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# The Crystal Structure of Lithium Tungstate*

By W. H. Zachariasen and H. A. Plettinger

*Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.*
*and Division of Physics, Argonne National Laboratory, Argonne, Illinois, U.S.A.*

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$Li_2WO_4$ has the phenacite type of structure, space group $R\bar{3}$, with six molecules in a rhombohedral cell with $a = 8{\cdot}888$ Å, $\alpha = 107{\cdot}78°$. The positions of all atoms have been found with considerable accuracy. The tungstate group is tetrahedral within experimental error with W–O = 1·79 Å. The configuration about lithium is also tetrahedral with an average bond length of Li–O = 1·96 Å.

Many years ago one of us reported (Zachariasen, 1926) that the compounds $Be_2SiO_4$ (mineral phenacite), $Zn_2SiO_4$ (willemite), $Li_2BeF_4$, $Li_2MoO_4$ and $Li_2WO_4$ were isostructural. Shortly afterwards Bragg (1927) described the structure of phenacite, and Bragg & Zachariasen (1930) the structure of willemite.

Recently Prof. R. J. Moon of this University asked the writers to examine inch long single crystals of lithium tungstate. The earlier statement that $Li_2WO_4$ has the phenacite type of structure was confirmed. Since no reliable results are available in the literature for the bond lengths of the tungstate group, a determination of all atomic coordinates in the lithium tungstate structure was carried out.

The dimensions of the hexagonal cell with 18 molecules and of the rhombohedral cell with 6 molecules are:

Hexagonal cell:

$$a = 14{\cdot}361 \pm 0{\cdot}003,\ c = 9{\cdot}602 \pm 0{\cdot}002 \text{ Å}.$$

Rhombohedral cell:

$$a = 8{\cdot}888 \pm 0{\cdot}002,\ \alpha = 107{\cdot}78 \pm 0{\cdot}03°.$$

The calculated density is 4·560 g.cm.$^{-3}$, whereas R. J. Moon reported to us a directly measured value of 4·535 g.cm.$^{-3}$. The space group is $R\bar{3}$, and all atoms are in general positions. Referred to hexagonal axes (in the following hexagonal axes are used unless otherwise specified) the equivalent coordinates are:

$$(0, 0, 0)\ (\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{3})\ (\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{2}{3}) +$$
$$\pm (x, y, z)\ (-y, x-y, z)\ (y-x, -x, z)\ .$$

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## Determination of the atomic positions

A single crystal fragment was ground into a nearly perfect sphere of radius 0·0215 cm. Precise intensities were measured on a General Electric XRD-3 spectrometer modified for single crystal work, using filtered Cu $K\alpha$-radiation and a proportional counter. Complete data were taken about the [010] axis for the layers $K = 0, 1, 2$ and about the [001] axis for the layers $L = 0, 1, 2, 3$. In this manner a total of about 750 distinct reflections were recorded.

The final parameter values were deduced with the aid of a least-squares refinement carried out on an IBM 704 machine using the Busing–Levi (1959) program. The atomic coordinates reported for the phenacite structure were used as a starting point and isotropic temperature factors were assumed. Because of the small effect of lithium no attempt was made to vary the temperature factor for these atoms, and a value of $B = 2{\cdot}5$ Å$^2$ was presupposed. The subsequent results for the temperature factors of tungsten and oxygen indicate that the assumed value for lithium is somewhat too high. The $f$-curves of Berghuis *et al.* (1955) were used for lithium and oxygen. For tungsten the Thomas–Fermi $f$-curve (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1935) was em-

Table 2. *Final parameters* (*rhombohedral axes*)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| W | 0·03497 | 0·44606 | 0·27104 |
| $O_I$ | 0·1505 | 0·4612 | 0·1383 |
| $O_{II}$ | −0·0783 | 0·5777 | 0·2512 |
| $O_{III}$ | −0·1154 | 0·2231 | 0·1902 |
| $O_{IV}$ | 0·1823 | 0·5263 | 0·4998 |
| $Li_I$ | 0·386 | 0·782 | 0·605 |
| $Li_{II}$ | 0·697 | 0·098 | 0·938 |

