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# Characterization and Structure of $La_4Re_6O_{19}$, a New Metal Cluster Compound

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Crystals of $La_4Re_6O_{19}$ have been prepared hydrothermally, and their structure has been solved and refined by least squares to an $R$ of 0.027. The crystals are cubic with $a = 9.0308$ (2) A at 25°, $d_o = 8.92$ (6) and $d_c = 8.91$ for $Z = 2$ and space group I23. The data consisted of 56 reflections collected from the powder using a diffractometer. Rhenium–oxygen octahedra share edges in pairs to form binuclear clusters; in each cluster there is a short Re–Re distance of 2.42 A. These clusters are joined, by sharing corners of the octahedra, to form a three-dimensional network. Within voids of this network there are $La_4O$ tetrahedra. Magnetic and electrical transport properties of $La_4Re_6O_{19}$ have also been studied.

## Introduction

A lanthanum rhenium oxide with body-centered-cubic symmetry ($a \sim 9.0$ A) was discovered by one of us several years ago.[3] At that time a single-crystal X-ray study established that the space group was $I2_13$, I23, or Im3, but the lack of a sufficiently large single-phase sample prevented characterization and structure determination. Now, a new method of preparation has led to a product which is readily purified. A characterization, including a structure determination, has been carried out. The composition of this new lanthanum rhenium oxide has been found to be $La_4Re_6O_{19}$.

## Preparation and Characterization

Although the preparation of $La_4Re_6O_{19}$ can be carried out in evacuated silica ampoules at 1000°,[3] a hydrothermal preparation has been found to offer the advantage of a product which is readily purified. Single-phase $La_4Re_6O_{19}$ has never been obtained in one step by any method, even when the reaction below was attempted.

$$6La_2O_3 + 13ReO_3 + 5Re \longrightarrow 3La_4Re_6O_{19}$$

A typical hydrothermal charge was 1.955 g of $La_2O_3$ (99.999%), 4.216 g of $ReO_3$ (from Alfa Inorganics), and 3 ml of water. The container was a $^3/_8$-in. diameter gold tube, about 5 in. long and sealed by welding at both ends. Reaction conditions were generally 700° for 12 hr with 3000 atm of external pressure applied to the gold tube. The product was multiphase, but only crystals of $La_4Re_6O_{19}$ remained after washing with 6 $N$ HCl. Although some of these crystals had well-developed faces, most were irregular with roughly a spherical shape. The mean diameter of a crystal often was as large as ~0.5 mm.

Although the composition of the purified product was derived primarily from the structure determination, supporting analytical data were obtained. Chemical analysis for lanthanum with EDTA gave 28.0% (28.10% calcd). Thermogravimetric analysis in an $H_2$–Ar (15%) atmosphere showed that 10.5% of the sample was associated with the reducible rhenium; a weight loss of 10.52% is calculated. The density of the $La_4Re_6O_{19}$ crystals was determined by the standard pycnometer method using benzene at 25° (obsd, 8.92 ± 0.06 g/cm$^3$; calcd, 8.91 g/cm$^3$, for $Z = 2$).

Resistivity measurements by the four-probe method were carried out on two crystals from two separate preparations. Metallic behavior was observed from 4.2° ($\rho \sim 10^{-5}$ ohm-cm) to room temperature ($\rho \sim 10^{-4}$ ohm-cm). Thermoelectric power measurements at 298°K showed a Seebeck coefficient *vs.* copper of +1.6 $\mu$v/deg.

Magnetic susceptibility measurements were performed using a Faraday balance at 298, 77, and 4.2°K. Between fields of $1 \times 10^3$ and $8 \times 10^3$ oersteds the expression $\chi_m = \chi_m^0 + (a/H)$ was followed very well. The values of $\chi_m^0 \times 10^3$ and $a$ were: at 298°K, 0.25 and 0.52; at 77°K, 0.43 and 2.15; and at 4.2°K, 2.34 and 0.65, respectively. The field dependence observed could easily be due to a very small amount of an unknown ferromagnetic contamination.

## X-Ray Data

Integrated X-ray powder intensity data were gathered with a Norelco diffractometer using Cu K$\alpha$ radiation and an LiF bent-crystal monochromator. The intensity of each peak was determined by scanning at 0.25°/min and accumulating both time and counts. The background subtracted from a peak was determined from a plot of background *vs.* 2$\theta$. No extraneous peaks were observed, and, since the symmetry is cubic, resolution problems were not encountered.

The sample was prepared by repeatedly grinding it and passing it through a 325-mesh sieve. The powder was then packed in a tray by several different methods and X-ray data were taken to determine if preferred orientation was a serious problem. Comparison of the several sets of data led to the conclusion that preferred orientation was not significant. The depth of the flat sample tray was about 1 mm, which effectively prohibits any X-rays from passing through the sample. The dimensions of the tray and beam slits were such that the entire beam was intercepted by the sample for all

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[1] Operated with support from the U. S. Air Force.

