# Short Communications

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## On the space group of the rare earth orthoferrites and related compounds. By M. MAREZIO,* J. P. REMEIKA and

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The anomalous dispersion effect and a full-matrix least-squares refinement strongly indicate that the structure of the rare-earth orthoferrites should be described in the centrosymmetrical space group *Pbnm*, as found by Geller and Bertaut & Forrat. The space groups suggested by subsequent authors do not appear to be valid.

Many $ABO_3$ compounds, including all rare earth orthoferrites, crystallize with an orthorhombic distortion of the perovskite structure. Geller (1956) determined the structure of $GdFeO_3$ which can be considered the prototype of this series, and found that the probable space groups for these compounds were either *Pbnm* or *Pbn2_1*. The structure of $GdFeO_3$ was solved on the basis of the space group *Pbnm* with four molecules per unit cell. Four Gd atoms were placed in the special positions $4(c)$ $(x,y,\frac{1}{4})$, 4 Fe atoms in the special positions $4(b)$ $(0,\frac{1}{2},0)$, 4 of the oxygen atoms in the special positions $4(c)$ $(x,y,\frac{1}{4})$ and the remaining 8 oxygen atoms in the general positions. Exactly the same arrangement could be obtained in the space group symmetry *Pbn2_1* by placing all atoms in the general positions and moving some of them away from mirror planes. The main difference between the two arrangements would be in the number of degrees of freedom of the atoms. The X-ray intensities showed that the deviations of the atoms from their respective *Pbnm* mirror planes, if any, were extremely small. Therefore, it seemed reasonable to discuss the structure as though the most probable space group were *Pbnm*. Geller also pointed out that it is by no means unreasonable to expect these compounds to be non-centrosymmetric, because their magnetic characters (the Fe sublattices are imperfectly antiferromagnetic at room temperature) would require lower symmetry than *Pbnm*, though not necessarily *Pbn2_1*.

Coppens & Eibschütz (1965) refined the structure of $YFeO_3$ using both space groups. They found that the differences in the positional and thermal parameters between the two refinements were again too small to be able to decide whether or not the structure contains a center of symmetry.

Brusset, Gillier-Pandraud & Berdot (1967) redetermined the structure of $NdGaO_3$, which had also been reported to be isostructural with $GdFeO_3$. By the Patterson method and a full-matrix least-squares refinement these authors have been able to show that the structure of $NdGaO_3$ can only be described in the acentric space group symmetry *Pbn2_1*. The acentric arrangement of $NdGaO_3$ is slightly

different from that proposed by Coppens & Eibschütz for $YFeO_3$.

Okazaki, Iwanaga & Tsukuda (1968), pointed out that the space group of $NaNiF_3$ and $NaCoF_3$ was $P2_12_12_1$ and not *Pbnm* or *Pbn2_1* as reported earlier by Rüdorff, Dincke & Babel (1963), who had found that the crystal structure of $NaCoF_3$ was of $GdFeO_3$ type. In their note Okazaki *et al.* also doubted the space group and therefore the structure of $GdFeO_3$ itself.

In order to eliminate some of these doubts concerning the space group of rare earth orthoferrites, it was decided to redetermine the crystal structure of $LuFeO_3$. This compound was chosen because it should have the most distorted arrangement as a perovskite and the largest anomalous dispersion effect.

A single crystal of $LuFeO_3$,* having the shape of a small parallelepiped, was oriented on a precession camera with the [001] as the precessing axis. Long exposure photographs taken with Mo $K\alpha$ radiation showed that the only systematically absent reflections were $h0l$ when $h+l=2n+1$ and $0kl$ when $k=2n+1$. This confirms the space groups assigned by Geller (1956) and Bertaut & Forrat (1956). The intensity measurements were made by use of the same diffractometer and by following the same procedure described in an earlier paper (Marezio, Remeika & Dernier, 1969). The specimen was a sphere of radius $R=0.073$ mm, which was oriented with the [010] zone axis parallel to the $\theta$ axis of the goniostat. All reflections having $2\theta \leq 90°$ included in the upper hemisphere were measured. No difference in intensity was noted between pairs of reflections $hkl$ and $\bar{h}k\bar{l}$. All fluctuations were well within the counting statistics indicating that the structure of $LuFeO_3$ should contain a center of symmetry. Any systematic violation of Friedel's law was not observed among the intensities of all the other rare-earth orthoferrites (Marezio, Remeika & Dernier, 1970). Although this observation is a strong indication that at least the rare-earth orthoferrites have a centric structure, unfortunately it is not conclusive. The magnitude of the inequalities $(I_{hkl}-I_{\bar{h}k\bar{l}})$ not only depends upon the values of the $\Delta f''$ of the atoms present in the compound, but also upon the magnitude of the displacements of the atoms from their centric positions. The absorption and Lorentz-

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* Details of the crystal growth technique will be reported later.

polarization corrections were applied in order to convert the integrated intensities into structure factors.

