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On the structure of lithium peroxide, Li_2O_2

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The two published lithium peroxide structures, both ascribed to the hexagonal $P\bar{6}$ space group, were subjected to reinterpretation, and another more symmetric structure, now belonging to the $P6_3/mmc$ space group, was found. Detailed density-functional quantum mechanical calculations and crystal structure optimizations were carried out on both structures and the energetic arguments obtained therewith helped to rule out one of them.

1. Introduction

Despite its use as an oxidizing agent, as a regenerator for confined breathable atmospheres and as a fuel cell material, lithium peroxide has seemingly not been sufficiently studied, to the point that even its crystalline structure has not been unambiguously determined. Crystallographic databases give two different accounts of the lithium peroxide structure, the first proposed by Féher *et al.* (1953) and the other by Föppl (1957). Whether these two structures represent isomorphs is not substantiated by any experimental evidence other than the interpretation of X-ray diffraction data, which is not entirely suitable to lithium compounds due to the fact that lithium is a poor X-ray scatterer. Therefore, since the issue of choosing one of the proposed structures is not completely resolved, further argumentation is in order.

In the course of a density-functional quantum mechanical study of lithium peroxide, we found out that both proposed structures could be better accounted for by another more symmetric hexagonal space group. On the other hand, optimization of atomic coordinates and cell parameters shows that the Föppl structure is substantially more favourable in terms of energy and in terms of its ability to reproduce the experimental X-ray spectrum of the peroxide.

This study relies on the fact that modern high-quality DFT calculations are nowadays very much able to make not only qualitative but also accurate quantitative predictions.

2. Calculation details

The calculations were carried out using the *WIEN2k* code (Blaha *et al.*, 2001), which is a full potential-linearized augmented plane-wave (FP-LAPW) method based on the density functional theory (DFT). The generalized gradient approximation (Perdew *et al.*, 1996) was used for the treatment of the exchange–correlation interactions. The number of k points used was 1000 (72 in the irreducible wedge).

For the number of plane waves the applied criterion was $R_{\rm MT}^{\rm max}$ (muffin–tin radius) $\times$ $K^{\rm max}$ (for the plane waves) $= 8$. The same $R_{\rm MT}$ was used for each atom in all the crystal structures, $R_{\rm MT}({\rm Li}) = 1.8$ a.u., $R_{\rm MT}({\rm O}) = 1.4$ a.u., except for the

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Table 1
Structure 1, original (Féher *et al.*, 1953).

Space group: $P\bar{6}$ (space group #174), hexagonal; unit cell: a = 6.305, b = 6.305, c = 7.71 Å; α = 90, β = 90, γ = 120°.

	Site	x	y	z
Li1	2(g)	0	0	±0.158
Li2	2(d)	−1/3	1/3	1/2 ± 0.158
Li3	6(l)	1/2	1/2	±0.158
		0	1/2	±0.158
		1/2	0	±0.158
Li4	6(l)	1/6	−1/6	1/2 ± 0.158
		−1/3	−1/6	1/2 ± 0.158
		1/6	1/3	1/2 ± 0.158
O1	2(g)	0	0	1/2 ± 0.083
O2	2(i)	−1/3	1/3	±0.083
O3	6(l)	1/2	1/2	1/2 ± 0.083
		0	1/2	1/2 ± 0.083
		1/2	0	1/2 ± 0.083
O4	6(l)	1/6	−1/6	±0.083
		−1/3	−1/6	±0.083
		1/6	1/3	±0.083

Table 2
Structure 1, reduced.

Space group: $P\bar{6}$ (space group #174), hexagonal; unit cell: a = 3.1525, b = 3.1525, c = 7.71 Å; α = 90, β = 90, γ = 120°.