[2] Contribution No. 1375.

[3] J. M. Longo, Ph.D. Dissertation, University of Connecticut, 1964.

peaks except the 110 (which was rejected from the refinement for this reason).

The intensity of a group of equivalent reflections was taken to be $I = F^2SLpM$, where $F$ has its usual definition, $S$ is the scale factor, $L$ is the Lorentz factor of $1/(\sin^2\theta\cos\theta)$, $p$ is the polarization factor of $(1 + \cos^2 2\theta_M \cos^2 2\theta)/2$, and $M$ is the multiplicity factor. $\theta_M$ equals 22.5° for the LiF monochromator used. The observed intensity is compared to the sum of nonequivalent reflections which fall at the same $2\theta$ value. The scattering factor for $O^{2-}$ was taken from Tokonami.[4] The scattering factors for neutral La and Re are those of Cromer and Waber,[5] and the anomalous dispersion corrections for La, Re, and O, were taken from Cromer.[6]

The cell edge of $La_4Re_6O_{19}$ was determined by use of a Guinier camera using strictly monochromatic Cu K$\alpha_1$ radiation. A potassium chloride ($a$ = 6.29310 A) internal standard was used, and a least-squares refinement was carried out. At 25° the unit cell edge is 9.0308 (2) A.

## Structure Determination and Refinement

The preliminary single-crystal investigation showed no reflections in violation of the body-centered requirement of $h + k + l = 2n$. There were no other systematic absences observed. This information and the Laue group limited the space group to the three mentioned below.

Initial computations for structure determination and refinement were made using a program[7] developed at Lincoln Laboratory. Trial atomic positions for La and Re were obtained from compositional and geometrical considerations within the possible space groups $I2_13$, I23, and Im3. Using only the first 14 lines, good results were obtained for La in 8(c) and Re in 12(e) of space group I23. Assuming octahedral coordination of rhenium by oxygen, 36 oxygens were placed in 12(d) and 24(f). Refinement of this model led to an $R$ value of about 6%.

It was now apparent that this structure could be viewed as a three-dimensional network in which rhenium–oxygen octahedra are connected by sharing edges and corners as shown in Figure 1. The lanthanums are located within voids of this network, and the formula at this point was $La_4Re_6O_{18}$.

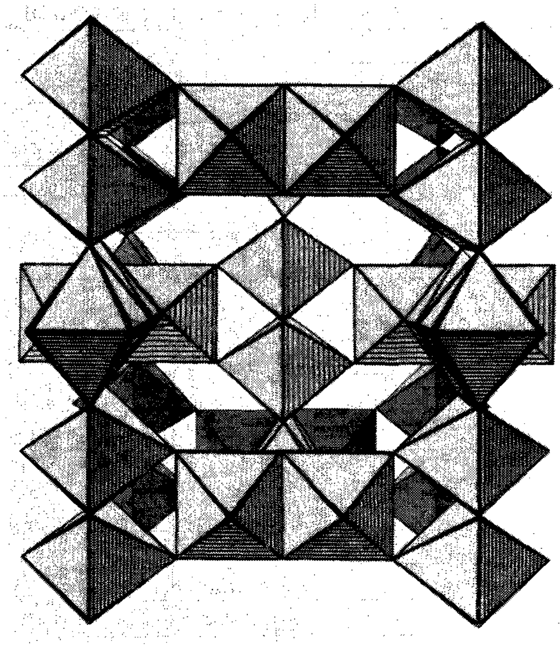
Figure 1.—The rhenium–oxygen octahedra network.

The final refinements were performed using a least-squares program written by C. T. Prewitt. All possible reflections, except the 110, which occurred from 0 to 160° $2\theta$ were used. Real and imaginary anomalous dispersion corrections were made to $A$ and $B$ for all atoms. Since there still appeared to be space available within the voids of the network, additional oxygens were placed at 2(a) and at 8(c) with $x$ = 0.34. Several cycles of least squares indicated that there was an oxygen at 2(a) but that there was no significant scattering power at 8(c) with $x \sim 0.34$. Therefore, the formula was now $La_4Re_6O_{19}$. The $R$ which was minimized was $R = \sqrt{\Sigma(I_o - I_c)^2}/\sqrt{\Sigma I_o^2}$. No weighting scheme was used since data collected by counting and refined on intensities are weighed naturally (*i.e.*, the strongest peak is assumed to have the best accuracy). Based on 56 reflections the final $R$ was 0.027. The corresponding $R'$ was 0.038 where $R' = \Sigma|I_o - I_c|/\Sigma I_o$.