A three-dimensional Patterson synthesis was computed using the program *Four* written by Fritchie (1967) and modified by L. Guggenberger and P. B. Jamieson. The squares of the 634 observed structure factors on an arbitrary scale were the input terms. Since there was no difference between the pairs $F_{hkl}$ and $F_{\bar{h}kl}$ their average was used. All the peaks in the Patterson synthesis could be explained by the structural arrangements, as described by Coppens & Eibschütz (1965), in both space groups *Pbnm* or *Pbn2₁*. The failure of the Patterson synthesis to distinguish between the two arrangements is due to their similarity. However, the Patterson function did show that the arrangement, described by Brusset *et al.* (1967), for NdGaO$_3$ could be discarded as a possible one for rare earth orthoferrites. The difference between the acentric arrangement of Coppens & Eibschütz (1965) and that of Brusset *et al.* (1967) is mainly in the positions of the atoms O(2) and O(3).

The positional parameters of LuFeO$_3$ obtained from the Patterson synthesis were refined with a full-matrix, least-squares program written by Prewitt (1966). In this program the function minimized is $\Sigma w||F_o| - |F_c||^2$, and the discrepancy index, $R$, is equal to $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. The $f$ curves for neutral Lu, Fe and O given by Cromer & Waber (1965) were used together with the values of $\Delta f'$ and $\Delta f''$ for Lu and Fe reported by Cromer (1965). An average value of 0·4 Å$^2$ for each isotropic thermal parameter was assigned as a starting value. Each observed structure factor was weighted by $w = 1/\sigma^2$ where $\sigma = 2\cdot5$ when $|F| \le 25$ and $\sigma = 0\cdot1|F|$ when $|F| > 25$. Two independent refinements carried out simultaneously, one with the space group *Pbnm*, and the other with *Pbn2₁*. The secondary extinction correction was applied according to the formula $F_{corr} = F_o(1 + \beta CI)$ (Zachariasen, 1963). In both cases $F_{obs}$ represented the average of the four values $F_{hkl}$, $F_{\bar{h}kl}$, $F_{hk\bar{l}}$, and $F_{\bar{h}k\bar{l}}$. Convergence was attained after three cycles in both refinements. But, while in the case of *Pbnm* the parameters remained constant with further refinement, in the case of *Pbn2₁* the refinement fell into a loop: O(1) started to oscillate above and below the pseudomirror plane at $l = \frac{1}{4}$,

while the standard deviation of the $z$ parameter was abnormally large. Furthermore, the two refinements yielded the same $R$ index, 0·034, even though the centric structure has a smaller number of variables, indicating that the REFeO$_3$ structure as determined by X-ray has a centric arrangement. The final values of the two refinements are reported in Table 1 for comparison. The centric refinement was carried on further by introducing anisotropic thermal parameters. These results will be reported together with the refinements of all the other rare earth orthoferrites. (Marezio, Remeika & Dernier, 1970).

In order to determine if displacement of the Fe atoms in the centric refinement gives rise to measurable differences between some of the weak pairs $F_{hkl}$ and $F_{\bar{h}kl}$, these two values were calculated for all possible reflections using the final values reported in Table 1. The results showed that the differences were in all cases within the experimental errors.

The crystals of the rare earth orthoferrites are known to grow in the form of polytwins. We have investigated this feature in LaFeO$_3$, PrFeO$_3$, NdFeO$_3$, EuFeO$_3$ and LuFeO$_3$. Our data indicate that twinning occurs as a rotation of 90° around the c* axis. Therefore, along a* there is a certain percentage of b* and *vice versa*, whereas c* is uniquely determined.

In LaFeO$_3$ it was found that along a* about 27% is b* and 73% a* and *vice versa* along b*. No dispersion of the c* (orthorhombic) among the three a* of the pseudo-cubic cell has been found indicating that these compounds grow from the flux melt as orthorhombic crystals. Some preliminary results are reported in Table 2. Some forbidden reflections (h0l) with $h + l = 2n + 1$ are present, such as 201, 401, 601, 203, *etc.* If our twinning hypothesis is correct, these reflections are the allowed reflections 021, 041, *etc.* A few forbidden reflections (0kl) were observed. They were extremely weak because the allowed h0l's with $h = 2n + 1$ and $l = 2n + 1$ are very weak. Of course, the presence of the extra reflections could be easily justified by assigning a different space group, such as the one proposed by Okazaki *et al.* (1968), $P2_12_12_1$. But two striking features suggest that these extra reflections are due to twinning: (1) A constant ratio between $I_{h0l}$ and $I_{0kl}$ when $h = k = 2n$ and $l = 2n + 1$ was observed. Whereas the same ratio of the reflections with $h = k = 2n$ and $l = 2n$, which are both allowed by the space group *Pbnm*, varies over a very large range. (2) The reflections h0l with $h = 2n + 1$ and $l = 2n$ are all absent. This is due to the fact that the corresponding reflections 0kl are systematically absent.