	Site	x	y	z
Li1	2(g)	0	0	±0.158
Li2	2(d)	1/3	−1/3	1/2 ± 0.158
O1	2(g)	0	0	1/2 ± 0.083
O2	2(d)	1/3	−1/3	±0.083

original Féher *et al.* (1953) structure, where $R_{\rm MT}$(O) = 1.2 a.u., was used. The space-group analysis was carried out with the program *SGROUP* (Yanchitsky & Timoshevskii, 2001) contained in the *WIEN2k* package. For crystal structure visualization the *XCrySDen* package (Kokalj, 1999) was used.

3. Discussion

3.1. Crystal structure simplification

The crystal structure of lithium peroxide was reported some 50 years ago by Féher *et al.* (1953; from hereon *Str*1) and by Föppl (1957; from hereon *Str*2). Both authors proposed their respective structural models based on the good agreement of their respective X-ray data. Föppl, however, based on a systematic study of several alkali peroxides, claimed that his structural assignment was more in accordance with the general peroxide construction principles, although he provided no further evidence pertaining to lithium peroxide itself.

*Str*1 is presented in Table 1. From the atomic positions it can readily be seen that by shifting the three Li3 atoms by half a cell in the a or b direction, they fall into the Li1 positions, and the same is valid for the other atoms, such that Li4 becomes Li2, O3 becomes O1 and O4 becomes O2. This clearly suggests that the unit cell can be reduced to $a' = a/2$ and $b' = b/2$ ($a' = b'$ = 3.1525 Å), the 2(g) (00z) positions remain the same and the 2(i) $(\frac{1}{3}\frac{\bar{1}}{3}z)$ positions change to 2(d) $(\frac{\bar{1}}{3}\frac{1}{3}z)$. The reduced structure is therefore as in Table 2.

Table 3
Structure 1, symmetrized.

Space group: $P6_3/mmc$ (space group # 194), hexagonal; unit cell: a = 3.1525, b = 3.1525, c = 7.71 Å; α = 90, β = 90, γ = 120°.

	Site	x	y	z
Li1	4(f)	1/3	−1/3	1/4 ± 0.158
		−1/3	1/3	−1/4 ± 0.158
O1	4(f)	1/3	−1/3	−1/4 ± 0.083
		−1/3	1/3	1/4 ± 0.083

Table 4
Structure 2, original (Föppl, 1957).

Space group: $P\bar{6}$ (space group #174), hexagonal; unit cell: a = 3.142, b = 3.142, c = 7.65 Å; α = 90, β = 90, γ = 120°.

	Site	x	y	z
Li1	1(a)	0	0	0
Li2	1(d)	1/3	−1/3	1/2
Li3	2(i)	−1/3	1/3	±1/4
O1	2(g)	0	0	1/2 ± 0.102
O2	2(h)	1/3	−1/3	±0.102

This simpler cell, with only four Li and four O atoms has no inversion symmetry. However, by shifting all atoms by $(\frac{1}{3}\frac{\bar{1}}{3}\frac{1}{4})$, Li1 and Li2 are now connected by inversion as well as O1 and O2. The new cell belongs to a different space group, as is shown in Table 3.

Li atoms are arranged as in the wurtzite structure, which is similar to the h.c.p. (hexagonal close packed) structure, but rather than having alternating triangular layers, *BCBC*..., the layers are repeated twice, *BBCCBBCC*... . At the same time, O atoms occupy alternate sites, that is, *CCBBCCBB*...; therefore, the new structure can be viewed as two interpenetrating wurtzite structures, one shifted from the other by half a cell in the c direction. This is indeed an open structure with the A sites vacant. In this structure the vertical distances between two lithium atoms and between two O atoms cannot be determined by symmetry [these distances, which will be referred to as 2α, are 2α(Li) = 0.316 (2.43 Å) and 2α(O) = 0.166 (1.28 Å)].