TABLE I

FINAL ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS[a]

| Atom | Position | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|---|
| La | 8(c) | 0.1613 (4) | 0.1613 | 0.1613 | 0.01 |
| | | 0.1599[b] | | | |
| Re | 12(e) | 0.3659 (4) | 0.5 | 0.0 | 0.01 |
| | | 0.3663 | | | |
| $O_1$ | 12(d) | 0.331 (5) | 0.0 | 0.0 | 0.97 (99) |
| | | 0.322 | | | |
| $O_2$ | 24(f) | 0.340 (4) | 0.272 (4) | 0.979 (5) | 1.24 (83) |
| | | 0.341 | 0.284 | 0.974 | |
| $O_3$ | 2(a) | 0.0 | 0.0 | 0.0 | 0.01 |

[a] Parameters are expressed as fractions of the cell edge. Standard deviations are in parentheses. [b] Single-crystal work of N. Morrow and L. Katz, American Crystallographic Association Meeting, 1967, Paper R-6.

The final values of the atomic parameters are given in Table I. The population factors of the atoms within the voids of the network (O at 2(a) and La) were allowed to vary, but these sites remained fully occupied within their standard deviations. The temperature factors of La, Re, and $O_3$ tended to become negative: −0.04 (11), −0.02 (3), and −4.85 (279), respectively. This is apparently caused by the very high absorption of $La_4Re_6O_{19}$ with Cu radiation ($\mu$ = 1768.7). Although absorption is generally taken to be constant with $\theta$ for the powder diffractometer method,[8] this is

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[4] M. Tokonami, *Acta Cryst.*, **19**, 486 (1965).

[5] D. T. Cromer and J. T. Waber, *ibid.*, **18**, 1041 (1965).

[6] D. T. Cromer, *ibid.*, **18**, 20 (1965).

[7] P. M. Raccah and J. B. Goodenough, *Phys. Rev.*, **155**, 932 (1967).

[8] B. D. Culity, "Elements of X-Ray Diffraction," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1956.

not strictly true.[9] The effect of surface roughness in high absorbers causes absorption to be somewhat greater at small values of $\theta$, which, if not corrected for, could easily cause negative temperature factors. However, the temperature factors were not allowed to be negative in the refinement as may be seen in Table I.

A concurrent independent structure analysis[10] using single-crystal data is in good agreement with our results. The final positional parameters of that analysis are also given in Table I.

The observed and calculated intensities given in Table II are based on the parameters in Table I and a scale factor of $1.529 \times 10^{-5}$. The imaginary part of the anomalous dispersion for this noncentrosymmetric structure led to significant deviations from Friedel's law; consequently, the calculated values for $A$ and $B$ are also given.

Bond distances and angles with errors were calculated using a program written by L. W. Finger in which correlations (maximum found, 0.34) are used. Some of these are given in Table III. The lanthanum–oxygen coordination is shown in Figure 2, and a rhenium–oxygen octahedra pair is shown in Figure 3.

## Discussion

The structure of $La_4Re_6O_{19}$ contains rhenium–oxygen octahedra which share edges in pairs. Since there is a short Re–Re distance of 2.42 A across this edge, there is presumed to be a homopolar metal–metal bond. The Re–Re distance in rhenium metal is 2.75 A, and according to Cotton[11] an Re–Re distance of 2.42 A would correspond approximately to a double bond. The octahedra are further linked by sharing corners to form a three-dimensional network in which there are sizable voids. Within the voids there are $La_4O$ tetrahedra centered at the origin and at the body center. The lanthanum–oxygen coordination may be described as a trigonal prism which is capped on all three rectangular faces and one triangular face.

The compounds $KSbO_3$[12] and $KBiO_3$[13] are reported to have the same type of octahedral network as shown in Figure 1, but the voids are occupied in a different manner. The bonding in the octahedral network is undoubtedly highly covalent in $KBiO_3$, $KSbO_3$, and $La_4Re_6O_{19}$. This is particularly evident from the close oxygen–oxygen contacts for those oxygens making up the octahedron around rhenium. As shown in Table III, some of these distances are less than twice the ionic radius of $O^{2-}$ but are consistent with oxygen–oxygen distances found in certain more covalent oxides.