Table 1. *Final values of the positional and thermal parameters of* LuFeO$_3$

| | | *Pbn2₁* | *Pbnm* |
|---|---|---|---|
| Lu | x | −0·02000 (8) | −0·02000 (6) |
| | y | 0·07136 (8) | 0·07143 (7) |
| | z | (0·25) | (0·25) |
| | B | 0·506 (9) | 0·503 (9) |
| Fe | x | −0·0054 (11) | (0) |
| | y | 0·5075 (9) | (0·50) |
| | z | 0·0016 (9) | (0) |
| | B | 0·44 (2) | 0·503 (1) |
| O(1) | x | 0·1197 (15) | 0·1203 (13) |
| | y | 0·4520 (16) | 0·4529 (13) |
| | z | 0·2546 (60)* | (0·25) |
| | B | 0·76 (14) | 0·68 (7) |
| O(2) | x | −0·3131 (25) | −0·3112 (9) |
| | y | 0·3109 (25) | 0·3072 (9) |
| | z | 0·0575 (22) | 0·0619 (7) |
| | B | 0·32 (17) | 0·66 (5) |
| O(3) | x | 0·3108 (31) | |
| | y | −0·3013 (32) | |
| | z | −0·0699 (25) | |
| | B | 0·68 (24) | |

\* In the previous cycle it was $z = 0\cdot2462$.

Table 2. *Twinning data for* LaFeO$_3$

| Allowed reflections in the zone ⟨0kl⟩ | | | | Forbidden reflections in the zone ⟨h0l⟩ | | | | % of b* along a* |
|---|---|---|---|---|---|---|---|---|
| h | k | l | $I^*_{obs}$ | h | k | l | $I^*_{obs}$ | |
| 0 | 2 | 1 | 376 | 2 | 0 | 1 | 153 | 29 |
| 0 | 4 | 1 | 511 | 4 | 0 | 1 | 195 | 28 |
| 0 | 6 | 1 | 341 | 6 | 0 | 1 | 114 | 25 |
| 0 | 8 | 1 | 216 | 8 | 0 | 1 | 74 | 26 |
| 0 | 10 | 1 | 91 | 10 | 0 | 1 | 29 | 24 |
| 0 | 12 | 1 | 36 | 12 | 0 | 1 | 15 | 29 |
| 0 | 6 | 3 | 386 | 6 | 0 | 3 | 134 | 26 |
| 0 | 10 | 5 | 64 | 10 | 0 | 5 | 22 | 26 |
| 0 | 2 | 3 | 383 | 2 | 0 | 3 | 147 | 28 |
| | | | | | | | Average | 27 |

\* These values, which are net of background, were measured by using a single crystal of LaFeO$_3$ ground into a sphere.

We have investigated only one crystal for each compound and therefore we cannot make any generalization, but our results seem to indicate that the degree of twinning decreases drastically on going from $LaFeO_3$ to $LuFeO_3$. We have found that it is $\sim 27\%$ for $LaFeO_3$, $\sim 8\%$ for $PrFeO_3$, $\sim 3\%$ for $NdFeO_3$, barely observable in $EuFeO_3$, and absent in $LuFeO_3$.

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# Note on the space group of potassium hydrogeniodate(V), KIO₃.HIO₃.

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A pronounced piezolectric effect shows that the space group $P2_1/c$ indicated by X-ray evidence is incorrect.

Recent experience with acid potassium iodate $KIO_3.HIO_3$ has shown that one cannot rely on X-ray evidence alone for the determination of the symmetry of a compound, even if the refinement has given good agreement between the $F_o$ and $F_c$ values.

In agreement with the monoclinic symmetry and the systematic extinctions, $0k0$ absent for $k$ odd and $h0l$ absent for $l$ odd, the space group of $KIO_3.HIO_3$ was assumed to be $P2_1/c$. The unit cell with dimensions $a = 7.025(2)$, $b = 8.206(2)$, $c = 21.839(5)$ Å, $\beta = 97.98(1)°$, contains eight (two independent) formula units $KIO_3.HIO_3$. During a least-squares refinement in space group $P2_1/c$ based on 7516 accurately determined independent $F$ values, the weighted residual $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$ decreased to 0.043. For the standard deviations in the iodine and oxygen atom positions small values of 0.0003 and 0.0035 Å respectively were calculated by the least-squares program and reasonable values for the thermal parameters were found. Nonetheless the adopted space group is incorrect as the crystals exhibit a very pronounced piezoelectric effect (kindly measured by Professor W. G. Perdok). A discussion of the structure will be given after the deviations from centrosymmetry have been determined by means of neutron diffraction.

# International Union of Crystallography

## Opening of new Union office

The President of the Union, Professor A. Guinier, together with the Chairman of the Commission on Journals, the General Secretary, the Treasurer, employees of the Union and guests, attended a luncheon in Chester on 7 January to mark the opening of the new Union office. This office, incorporating the office of the Technical Editor and the office of the Executive Secretary, is at 13 White Friars, Chester CH1 1NZ, England. All correspondence for the Technical Editor, Mr S. A. Bryant, and the Executive Secretary, Dr J. N. King, should be sent to this address. Dr King has now taken over the day-to-day business of the Union from the General Secretary and the Treasurer.