*Str*2 is presented in Table 4. Again, inversion symmetry can be incorporated by shifting the atoms by $(\frac{1}{3}\frac{\bar{1}}{3}\frac{1}{4})$. Now Li1 and Li2 are connected by inversion and both therefore become Li2, Li3 becomes Li1, and finally O1 and O2 are also connected by inversion. The new cell is shown in Table 5. As can be seen, this structure is quite similar to the reduced *Str*1 cell (Table 3), where oxygen ions have the same 4(f) position, but with a larger separation, 2α(O) = 0.204 (1.56 Å). Li atoms, however, have different positions: instead of being on the oxygen planes they are between the planes. The arrangement can be described as *AcBcAbCbA*, where capital letters refer to lithium and small letters to oxygen. This can be seen as a close-packed arrangement, compressed in the c direction. The sequence *BcAbC* forms a cubic close-packed arrangement (c.c.p.), followed by the reverse sequence, *CbAcB*, which also forms a c.c.p. arrangement. Therefore, *Str*2 can be regarded as specular layers of c.c.p. arrangements. The Li atoms by

Table 5
Structure 2, symmetrized.

Space group: *P*6_3/*mmc* (space group #194), hexagonal; unit cell: *a* = 3.142, *b* = 3.142, *c* = 7.65 Å; *α* = 90, *β* = 90, *γ* = 120°.

	Site	*x*	*y*	*z*
Li1	2(*a*)	0	0	0
		0	0	1/2
Li2	2(*c*)	1/3	−1/3	1/4
		−1/3	1/3	−1/4
O1	4(*f*)	1/3	−1/3	−1/4 ± 0.102
		−1/3	1/3	1/4 ± 0.102

themselves form a close-packed structure, *ABACA*, which is still compressed in the *c* direction, with $c/a = 2.43$, compared with the ideal hard sphere packing of 3.26.

Table 6
Optimization of structure 1 (forces are given in mRy a.u.$^{-1}$, energies in Ry and bond distances in Å).

Structure	*a*	*c*	2*α*(Li)	2*α*(O)	O—O	Energy
Unrelaxed	3.1525	7.71	0.316	0.166	1.28	−662.2907
Force relaxed	3.1525	7.71	0.2952	0.1943	1.50	−662.4002
Fully relaxed	3.3339	7.9300	0.2937	0.1923	1.53	−662.4262

Table 7
Optimization of structure 2 (forces are given in mRy a.u.$^{-1}$, energies in Ry and bond distances in Å).

Structure	*a*	*c*	2*α*(O)	O—O	Energy
Unrelaxed	3.142	7.65	0.204	1.5606	−662.5025
Fully relaxed	3.1830	7.7258	0.2006	1.5500	−662.5043

3.2. Crystal structure optimization

To elucidate whether these two crystal structures represent isomorphs of Li_2O_2, electronic structure calculations were performed on the symmetry-optimized version of each peroxide structure. Both structures were found to be strained (*i.e.* the calculations showed that there were non-negligible net forces acting on the atoms), therefore, a full optimization of the atomic coordinates and cell parameters was performed.

3.2.1. Féher *et al.* (1953) structure, *Str1*. This structure showed large forces on its atoms, with $F(\mathrm{Li}) = -10$ mRy a.u.$^{-1}$ and $F(\mathrm{O}) = -374$ mRy a.u.$^{-1}$, according to our calculations. Relaxing the atomic coordinates (until the forces became negligible, that is, less than 1 mRy a.u.$^{-1}$) produced drastic changes (see Table 6): there is a total energy reduction of −0.11 Ry, while the O—O bond length increases from 1.28 to 1.50 Å.