The formal oxidation state of rhenium in $La_4Re_6O_{19}$ is $+4^1/_3$. This implies that if the crystallographically equivalent rheniums are all chemically equivalent, delocalization of some electrons must occur. The electrical resistivity (~$10^{-5}$ ohm-cm at 4.2°K), the Seebeck coefficient (~+1.6 $\mu$v/deg), and the low, nearly temperature-independent magnetic susceptibility are

Table II

Observed and Calculated Intensities for $La_4Re_6O_{19}$

| H | K | L | $I_{OBS}$ | $I_{CAL}$ | $A_{CAL}$ | $B_{CAL}$ |
|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 221 | 299 | -178 | -1 |
| 2 | 0 | 0 | 288 | 290 | 354 | 9 |
| 2 | 1 | 1 | | 191 | 36 | -248 |
| -2 | -1 | -1 | | 177 | -55 | 235 |
| | | | 366 | 368 | | |
| 2 | 2 | 0 | 113 | 112 | 221 | 30 |
| 3 | 1 | 0 | | 999 | -745 | -90 |
| 1 | 3 | 0 | | 1 | 13 | -27 |
| | | | 1000 | 1001 | | |
| 2 | 2 | 2 | | 33 | -27 | -259 |
| -2 | -2 | -2 | | 34 | -130 | 232 |
| | | | 73 | 67 | | |
| 3 | 2 | 1 | | 212 | 415 | -1 |
| -3 | -2 | -1 | | 214 | 404 | 102 |
| 1 | 2 | 3 | | 56 | -210 | -37 |
| -1 | -2 | -3 | | 60 | -221 | 11 |
| | | | 552 | 544 | | |
| 4 | 0 | 0 | 8 | 7 | 117 | -21 |
| 4 | 1 | 1 | | 53 | 88 | 220 |
| -4 | -1 | -1 | | 65 | 169 | -203 |
| 3 | 3 | 0 | | 60 | 247 | 48 |
| | | | 186 | 179 | | |
| 4 | 2 | 0 | | 12 | 121 | 17 |
| 2 | 4 | 0 | | 0 | 9 | 17 |
| | | | 18 | 12 | | |
| 3 | 3 | 2 | | 7 | -100 | -21 |
| -3 | -3 | -2 | | 8 | -101 | -35 |
| | | | 22 | 16 | | |
| 4 | 2 | 2 | | 94 | -333 | 164 |
| -4 | -2 | -2 | | 77 | -243 | -232 |
| | | | 160 | 172 | | |
| 5 | 1 | 0 | | 109 | -417 | -32 |
| 1 | 5 | 0 | | 5 | 93 | 16 |
| 4 | 3 | 1 | | 1 | -27 | 37 |
| -4 | -3 | -1 | | 0 | -18 | -13 |
| 1 | 3 | 4 | | 264 | 643 | 93 |
| -1 | -3 | -4 | | 268 | 652 | 57 |
| | | | 651 | 649 | | |
| 5 | 2 | 1 | | 45 | 184 | 224 |
| -5 | -2 | -1 | | 61 | 286 | -182 |
| 1 | 2 | 5 | | 57 | -279 | 171 |
| -1 | -2 | -5 | | 44 | -177 | -227 |
| | | | 209 | 208 | | |
| 4 | 4 | 0 | 4 | 3 | -80 | 6 |
| 5 | 3 | 0 | | 19 | -200 | -38 |
| 3 | 5 | 0 | | 59 | -353 | -53 |
| 4 | 3 | 3 | | 2 | 72 | -28 |
| -4 | -3 | -3 | | 2 | 73 | -16 |
| | | | 79 | 84 | | |
| 6 | 0 | 0 | | 148 | 815 | 119 |
| 4 | 4 | 2 | | 103 | -431 | -223 |
| -4 | -4 | -2 | | 119 | -511 | 111 |
| | | | 371 | 371 | | |
| 5 | 3 | 2 | | 6 | 114 | 42 |
| -5 | -3 | -2 | | 6 | 126 | -1 |
| 2 | 3 | 5 | | 0 | -12 | 46 |
| -2 | -3 | -5 | | 0 | -0 | -34 |
| 6 | 1 | 1 | | 2 | 17 | 67 |
| -6 | -1 | -1 | | 1 | 38 | -43 |
| | | | 21 | 17 | | |
| 6 | 2 | 0 | | 3 | 91 | -4 |
