the error was on the second decimal of the bond distances), those two samples have two different kinds of trigonal bipyramids for the Fe2 site: one has the same kind of distortion reported for the $\text{LuFeO}_3(\text{ZnO})_m$ series and q/Q values similar to those reported here (Yb, 1.09; Fe1, 0.93; Fe2, 0.95), whereas in the other case (23) neither such distortion nor such unsatisfactory q/Q values (Yb, 1.02; Fe1, 0.96; Fe2, 1.00) are present (21).

For higher members of the accretional homologous series $\text{InFeO}_3(\text{ZnO})_m$ (isostructural with $\text{LuFeO}_3(\text{ZnO})_m$) extra reflections in the selected area electron diffraction (SAED) pattern were reported (25–28), and were interpreted in terms of superspace group analysis (27). Transmission electron microscope (TEM) observations have revealed the existence of a modulation wave involving the octahedral cation (26–29). Correspondingly, the symmetry lowered to monoclinic and orthorhombic, respectively, instead of rhombohedral and hexagonal, respectively. The distortion of the trigonal bipyramids and its effect on the location of the octahedral cation, as shown in the present research, may play a significant role in the observed anomalies. It is, however, not clear why such anomalies are observed in higher members only. Structural studies of a larger number of members of these series, especially of higher members, are necessary to explain the features revealed by SAED/TEM studies.

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