Table 1. *Final parameters* (*hexagonal axes*)

| | $x$ | $y$ | $z$ | $B$ in Å$^2$ |
|---|---|---|---|---|
| W | −0·02035 ± 7 | 0·19537 ± 7 | 0·25069 ± 10 | 0·176 ± 25 |
| $O_I$ | 0·1117 ± 16 | 0·2112 ± 16 | 0·2500 ± 21 | 1·11 ± 36 |
| $O_{II}$ | −0·0010 ± 16 | 0·3275 ± 16 | 0·2502 ± 21 | 1·04 ± 35 |
| $O_{III}$ | −0·0909 ± 16 | 0·1238 ± 16 | 0·0993 ± 21 | 1·68 ± 35 |
| $O_{IV}$ | −0·0970 ± 16 | 0·1235 ± 16 | 0·4028 ± 21 | 0·95 ± 34 |
| $Li_I$ | −0·014 ± 4 | 0·191 ± 4 | 0·591 ± 5 | (2·5) |
| $Li_{II}$ | −0·027 ± 4 | 0·187 ± 4 | 0·911 ± 5 | (2·5) |

Table 3. *Observed and calculated structure factors*

| *HKL* | $F_o$ | $F_c$ | *HKL* | $F_o$ | $F_c$ | *HKL* | $F_o$ | $F_c$ | *HKL* | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 101 | 0 | 37 | $30\bar{3}$ | 34 | −13 | $29\bar{4}$ | 342 | −322 | $13,1,\bar{6}$ | 235 | −255 |
| 110 | 206 | −180 | $32\bar{2}$ | 51 | −40 | 10,2,2 | 27 | 20 | 1,13,6 | 201 | 203 |
| $20\bar{1}$ | 215 | −181 | 232 | 308 | 296 | $2,10,\bar{2}$ | 165 | 161 | $1,13,\bar{6}$ | 191 | 196 |
| $10\bar{2}$ | 589 | −585 | $50\bar{1}$ | 0 | 18 | 707 | 348 | −331 | 1,1,12 | 74 | −75 |
| 211 | 599 | −628 | 330 | 55 | −32 | $93\bar{3}$ | 54 | −68 | $1,1,\bar{12}$ | 52 | −50 |
| $12\bar{1}$ | 786 | 899 | $22\bar{3}$ | 479 | 515 | $93\bar{3}$ | 54 | 61 | 8,10,1 | 86 | 74 |
| 300 | 281 | −269 | $22\bar{3}$ | 494 | −525 | $39\bar{3}$ | 342 | −305 | $10,8,\bar{1}$ | 391 | 437 |
| 202 | 279 | 250 | 104 | 455 | 448 | $39\bar{3}$ | 348 | 297 | 6,1,11 | 99 | 108 |
| 220 | 498 | −518 | 167 | 318 | 307 | 508 | 543 | 539 | $1,6,\bar{11}$ | 278 | −304 |
| 122 | 498 | 510 | $61\bar{7}$ | 151 | −147 | 915 | 29 | −8 | 10,1,9 | 29 | −7 |
| $21\bar{2}$ | 420 | 420 | 2,10,1 | 187 | 186 | $19\bar{5}$ | 256 | −244 | $10,1,\bar{9}$ | 29 | −18 |
| 131 | 462 | −488 | $10,2,\bar{1}$ | 288 | 279 | 672 | 250 | 253 | 1,10,9 | 112 | 120 |
| $31\bar{1}$ | 311 | 279 | 10,1,3 | 41 | −15 | $76\bar{2}$ | 20 | 23 | $1,10,\bar{9}$ | 109 | −109 |
| 003 | 0 | 12 | $10,1,\bar{3}$ | 52 | 26 | 627 | 498 | 468 | 15,1,2 | 213 | −230 |
| 401 | 86 | 84 | 1,10,3 | 164 | −154 | 267 | 279 | −274 | $1,15,\bar{2}$ | 163 | 187 |
| 113 | 530 | 553 | $1,10,\bar{3}$ | 164 | 147 | 11,1,1 | 43 | 43 | 3,14,1 | 123 | 120 |
| $11\bar{3}$ | 525 | −560 | $23\bar{8}$ | 215 | −190 | 1,11,1 | 348 | 342 | $14,3,\bar{1}$ | 129 | 137 |
| $31\bar{2}$ | 164 | −155 | $32\bar{8}$ | 54 | 51 | 8,1,10 | 191 | −192 | 11,7,1 | 240 | −263 |
| $13\bar{2}$ | 185 | 180 | 10,0,4 | 396 | 391 | $1,8,\bar{10}$ | 156 | 152 | $7,11,\bar{1}$ | 17 | 12 |
| 321 | 57 | 49 | 11,0,2 | 30 | −24 | 13,2,5 | 47 | −22 | 3,0,12 | 86 | −86 |
| $23\bar{1}$ | 167 | −170 | 761 | 66 | −61 | $2,13,\bar{5}$ | 281 | −316 | $3,0,\bar{12}$ | 93 | −91 |
| 410 | 750 | 884 | $67\bar{1}$ | 487 | 482 | 0,0,12 | 547 | 584 | 13,0,7 | 232 | −282 |
| 140 | 140 | 143 | 850 | 111 | 86 | 1,15,1 | 174 | 189 | $7,0,\bar{11}$ | 249 | 281 |
| $40\bar{2}$ | 548 | −550 | 580 | 337 | −317 | $15,1,\bar{1}$ | 106 | −87 | 12,6,0 | 29 | 10 |
| 303 | 40 | 11 | 924 | 362 | 357 | 13,1,6 | 242 | −256 | 6,12,0 | 96 | −119 |