| 2 | 6 | 0 | | 9 | 153 | -4 |
| | | | 15 | 12 | | |
| 5 | 4 | 1 | | 65 | 404 | -118 |
| -5 | -4 | -1 | | 50 | 314 | 193 |
| 1 | 4 | 5 | | 13 | -28 | -188 |
| -1 | -4 | -5 | | 15 | -118 | 165 |
| | | | 151 | 145 | | |
| 6 | 2 | 2 | | 2 | 58 | 67 |
| -6 | -2 | -2 | | 2 | 82 | -36 |
| | | | 5 | 5 | | |
| 6 | 3 | 1 | | 66 | -436 | -75 |
| -6 | -3 | -1 | | 65 | -433 | -76 |
| 1 | 3 | 6 | | 2 | 74 | -18 |
| -1 | -3 | -6 | | 2 | 77 | -6 |
| | | | 136 | 135 | | |
| 4 | 4 | 4 | | 49 | -671 | 66 |
| -4 | -4 | -4 | | 44 | -601 | -224 |
| | | | 97 | 93 | | |
| 7 | 1 | 0 | | 0 | -16 | 10 |
| 1 | 7 | 0 | | 7 | -151 | -1 |
| 5 | 5 | 0 | | 7 | -155 | -12 |
| 5 | 4 | 3 | | 8 | 161 | -3 |
| -5 | -4 | -3 | | 8 | 150 | 60 |
| 3 | 4 | 5 | | 33 | 325 | 38 |
| -3 | -4 | -5 | | 31 | 314 | 47 |
| | | | 93 | 96 | | |
| 6 | 4 | 0 | | 1 | -72 | -34 |
| 4 | 6 | 0 | | 0 | -27 | -34 |
| | | | 2 | 2 | | |
| 7 | 2 | 1 | | 9 | -30 | -175 |
| -7 | -2 | -1 | | 9 | -109 | 146 |
| 1 | 2 | 7 | | 7 | 56 | -144 |
| -1 | -2 | -7 | | 5 | -22 | 138 |
| 6 | 3 | 3 | | 16 | 230 | 57 |
| -6 | -3 | -3 | | 16 | 230 | 65 |
| 5 | 5 | 2 | | 14 | 63 | -215 |
| -5 | -5 | -2 | | 13 | -48 | 212 |
| | | | 87 | 93 | | |
| 6 | 4 | 2 | | 0 | -17 | -29 |
| -6 | -4 | -2 | | 0 | -38 | 34 |
| 2 | 4 | 6 | | 1 | -60 | -44 |
| -2 | -4 | -6 | | 2 | -80 | 49 |
| | | | 6 | 5 | | |
| 7 | 3 | 0 | | 0 | -0 | -32 |
| 3 | 7 | 0 | | 108 | -620 | -107 |
| | | | 100 | 108 | | |
| 7 | 3 | 2 | | 38 | 380 | 45 |
| -7 | -3 | -2 | | 37 | 371 | 77 |
| 2 | 3 | 7 | | 7 | -166 | -19 |
| -2 | -3 | -7 | | 8 | -175 | -7 |
| 6 | 5 | 1 | | 11 | -196 | -77 |
| -6 | -5 | -1 | | 12 | -218 | 39 |
| 1 | 5 | 6 | | 11 | 205 | 3 |
| -1 | -5 | -6 | | 9 | 182 | 56 |
| | | | 132 | 136 | | |
| 8 | 0 | 0 | 29 | 27 | 460 | -4 |
| 8 | 1 | 1 | | 12 | -130 | -182 |
| -8 | -1 | -1 | | 17 | -229 | 133 |
| 5 | 5 | 4 | | 10 | 91 | 180 |
| -5 | -5 | -4 | | 14 | 190 | -148 |
| 7 | 4 | 1 | | 3 | 6 | 125 |
| -7 | -4 | -1 | | 5 | 75 | -126 |
| 1 | 4 | 7 | | 7 | 97 | 140 |
| -1 | -4 | -7 | | 10 | 166 | -119 |
| | | | 80 | 82 | | |
| 8 | 2 | 0 | | 27 | 333 | 46 |
| 2 | 8 | 0 | | 24 | 312 | 46 |
| 6 | 4 | 4 | | 7 | -168 | 23 |
| -6 | -4 | -4 | | 5 | -150 | -40 |
| | | | 67 | 65 | | |
| 6 | 5 | 3 | | 1 | -81 | -17 |
| -6 | -5 | -3 | | 1 | -83 | -30 |
| 3 | 5 | 6 | | 7 | -171 | -39 |
| -3 | -5 | -6 | | 7 | -174 | -37 |
| | | | 16 | 18 | | |
| 6 | 6 | 0 | | 68 | 525 | 103 |
| 8 | 2 | 2 | | 12 | 146 | -173 |
| -8 | -2 | -2 | | 9 | 35 | 195 |
| | | | 90 | 90 | | |
| 8 | 3 | 1 | | 29 | -348 | -53 |