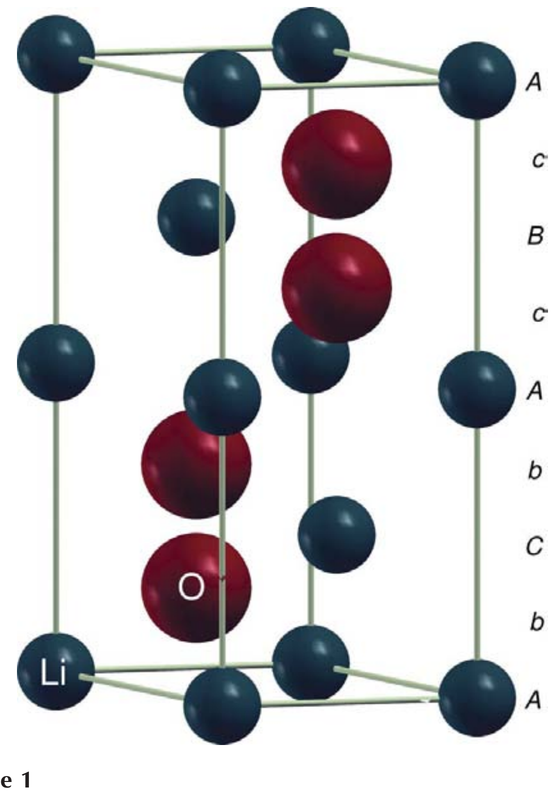

Figure 1
Optimized Li_2O_2 structure. The letters on the right refer to hexagonal packing, see text.

For his part, Föppl (1957) argued that such a short (1.28 Å) O—O bond in the Féher *et al.* (1953) structure would reproduce the X-ray diffraction pattern well. However, in analogy with his homologous peroxide determinations, Föppl concluded that this O—O bond should be of the order of 1.5 Å and with such a large bond the X-ray diffraction pattern would be discernibly different. Therefore, according to Föppl (1957), *Str*1 must be wrong.

Full optimization of this structure was carried out in sucessive cycles of force, cell volume and c/a optimization steps. In the last cycle the changes in cell volume and c/a were 0.39 and 0.29%, respectively. The final forces were $F(\mathrm{Li})$ = 1.3 mRy a.u.$^{-1}$ and $F(\mathrm{O})$ = 2.8 mRy a.u.$^{-1}$. The optimization after the relaxation of the atomic coordinates did not have such a large impact on the energy or on the O—O bond length, but produced a considerable 15% cell volume increase and a 2.7% reduction in the c/a ratio. Such large discrepancies with the originally reported experimental values must necessarily entail a misinterpretation of the X-ray diffraction measurements, which should perhaps have been evident even in the X-ray diffraction patterns of 1953.

3.2.2. Föppl (1957) structure, *Str2*. Our calculations show that there is a moderate force on the O atom, of 11 mRy a.u.$^{-1}$, in this structure. Full optimization of the structure (see Table 7) produces a moderate volume increase of 3.6% and some other quite small changes: 1.8 mRy total energy reduction, an O—O bond length reduced from 1.56 to 1.55 Å and a c/a ratio change of 0.31%. The changes in volume and c/a were 0.22 and 0.15%, respectively, in the last cycle of optimization. The final force was $F(\mathrm{O})$ = 1.6 mRy a.u.$^{-1}$.

There is a large initial energy difference between *Str2* and *Str1* of −110 mRy per peroxide unit, which reduces after optimization to only −39 mRy per peroxide. However, this energy difference is still large enough (Fournier, 1993), which constitutes further evidence that lithium peroxide does not have the *Str1* structure.

Therefore, our results show that lithium peroxide has the same crystal structure proposed by Föppl (1957), but now with inversion symmetry (space group 194) and slightly modified atomic positions (Fig. 1 and Table 5). The optimized structure has the following cell parameters: $a = 3.1830$ and $c = 7.7258$ Å, with $\alpha = 1.003^\circ$ (rather than $\alpha = 1.02^\circ$).

4. Conclusions

Two crystal structures have been proposed for lithium peroxide. These structures were formerly assigned to the space group $P\bar{6}$ (space group #174). It was found that they could be better described by the $P6_3/mmc$ space group (space group #194).

The results presented in this work, performed with high-quality DFT codes, offer a strong argument against the viability of the structure proposed by Féher *et al.* (1953). They do, however, confirm the correctness of the structure proposed by Föppl (1957). Furthermore, on these grounds it was possible to present improved values for the Li_2O_2 cell parameters.

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