ployed, but corrected for anomalous dispersion (Dauben & Templeton, 1955).

The refinement process gave an $R$-factor of 0·065 (including zeros) and the results shown in Tables 1 and 2. The degree of agreement between observed and calculated structure factors is illustrated in Table 3. Included in this table are groups of consecutive reflections on the sin $\theta/\lambda$ scale, taken from the beginning, the middle and the end of the complete table of data.

Inspection of the data shows that there are secondary extinction effects for which no correction was made. Were extinction effects taken into account, an appreciable reduction in the $R$-factor could be attained and there would be greatly increased accuracy in the determination of the lithium positions. However, it was felt that this correction and other modifications in the refinement process would not yield results of sufficient added value to justify further expenditure of effort and computer time.

## The bond lengths

The atomic coordinates of tungsten have been found with a precision of 0·001 Å. The corresponding accuracy is 0·02 Å for oxygen and 0·05 Å for lithium atoms.

The bond lengths in the oxygen tetrahedra about tungsten and lithium are:

$$\begin{aligned} W\text{–}O_I &= 1{\cdot}79 \pm 0{\cdot}02 \text{ Å} \\ \text{–}O_{II} &= 1{\cdot}77 \pm 0{\cdot}02 \\ \text{–}O_{III} &= 1{\cdot}78 \pm 0{\cdot}02 \\ \text{–}O_{IV} &= 1{\cdot}81 \pm 0{\cdot}02 \end{aligned}$$

$$\begin{aligned} Li_I\text{–}O_I &= 1{\cdot}87 \pm 0{\cdot}08 \text{ Å} \\ \text{–}O_{II} &= 2{\cdot}10 \pm 0{\cdot}08 \\ \text{–}O_{IV} &= 1{\cdot}80 \pm 0{\cdot}08 \\ \text{–}O_{IV} &= 1{\cdot}80 \pm 0{\cdot}08 \end{aligned} \qquad \begin{aligned} Li_{II}\text{–}O_I &= 1{\cdot}88 \pm 0{\cdot}08 \text{ Å} \\ \text{–}O_{II} &= 1{\cdot}98 \pm 0{\cdot}08 \\ \text{–}O_{III} &= 2{\cdot}00 \pm 0{\cdot}08 \\ \text{–}O_{III} &= 2{\cdot}02 \pm 0{\cdot}08 \end{aligned}$$

The $WO_4$-tetrahedron is regular within experimental error, the W–O bond angles ranging from 106 to 112°.

The Li–O average bond length of 1·96 Å is slightly smaller than the value 2·00 Å observed in $Li_2O$. However, in the latter structure each oxygen is bonded to eight lithium atoms, so that the Li–O bond length presumably is increased due to lithium–lithium repulsion.

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