| -8 | -3 | -1 | | 31 | -360 | -30 |
| 1 | 3 | 8 | | 4 | 141 | -14 |
| -1 | -3 | -8 | | 4 | 130 | 58 |
| 7 | 4 | 3 | | 0 | -23 | 19 |
| -7 | -4 | -3 | | 0 | -14 | 6 |
| 3 | 4 | 7 | | 70 | 536 | 94 |
| -3 | -4 | -7 | | 72 | 545 | 81 |
| 7 | 5 | 0 | | 4 | 142 | 25 |
| 5 | 7 | 0 | | 28 | -345 | -34 |
| | | | 253 | 246 | | |
| 6 | 6 | 2 | | 0 | -6 | -20 |
| -6 | -6 | -2 | | 0 | -11 | -15 |
| | | | 7 | 0 | | |
| 7 | 5 | 2 | | 14 | 171 | 177 |
| -7 | -5 | -2 | | 19 | 258 | -126 |
| 2 | 5 | 7 | | 19 | -272 | 98 |
| -2 | -5 | -7 | | 14 | -185 | -169 |
| | | | 64 | 68 | | |
| 8 | 4 | 0 | | 8 | 184 | 30 |
| 4 | 8 | 0 | | 8 | 185 | 30 |
| | | | 15 | 16 | | |
| 9 | 1 | 0 | | 27 | -335 | -65 |
| 1 | 9 | 0 | | 7 | -172 | -48 |
| 8 | 3 | 3 | | 7 | -171 | -34 |
| -8 | -3 | -3 | | 7 | -173 | -38 |
| | | | 46 | 49 | | |
| 8 | 4 | 2 | | 6 | -101 | 137 |
| -8 | -4 | -2 | | 5 | -3 | -154 |
| 2 | 4 | 8 | | 7 | -105 | 145 |
| -2 | -4 | -8 | | 6 | -8 | -163 |
| | | | 22 | 26 | | |
| 9 | 2 | 1 | | 5 | 144 | -35 |
| -9 | -2 | -1 | | 4 | 112 | 89 |
| 1 | 2 | 9 | | 0 | 34 | -43 |
| -1 | -2 | -9 | | 0 | 1 | 63 |
| 7 | 6 | 1 | | 0 | -12 | 37 |
| -7 | -6 | -1 | | 0 | 4 | -12 |
| 1 | 6 | 7 | | 2 | 81 | 51 |
| -1 | -6 | -7 | | 2 | 98 | -3 |
| 6 | 5 | 5 | | 0 | -36 | 41 |
| -6 | -5 | -5 | | 0 | -11 | -39 |
| | | | 21 | 17 | | |
| 6 | 6 | 4 | | 6 | -158 | -46 |
| -6 | -6 | -4 | | 6 | -154 | -49 |
| | | | 18 | 12 | | |
| 9 | 3 | 0 | | 15 | 249 | 69 |
| 3 | 9 | 0 | | 1 | -76 | 22 |
| 8 | 5 | 1 | | 38 | -382 | 118 |
| -8 | -5 | -1 | | 28 | -273 | -212 |
| 1 | 5 | 8 | | 7 | -34 | 171 |
| -1 | -5 | -8 | | 8 | 75 | -167 |
| 7 | 5 | 4 | | 32 | 357 | -84 |
| -7 | -5 | -4 | | 25 | 281 | 165 |
| 4 | 5 | 7 | | 5 | -71 | -126 |
| -4 | -5 | -7 | | 7 | -148 | 86 |
| | | | 188 | 169 | | |
| 9 | 3 | 2 | | 2 | 108 | -13 |
| -9 | -3 | -2 | | 2 | 105 | 5 |
| 2 | 3 | 9 | | 14 | -242 | -46 |
| -2 | -3 | -9 | | 15 | -246 | -54 |
| 7 | 6 | 3 | | 46 | -425 | -94 |
| -7 | -6 | -3 | | 45 | -423 | -89 |
| 3 | 6 | 7 | | 1 | 79 | -21 |
| -3 | -6 | -7 | | 1 | 81 | -13 |
| | | | 136 | 131 | | |
| 8 | 4 | 4 | | 11 | -147 | -155 |
| -8 | -4 | -4 | | 15 | -233 | 97 |
| | | | 33 | 27 | | |
| 9 | 4 | 1 | | 21 | 274 | 105 |
| -9 | -4 | -1 | | 23 | 303 | -2 |
| 1 | 4 | 9 | | 7 | 146 | 85 |
| -1 | -4 | -9 | | 7 | 174 | -17 |
| 8 | 5 | 3 | | 1 | -61 | 20 |
| -8 | -5 | -3 | | 0 | -48 | -32 |
| 3 | 5 | 8 | | 7 | -172 | 3 |
| -3 | -5 | -8 | | 6 | -159 | -44 |
| 7 | 7 | 0 | | 0 | -45 | 12 |
| | | | 91 | 76 | | |
| 10 | 0 | 0 | | 0 | 56 | -22 |
| 8 | 6 | 0 | | 23 | 298 | 30 |
| 6 | 8 | 0 | | 21 | 286 | 30 |
| | | | 58 | 44 | | |
| 10 | 1 | 1 | | 5 | -1 | 105 |
| 7 | 7 | 2 | | 3 | -3 | -110 |
| -7 | -7 | -2 | | 3 | -70 | 86 |
| | | | 20 | 12 | | |
| 10 | 2 | 0 | | 4 | 131 | 31 |
| 2 | 10 | 0 | | 3 | 114 | 31 |
| 8 | 6 | 2 | | 8 | 169 | 63 |
| -8 | -6 | -2 | | 10 | 193 | -3 |
| 2 | 6 | 8 | | 10 | 183 | 78 |
| -2 | -6 | -8 | | 11 | 208 | -15 |
| | | | 55 | 50 | | |
| 9 | 5 | 0 | | 3 | -109 | -28 |
| 5 | 9 | 0 | | 25 | -296 | -60 |
| 9 | 4 | 3 | | 5 | -127 | -45 |
| -9 | -4 | -3 | | 4 | -124 | -42 |
| 3 | 4 | 9 | | 10 | 198 | 7 |
| -3 | -4 | -9 | | 11 | 202 | -1 |
| | | | 57 | 60 | | |
| 10 | 2 | 2 | | 10 | -170 | 87 |
| -10 | -2 | -2 | | 8 | -96 | -141 |
| 6 | 6 | 6 | | 12 | 346 | 85 |
| -6 | -6 | -6 | | 12 | 347 | 91 |
| | | | 47 | 43 | | |
| 7 | 6 | 5 | | 10 | -183 | -46 |
| -7 | -6 | -5 | | 12 | -203 | 5 |
| 5 | 6 | 7 | | 15 | 225 | 20 |
| -5 | -6 | -7 | | 13 | 206 | 58 |
| 9 | 5 | 2 | | 7 | 135 | 82 |
| -9 | -5 | -2 | | 8 | 171 | -25 |
| 2 | 5 | 9 | | 2 | -76 | 40 |
| -2 | -5 | -9 | | 1 | -40 | -46 |
| 10 | 3 | 1 | | 0 | -51 | 16 |
| -10 | -3 | -1 | | 0 | -43 | -0 |
| 1 | 3 | 10 | | 41 | 367 | 77 |
| -1 | -3 | -10 | | 42 | 375 | 66 |
| | | | 158 | 157 | | |
| 8 | 7 | 1 | | 6 | -72 | -128 |
| -8 | -7 | -1 | | 10 | -156 | 88 |
| 1 | 7 | 8 | | 15 | -148 | -165 |
| -1 | -7 | -8 | | 20 | -232 | 103 |
| 8 | 5 | 5 | | 16 | -76 | -213 |
| -8 | -5 | -5 | | 21 | -196 | 171 |
| 7 | 7 | 4 | | 2 | 29 | 82 |
| -7 | -7 | -4 | | 4 | 88 | -82 |
| | | | 93 | 99 | | |
| 10 | 4 | 0 | | 0 | 17 | 21 |
| 4 | 10 | 0 | | 0 | 25 | 21 |
| 8 | 6 | 4 | | 2 | 84 | -4 |
| -8 | -6 | -4 | | 1 | 62 | 37 |
| 4 | 6 | 8 | | 2 | 86 | -23 |
| -4 | -6 | -8 | | 2 | 64 | 55 |
| | | | 10 | 9 | | |
| 10 | 3 | 3 | | 2 | -68 | -44 |
| -10 | -3 | -3 | | 2 | -67 | -39 |
| 9 | 6 | 1 | | 2 | -85 | -19 |
| -9 | -6 | -1 | | 2 | -78 | -48 |
| 1 | 6 | 9 | | 14 | -200 | -43 |
| -1 | -6 | -9 | | 14 | -192 | -58 |
| | | | 31 | 39 | | |
| 10 | 4 | 2 | | 28 | -238 | -139 |
| -10 | -4 | -2 | | 35 | -304 | 40 |
| 2 | 4 | 10 | | 27 | -226 | -150 |
| -2 | -4 | -10 | | 32 | -291 | 51 |
| | | | 122 | 123 | | |
| 11 | 1 | 0 | | 44 | -329 | -51 |
| 1 | 11 | 0 | | 4 | 101 | 19 |
| 9 | 5 | 4 | | 33 | 291 | 5 |
| -9 | -5 | -4 | | 30 | 260 | 97 |
| 4 | 5 | 9 | | 4 | 101 | -19 |
| -4 | -5 | -9 | | 3 | 70 | 58 |
| 8 | 7 | 3 | | 10 | 157 | 13 |
| -8 | -7 | -3 | | 9 | 147 | 46 |
| 3 | 7 | 8 | | 40 | -313 | -49 |
| -3 | -7 | -8 | | 42 | -323 | -39 |
| | | | 220 | 222 | | |

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TABLE III

Bond Distances (A)

| | | | |
|---|---|---|---|
| Re–Re | 1 × 2.422 (7) | $O_{1a}$–$O_{1b}$ | 1 × 3.053 (95) |
| | 4 × 3.519 (2) | $O_{2a}$ | 2 × 2.464 (34) |
| La–Re | 3 × 3.397 (2) | $O_{2b}$ | 2 × 2.849 (41) |
| | 3 × 3.859 (4) | $O_{2d}$ | 2 × 3.042 (41) |
| Re–$O_{1a}$ | 2 × 1.948 (37) | $O_{2c}$ | 2 × 3.126 (36) |
| $O_{2a}$ | 2 × 1.913 (36) | $O_{2a}$–$O_{2b}$ | 2 × 2.766 (23) |
| $O_{2b}$ | 2 × 2.081 (34) | $O_{2e}$ | 2 × 2.907 (72) |
| La–$O_{1a}$ | 3 × 2.567 (28) | $O_{2d}$ | 2 × 2.681 (15) |
| $O_{2a}$ | 3 × 2.513 (46) | $O_3$–$O_{1a}$ | 6 × 2.989 (48) |
| $O_{2b}$ | 3 × 2.934 (46) | $O_{2a}$ | 12 × 3.939 (36) |
| $O_3$ | 1 × 2.523 (7) | | |

Bond Angles (Deg)

| | | | |
|---|---|---|---|
| $O_{1a}$–Re–$O_{2e}$ | 2 × 174 (12) | $O_{1a}$–Re–$O_{2b}$ | 2 × 90 (1) |
| $O_{2b}$–Re–$O_{2d}$ | 1 × 167 (9) | $O_{1a}$–Re–$O_{2d}$ | 2 × 98 (1) |
| | | $O_{2a}$–Re–$O_{2b}$ | 2 × 88 (1) |
| $O_{1a}$–Re–$O_{1b}$ | 1 × 103 (1) | $O_{2a}$–Re–$O_{2d}$ | 2 × 84 (1) |
| $O_{1a}$–Re–$O_{2a}$ | 2 × 79 (1) | $O_{2a}$–Re–$O_{2c}$ | 1 × 99 (2) |

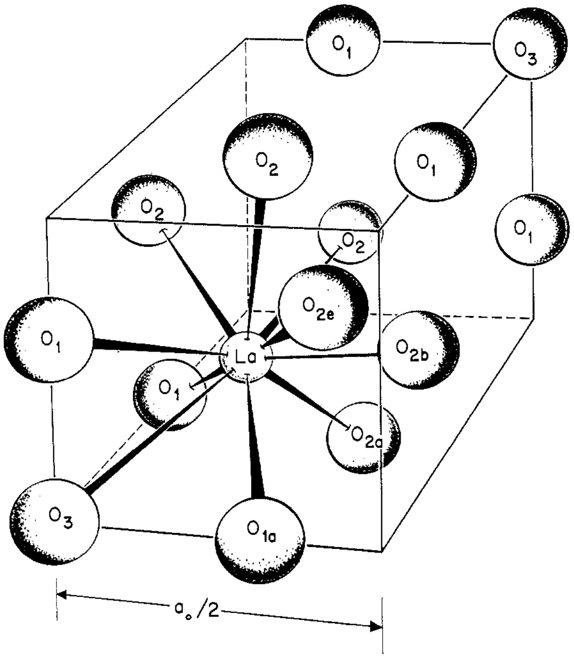

Figure 2.—The lanthanum–oxygen coordination.

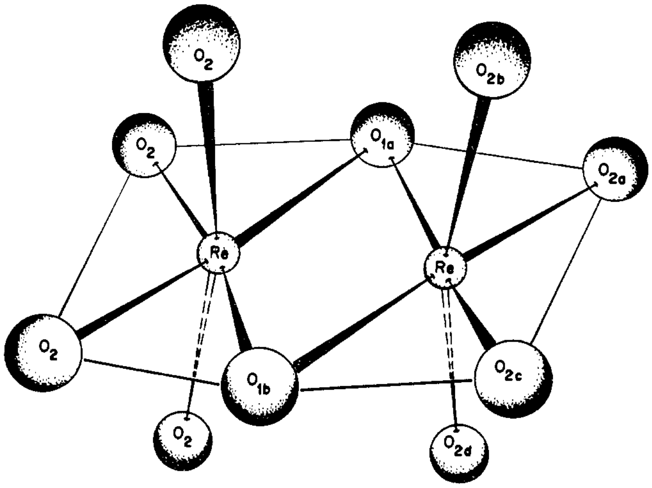

Figure 3.—A rhenium–oxygen octahedra pair.

all typical of metals and clearly indicate that electron delocalization has occurred. The results of all three measurements are inconsistent with a hopping model which would require the rhenium atoms to be only statistically equivalent. If three-dimensional delocalization is to occur only by metal–metal interaction, then direct overlap of the rhenium 5d orbitals must occur not only at the 2.42-A distance but also at a distance of 3.52 A. It is, however, likely that the delocalization involves orbitals of oxygen in a manner similar to that which has been proposed for $ReO_3$.[14]

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